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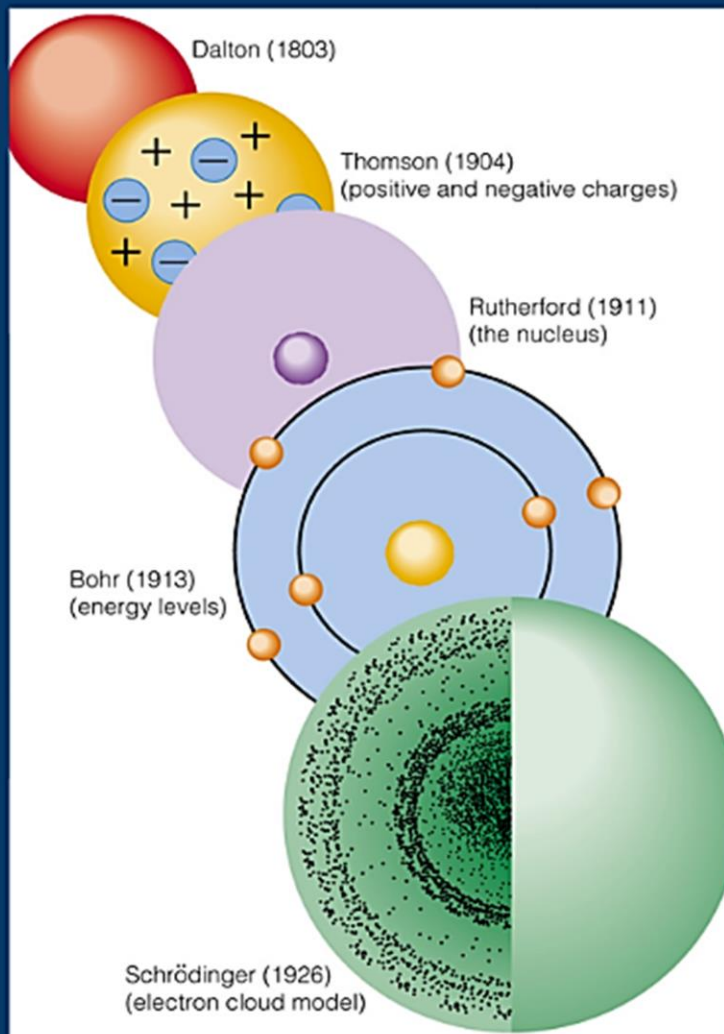

Atoms are the fundamental building blocks of matter, serving as the basic units that make up all elements and substances in the universe. These microscopic particles are the foundation of chemistry and play a crucial role in understanding the nature of our physical world.

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DISCOVERY OF ELECTRONS

Gases are normally bad conductors of electricity. However, under reduced pressure and/or at a high potential difference they conduct electricity. The liberation of energy from the passage of electric charge between two points (which are at different potentials) in a medium is called **electrical discharge.** Usually, the medium is a gas, often the atmosphere, and the potential difference is large. Some common examples of electrical discharges are lightning and the crackling sounds produced when synthetic clothes are separated in dry weather. Arc welding, fluorescent lamps, neon advertising signs, and mercury and sodium lamps are some other examples.

Electrical discharge through gases is studied by using a specially designed glass tube commonly called a **discharge tube.** It is a cylindrical glass tube with a metallic electrode at each end, as shown in Figure 2.1. These electrodes are connected to a high-tension power supply. Air from the tube is pumped out through a side tube connected to a vacuum pump. Using such a tube, Sir William Crookes found that gases conduct electricity at low pressures, hence the tube came to be known as **Crookes tube.**

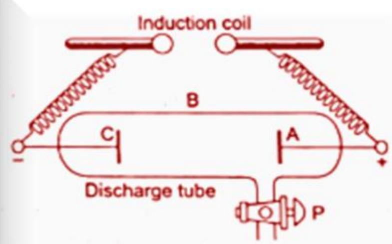


Fig. 2.1

◆◆ At low pressures, a gas conducts electricity (under a suitable voltage) because the mean free path of the electrons becomes longer, so they attain higher speeds before collision with an atom and are more likely to cause ionization. Table 2.1 shows the mean free path of an electron in various gases at different pressures.

Pressure (mmHg) → / Gases ↓	760.0	10.0	1.0	0.001
Hydrogen	1.83×10^{-7}	1.4×10^{-5}	1.4×10^{-4}	0.14
Oxygen	9.95×10^{-8}	7.56×10^{-6}	7.56×10^{-5}	0.076
Nitrogen	9.44×10^{-7}	7.17×10^{-6}	7.17×10^{-5}	0.017

◆ <u>When high voltage of the order of 10000 V is applied between the electrode of the tube , the following phenomena are observed at different pressure:</u>

1. At normal pressure (1 atm), no current flows between the electrodes.
2. At a pressure of about 20 mmHg, violet streamers of light pass between the cathode and the anode (Figure 2.2), accompanied by a crackling sound.

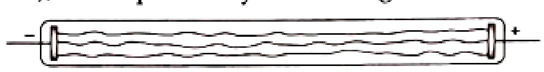


Fig. 2.2

3. At about 5 mmHg, the streamers of light change into a column of light referred to as the **positive column.** The colour of the column depends on the gas in the discharge tube. It is pinkish red for air.
4. At about 2 mmHg, a dark region, called the **Faraday dark space,** appears near the cathode and the cathode begins to glow, while the positive column diminishes in size. The glow at the cathode is referred to as the **negative glow** (Figure 2.3).

Fig. 2.3

5. At 1 mmHg, the positive column becomes shorter and the Faraday dark space grows in size. Another dark space, called the **Crookes dark space,** appears between the negative glow and the cathode (Figure 2.4). As the pressure is reduced to about 0.1 mmHg, the Crookes dark space expands and the positive column breaks up into a number of striations.

Fig. 2.4

6. At around 0.01 mmHg pressure or less, the Crookes dark space fills the whole tube and the wall of the tube glows or fluoresces (Figure 2.5). The colour of the glow depends on the material of the tube. For soda glass, it is yellowish green. As the pressure is reduced still further, the potential difference needed to maintain the discharge rises, and below about 10^{-3} mm of mercury the tube usually becomes a good insulator again.

Fig. 2.5

William Crookes, J J Thomson and others who studied the conduction of electricity in a discharge tube attributed the fluorescence of the walls of the tube to a radiation coming out of the cathode and falling on the walls. They called it **cathode rays.** By applying mutually perpendicular electric and magnetic fields across the discharge tube, Thomson was able to determine the speed and the specific charge (e/m or charge to mass ratio) of the cathode ray particles. He found that their speed ranged between 0.1 and 0.2 times the speed of light and that their specific charge was independent of the nature of the material of the cathode as well as the gas in the discharge tube. This led him to believe that the cathode ray particles were universal. Around the same time, it was experimentally found that certain metals, when heated to a high temperature or irradiated by ultraviolet light, emitted negatively charged particles, which were identical in nature to the cathode ray particles. This confirmed Thomson's surmise. He named the particles **electron**[1] and suggested that they are fundamental constitutents of matter.

Later, the American physicist R A Millikan found that the charge on an electron is 1.602×10^{-19} C. The accepted value of e/m at present is 1.76×10^{11} C kg^{-1}.

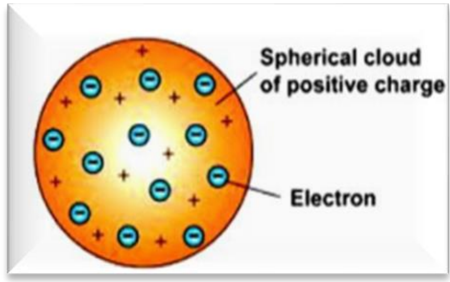
From the known values of charge and specific charge of an electron, its mass (m) can be determined as follows.

$$\frac{e}{e/m}=\frac{1.602\times10^{-19}\ \text{C}}{1.76\times10^{11}\ \text{C kg}^{-1}} \Rightarrow m=9.109\times10^{-31}\ \text{kg}.$$

PROPERTIES OF CATHODE RAYS

1. They are emitted normally from the cathode.
2. They travel in straight lines, which is proved by the fact that they produce a shadow of an object placed in their way.
3. They exert mechanical pressure, so they must consist of material particles.
4. They produce heat when they are stopped.
5. They are deflected by an electric field in a direction which shows that they are negatively charged.
6. They are deflected by a magnetic field.
7. They penetrate thin foils of aluminum, gold, etc.
8. They affect photographic plates.
9. They cause fluorescence and phosphorescence.
10. They are independent of the material of electrode and the nature of the gas in the tube.

◆◆ Thomson atomic model



As we have already discussed, the discovery of electrons implied the existence of positively charged particles in the atom. Thomson suggested that the atom is a positively charged sphere with a uniform charge distribution and that electrons are embedded in the sphere like the seeds in a watermelon or the plums in a pudding, as shown in Figure 2.6. This model is, therefore, known as the **watermelon model** or **plum-pudding model.** The arrangement of electrons is such that their mutual repulsion is balanced by their attraction by the positive charge.

The Thomson model was successful in explaining chemical reactions and radioactive disintegration. It also explained why only electrons are emitted when a metal is heated and not positively charged particles. However, it suffered from the following limitations.

1. It failed to explain the origin of the characteristic lines observed in the spectra emitted by hydrogen and other atoms.

The set-up for the experiment is shown in Figure 2.7. A radioactive source of α-particles (a doubly ionized helium atom denoted by ${}^{4}_{2}He$) such as polonium or ${}^{214}_{83}Bi$, is enclosed in a thick evacuated lead block with a narrow opening, which collimates the α-particles into a narrow beam. The α-particles are allowed to fall on a thin gold foil of thickness 21×10^{-7} m. After passing through the gold foil, they strike a zinc sulphide screen. Each strike produces a momentary flash, or scintillation. The screen and the detector (microscope) can be rotated. Thus, by counting the number of scintillations at different positions of the screen, the number of α-particles scattered (or deflected from their initial path) at different angles can be determined.

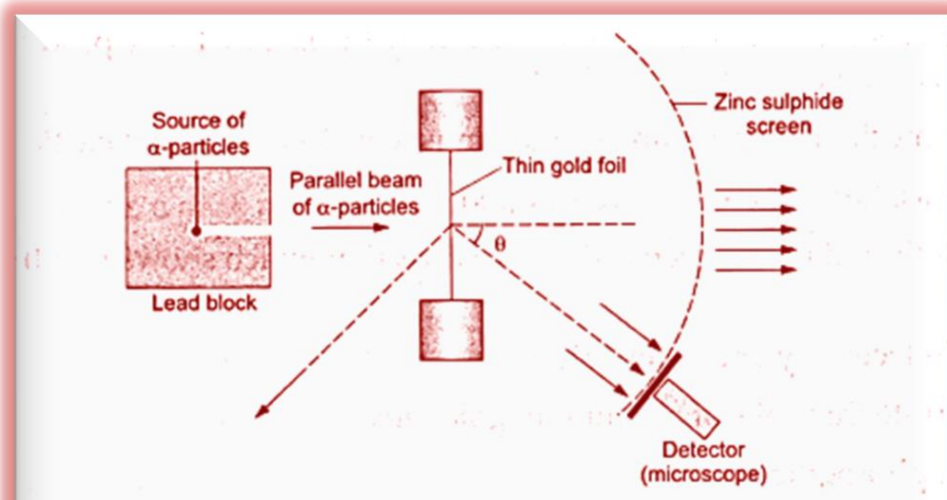


Fig. 2.7

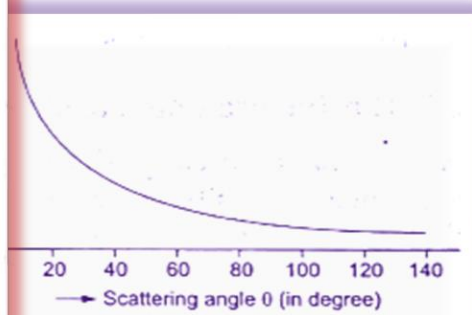


Fig. 2.8

When Rutherford and his associates plotted $N(\theta)$, the number of α-particles scattered, against θ, the angle of scattering, they obtained curves such as the one shown in Figure 2.8. The curves showed that

1. most of the α-particles passed straight through the gold foil or were undeflected,
2. a few α-particles, about 1 in 8000 (or about 0.125%), were deflected through 90° or more,
3. some even retraced their path, i.e., suffered a deflection of nearly 180°.

◆◆CONCLUSION:

1. As most of the α-particles passed undeviated through the gold foil, most of the space within the atom must be empty.
2. The α-particles which retraced their path suffered a large repulsive force due to a region of large positive charge. Thus, all the positive charge and the entire mass of the atom must be concentrated in a very small region at the centre of the atom.

Figure 2.9 explains the scattering of the α-particles on the basis of the Coulombian repulsion between them and the positively charged nucleus. Particles like 1 and 1′ pass through the atom at large distances from the nucleus and hence travel almost undeviated. Particles like 2 and 2′ or 3 and 3′, which pass closer to the nucleus, experience a large repulsive force and are deflected by large angles. Particles like 4 and 4′ which travel still closer to the nucleus are deflected by much larger angles, close to 180°. Finally, particles like 5, which approach the nucleus head on, are slowed down by the strong repulsive force, stop momentarily and retrace their path.

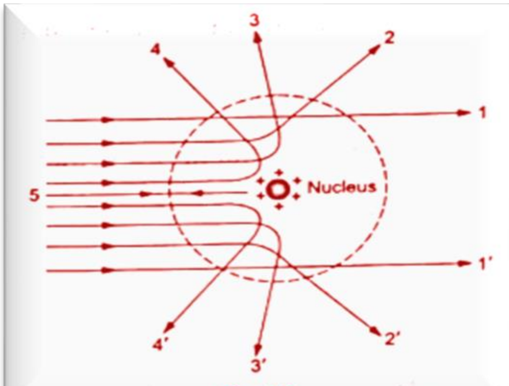


Fig. 2.9

◆◆ DISTANCE OF CLOSEST APPROACH:

The distance of closest approach is the closest that two charged particles can get to each other in a collision. Consider an α-particle of mass m and initial velocity v moving towards the nucleus of an atom, as shown in Figure 2.10. As it approaches the nucleus, it experiences a repulsive force, and its velocity and hence, its kinetic energy progressively decrease. The decrease in kinetic energy appears as an increase in the electrical potential energy of the system (that is, the α-particle and the nucleus), as the total energy remains conserved. At a certain distance r_0, which is the distance of closest approach, the α-particle comes momentarily to rest and then retraces its path. At this distance, the entire kinetic energy of the α-particle appears as the electrical potential energy of the system.

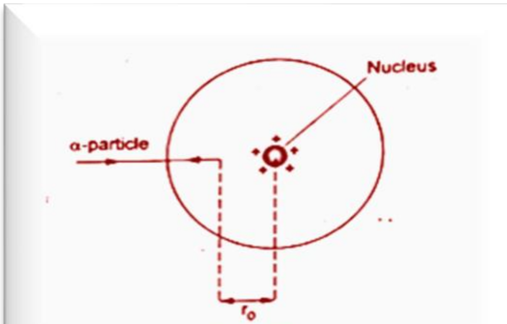


Fig. 2.10

The charge on the α-particle is $+2e$ and that on the scattering nucleus is $+Ze$, where Z is the atomic number of the scattering atom. The total initial energy of the system (α-particle plus scattering atom) is

$$E_i = \frac{1}{2}mv^2.$$

The total final energy of the system when the α-particle comes to rest is

$$E_f = \frac{1}{4\pi\epsilon_0}\frac{(2e)(Ze)}{r_0} = \frac{2Ze^2}{4\pi\epsilon_0 r_0}.$$

The application of the principle of conservation of energy gives

$$E_i = E_f \Rightarrow \frac{1}{2}mv^2 = \frac{2Ze^2}{4\pi\epsilon_0 r_0}$$

$$\Rightarrow \quad r_0 = \frac{Ze^2}{\pi\epsilon_0 mv^2}.$$

◆◆ IMPACT PARAMETER AND TRACJECTORY OF ALPHA PARTICLE

The impact parameter is the perpendicular distance between the velocity vector of the α-particle before it is deflected from its path and the centre of the scattering nucleus. it is Denoted 'b'.

Rutherford derived the following expression for the impact parameter in terms of the atomic number Z and the angle of scattering θ.

$$b = \frac{1}{4\pi\epsilon_0}\left(\frac{Ze^2 \cot\frac{\theta}{2}}{E_i}\right) = \left(\frac{Ze^2}{4\pi\epsilon_0 E_i}\right)\cot\frac{\theta}{2}.$$

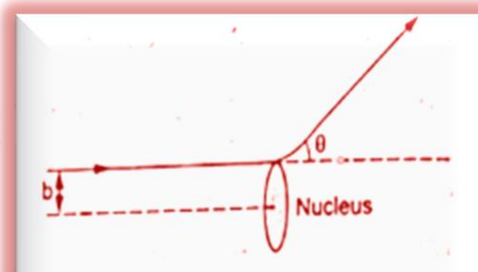


Fig. 2.11

Equation 2.4 shows that

$$b \propto \cot\frac{\theta}{2},$$

as the term within brackets is a constant. We can draw the following conclusions from Equation 2.4.

1. If the impact parameter is large, cot (θ/2) is large, which means that the scattering angle (θ) is small. Thus, α-particles which travel far away from the nucleus, suffer a small deflection.
2. If the impact parameter is small, cot (θ/2) is small, which means that the scattering angle is large. Thus, α-particles that come close to the nucleus, suffer a large deflection.
3. If the impact parameter is zero, cot (θ/2) is zero, which means that the scattering angle is 180°. Thus, α-particles approaching the nucleus head on, retrace their path.

◈ the trajectory of an α-particle depends upon the impact parameter.

◈◈ RUTHERFORD MODEL OF THE ATOM

The scattering of alpha – particle led Rutherford to propose a model of the ATOM.

◈ FEATURES

1. An atom consists of a central core where its entire positive charge and almost its entire mass is concentrated. This central core is known as the **nucleus** of the atom.
2. The size of the nucleus (diameter $\approx 10^{-15}$ m) is very small compared to the size of the atom (diameter $\approx 10^{-10}$ m).
3. The nucleus is surrounded by electrons. The number of electrons is such that their total negative charge just balances the total positive charge on the nucleus.
4. The electrons revolve round the nucleus in circular orbits just as planets revolve round the sun. The centripetal force necessary for their motion is provided by the force of attraction between the electrons and the nucleus.

In the case of the hydrogen atom, which has one proton in the nucleus with one electron revolving round it, the force of attraction between the two charges is

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}, \qquad \text{... 2.5}$$

where r is the radius of the orbit and ϵ_0 is the permittivity of vacuum. Since this force provides the centripetal force necessary to keep the electron revolving with a velocity v in a circular orbit of radius r,

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}. \qquad \text{... 2.6}$$

◈ DRAWBACKS

The Rutherford model could explain the electrical neutrality of an atom and the empty space within the atom indicated by the α-particle scattering experiment. However, it ran into the

1. In this model, an electron must move continuously round the nucleus in order not to be drawn into the nucleus by the Coulombian attraction. However, according to Maxwell's equations of electromagnetism, an accelerated charge must continuously emit electromagnetic radiation and since the revolving electron has a centripetal acceleration towards the nucleus, it should continuously emit radiation at all temperatures. If it did so, its energy would gradually decrease. Consequently, the radius of the circle described by it would gradually decrease until it fell into the nucleus. This is contrary to observation. Thus, the Rutherford model fails to explain the stability of the atom.

2. It had been observed that when hydrogen gas is heated, it emits radiation of certain definite frequencies. This could not be explained on the basis of the Rutherford model, according to which the revolving electron should emit a continuous spectrum. Besides, it should emit radiation at all temperatures, but hydrogen atoms emit radiation only when heated (or supplied with extra energy through other means).

◆◆ BOHR'S MODEL OF THE ATOM

According to quantum theory , radiation is emitted and absorbed in multiples of a basic unit , called quantum . The energy of each quantum is ....

$$E = h\nu, \quad \text{... 2.7}$$

where h is the Planck constant and ν is the frequency of the radiation.

Bohr imposed a quantum condition on the value of the angular momentum of an electron orbiting a nucleus. He showed that the experimental observations could be explained only if one assumed that the angular momentum is quantized. The Bohr model is based on the following postulates.

1. An electron moves in a circular orbit around the nucleus.
2. It can only revolve round the nucleus in orbits in which its angular momentum is an integral multiple of $\hbar$ or $h/2\pi$. These orbits are known as **stationary orbits** and as long as an electron is in any one of these orbits, it does not emit radiation. This is known as the **Bohr quantization rule.** According to this rule,

$$mv_n r_n = n\hbar = n\left(\frac{h}{2\pi}\right), \text{ where } n = 1, 2, 3, \ldots .$$

3. In each of the stationary orbits, an electron has a definite value of energy. An electron can jump from one stationary orbit to another. When it jumps from an orbit of higher energy E_2 to an orbit of lower energy E_1, it emits radiation of frequency ν, which is given by the Einstein–Planck equation

$$h\nu = E_2 - E_1. \quad \text{... 2.8}$$

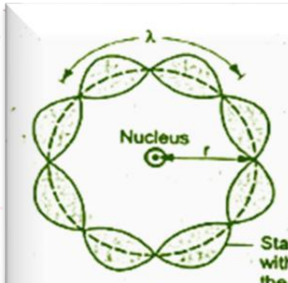
An electron can also absorb energy from some source and jump from an orbit of lower energy E_1 to an orbit of higher energy E_2.

◆ BOHR'S quantization rule And matter wave

The wave length of matter wave associated with a particle of mass m moving with velocity v is..

$$\lambda = \frac{h}{mv}. \quad \text{... 2.9}$$

According to the Bohr theory, when an electron revolves in a stationary orbit round the nucleus, it does not emit radiation. This means, the wave associated with it must be stationary, as transfer of energy does not occur only in the case of a stationary wave. You know that for stationary waves in a string, the length of the string is a multiple of the wavelength. Similarly, for stationary waves associated with an orbital electron, the circumference of the orbit must be an integral multiple of the wavelength λ, as shown in Figure 2.12. Thus, the condition for stationary waves associated with an orbital electron is



Stationary wave associated with electron revolving round the nucleus

Fig. 2.12

$$2\pi r = n\lambda = n\left(\frac{h}{mv}\right)$$

$$\Rightarrow \quad mvr = n\left(\frac{h}{2\pi}\right) = n\hbar, \quad \text{... 2.10}$$

which is the Bohr quantization condition.

◈◈ BOHR'S MODEL OF HYDROGEN ATOM

The hydrogen atom has only one proton in its nucleus with an electron revolving round it in a circular orbit.

◈ RADII OF STATIONARY ORBITS:

Consider an electron revolving round a nucleus of positive charge Ze (Z is the atomic number) with a constant speed v_n in a circular orbit of radius r_n. The centripetal force necessary for the circular motion is provided by the Coulomb attraction between the nucleus and the revolving electron. Hence,

$$\frac{(Ze)e}{4\pi\epsilon_0 r_n^2} = \frac{mv_n^2}{r_n} \quad \text{... 2.11}$$

$$\Rightarrow \quad r_n = \frac{Ze^2}{4\pi\epsilon_0 m v_n^2} \quad \text{... 2.12}$$

$$\Rightarrow \quad m r_n v_n^2 = \frac{Ze^2}{4\pi\epsilon_0}. \quad \text{... 2.13}$$

The angular momentum of the electron is $mv_n r_n$ which, according to the Bohr quantization rule, must be an integral multiple of $h/2\pi$. Hence,

$$mv_n r_n = n\left(\frac{h}{2\pi}\right), \quad \text{... 2.14}$$

where n is a positive integer.

Dividing Equation 2.13 by Equation 2.14,

$$v_n = \frac{Ze^2}{2\epsilon_0 nh}. \quad \text{... 2.15}$$

Substituting this value of v_n in Equation 2.12,

$$r_n = \left(\frac{\epsilon_0 h^2}{\pi m Z e^2}\right) n^2, \quad \text{... 2.16}$$

which shows that the radii of the orbits are proportional to n^2, and increase in the ratio 1 : 4 : 9 : 16 : ... . The parameter n is called the **principal quantum number.**

The period of revolution of an electron in the nth orbit is

$$T_n = \frac{2\pi r_n}{v_n}.$$

Inserting the values of r_n and v_n in the preceding equation,

$$T_n = 2\pi\left(\frac{\epsilon_0 n^2 h^2}{\pi m Z e^2}\right) \times \frac{2\epsilon_0 nh}{Ze^2} = \left(\frac{2\epsilon_0^2 h^3}{\pi m Z^2 e^4}\right) n^3.$$

The frequency of revolution in the nth orbit is

$$\nu_n = \frac{1}{T_n} = \left(\frac{\pi m Z^2 e^4}{2\epsilon_0^2 h^3}\right)\frac{1}{n^3}.$$

For hydrogen, $Z = 1$. Inserting the values of the physical constants in Equation 2.16, the radius of the first orbit ($n = 1$) is

$$r_1 = 0.053 \text{ nm}.$$

This is known as the **Bohr radius** and is usually denoted by a_0, i.e.,

$$a_0 = \frac{\epsilon_0 h^2}{\pi m e^2} = r_1. \qquad \text{... 2.17}$$

The radius of the nth orbit of hydrogen is, therefore,

$$r_n = a_0 n^2. \qquad \text{... 2.18}$$

To get the radius of the nth orbit of hydrogen-like ions, such as He^+, Li^{++} and Be^{+++} (which too have only one electron revolving around the nucleus), we just substitute the appropriate atomic number in the following equation.

$$r_n = \frac{n^2 a_0}{Z}. \qquad \text{... 2.19}$$

◈ Energy of STATIONARY ORBITS

Using Equation 2.13, the kinetic energy (KE) of an electron revolving around the nucleus with a constant speed v_n in an orbit of radius r_n is

$$\text{KE} = K_n = \frac{1}{2} m v_n^2 = \frac{Ze^2}{8\pi\epsilon_0 r_n}. \qquad \text{... 2.20}$$

The potential energy of the electron is equal to the product of the electric potential at the site of the electron and the charge on the electron. Hence,

$$\text{PE} = U_n = \frac{Ze}{4\pi\epsilon_0 r_n}(-e) = -\frac{Ze^2}{4\pi\epsilon_0 r_n}. \qquad \text{... 2.21}$$

The total energy of the electron in the nth orbit is, therefore,

$$E_n = K_n + U_n = \frac{Ze^2}{8\pi\epsilon_0 r_n} - \frac{Ze^2}{4\pi\epsilon_0 r_n} = -\frac{Ze^2}{8\pi\epsilon_0 r_n}. \qquad \text{... 2.22}$$

Substituting for r_n from Equation 2.16,

$$E_n = -\frac{mZ^2 e^4}{8\epsilon_0^2 h^2 n^2}. \qquad \text{... 2.23}$$

The total energy of the electron is thus negative, which indicates that the electron is bound to the nucleus. The innermost orbit, for which $n = 1$, has the lowest (that is, the most negative) energy and is known as the **ground state**. All the other states with higher energies are called **excited states.**

Equations 2.15 through 2.23 give various parameters of the atom when the electron is in the nth orbit or the atom is in the nth energy state.

◈ **For hydrogen , Z= 1 , inserting the value in equation 2.23**

$$E_1 = -\frac{me^4}{8\epsilon_0^2 h^2} = -13.6 \text{ eV}, \qquad \text{... 2.24}$$

where one electronvolt (eV) is the energy that an electron acquires in moving through a potential difference of 1 V and equals 1.6×10^{-19} J.

The energy of the electron in the nth orbit is, therefore,

$$E_n = \frac{E_1}{n^2} = -\frac{13.6}{n^2} \text{ eV}. \qquad \text{... 2.25}$$

From Equation 2.25, the energy of the electron in the nth orbit is proportional to $1/n^2$. The energy in the second orbit ($n = 2$) is $E_2 = E_1/4 = -3.4$ eV, in the third orbit ($n = 3$) is $E_3 = E_1/9 = -1.5$ eV, and so on. Thus, the energy of the electron increases (becomes less negative) with increase in the principal quantum number.

The energy of an electron in the nth orbit of a hydrogen-like ion with Z protons is

$$E_n = \frac{Z^2 E_1}{n^2}. \quad \text{... 2.26}$$

◈ Origin of SPECTRAL LINES

We know that for any system to be stable, its potential energy must be the minimum. When no energy is supplied to an atom from outside, its energy is the minimum and its electrons occupy the innermost orbits in accordance with the **Bohr–Bury scheme,** which has the following rules.

1. The maximum number of electrons that can be accommodated in a given orbit is given by the formula $2n^2$, where n is the principal quantum number of the orbit.
2. The outermost orbit can have at most 8 electrons, and the one next to the outermost (penultimate) can have at most 18 electrons, if permissible in accordance with Rule 1.
3. It is not always necessary for an orbit to be completely filled before the next higher orbit starts to be filled.

In the minimum-energy state, there is no available state of lower energy to which an electron can jump, so there can be no emission of radiation. When energy is supplied by some external source, some of the electrons absorb energy and jump to higher energy orbits. They remain in the excited state for about 10^{-8} s and then jump back to lower energy orbits in order to achieve equilibrium and in the process, radiate energy.

Let an electron jump from the mth orbit of energy E_m to the nth orbit ($m > n$) of energy E_n. The energy difference, $E_m - E_n$, between the two orbits is emitted as a photon of radiation of frequency ν, given by

$$\nu = \frac{E_m - E_n}{h}. \quad \text{... 2.27}$$

The corresponding wavelength, λ, is given by

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_m - E_n}{hc}, \quad \text{... 2.28}$$

where c is the velocity of electromagnetic radiation.

Substituting for E_m and E_n in Equation 2.28,

$$\frac{1}{\lambda} = \frac{mZ^2e^4}{8\epsilon_0^2 h^3 c}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = RZ^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \quad \text{... 2.29}$$

where

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c}, \quad \text{... 2.30}$$

is a constant, known as the **Rydberg constant.** Substituting the values of the physical constants appearing in Equation 2.30, the value of the Rydberg constant comes out to be $1.09737 \times 10^7\ \text{m}^{-1}$. In terms of the Rydberg constant, the energy of the atom in the nth state is

$$E_n = -\frac{RhcZ^2}{n^2}. \quad \text{... 2.31}$$

From Equation 2.24,

$$Rhc = \frac{me^4}{8\epsilon_0^2 h^2} = 13.6 \text{ eV}.$$

The rydberg = –13.6 eV is a unit, often used to express the energy of an atom.

For hydrogen, $Z = 1$, so Equation 2.29 reduces to

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right). \quad \text{... 2.32}$$

When electrons in hydrogen atoms jump to the first orbit from other orbits of higher energy, they emit radiation of wavelengths

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{m^2}\right), \quad \text{... 2.33}$$

where $m = 2, 3, 4, \ldots$. This series of lines in the spectrum of hydrogen was first observed by Lyman. Hence, it is called the **Lyman series.**

When electrons jump to the second orbit from orbits of higher energy, the wavelengths of the lines are given by

$$\frac{1}{\lambda}=R\left(\frac{1}{2^2}-\frac{1}{m^2}\right), \qquad \text{... 2.34}$$

where $m=3,4,5,\ldots$. This series of lines is called the **Balmer series.** Similarly, transitions from higher states to $n=3$ produce the **Paschen series,** to $n=4$ produce the **Brackett series,** to $n=5$ produce the **Pfund series,** to $n=6$ the **Humphreys series,** and so on. All these series have been detected and the wavelengths of the emitted radiations are found to be in excellent agreement with the Bohr theory for the hydrogen spectrum. Figure 2.13 shows the transitions corresponding to the series of lines of the hydrogen spectrum.

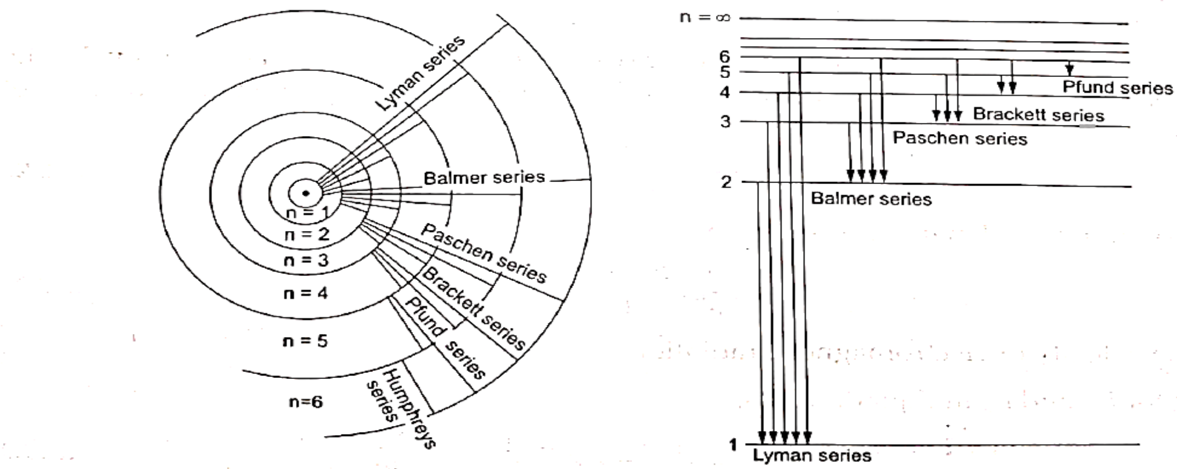


Fig. 2.13

Ionization Energy of an ATOM

When an atom loses an electron, the remaining orbital electrons no longer balance the positive charge of the nucleus, so the atom acquires a net positive charge and is known as a positive ion. Similarly, when an atom gains an electron by some means, it acquires a net negative charge, and is known as a negative ion. The process by which an atom is converted into an ion is called **ionization.**

In any atom, the revolving electrons are bound to the nucleus by an attractive force and their energy is negative. If the requisite amount of energy is supplied to the atom, these electrons may be completely detached from the nucleus or be moved to an infinite distance from the nucleus.

The minimum energy required to remove the electron in the hydrogen atom from the first orbit to infinity is called the ionization energy, E_i , of the hydrogen atom (or a hydrogen-like ion). It is equal to the difference in energy between the orbits $n=1$ and $n=\infty$ ($n=\infty$ means that the electron is completely detached from the nucleus). Thus,

$$E_i=E_\infty-E_1.$$

Using Equation 2.23, the preceding equation becomes

$$E_i=-\frac{mZ^2e^4}{8\epsilon_0 h^2}\left[\frac{1}{\infty}-\frac{1}{1}\right]=\frac{mZ^2e^4}{8\epsilon_0 h^2}. \qquad \text{... 2.35}$$

Inserting $Z=1$ and the values of the physical constants in Equation 2.35, the ionization energy of the hydrogen atom turns out to be

$$E_i^H=13.6\text{ eV}. \qquad \text{... 2.36}$$

Equation 2.36 is in agreement with the experimentally measured value. If more than +13.6 eV is supplied, the rest of the energy appears as the kinetic energy of the electron.

The potential difference through which an electron should be accelerated to acquire the ionization energy is called the **ionization potential.** The ionization potential of the hydrogen atom in the ground state is, therefore, 13.6 V.

➤ EXCITATION ENERGY OF AN ATOM

The energy required to take an atom from its ground state to an excited state is known as the excitation energy of the excited state.

The energy of a hydrogen atom in its ground state is –13.6 eV, and in its first excited state (when its electron is in the second orbit) is –3.4 eV. The hydrogen atom in the ground state, therefore, needs [–3.4 eV – (–13.6 eV)] = 10.2 eV of energy to reach its first excited state. In other words, the excitation energy of the hydrogen atom in the first excited state ($n = 2$) is, 10.2 eV.

The potential difference through which an electron must be accelerated to acquire the excitation energy is called the **excitation potential.** The excitation potential of the hydrogen atom in its first excited state is, therefore, 10.2 V.

➤ LIMITATION OF BOHR'S ATOMIC MODEL

The Bohr theory was able to explain the presence of particular wavelengths in the emission and absorption spectra of hydrogen corresponding to the transitions between various discrete orbits, as indicated by Equation 2.28. However, it could be applied to only one-electron systems such as the hydrogen atom or hydrogen-like ions. Besides, it failed to explain the fine structure (components with slightly different wavelengths) of the lines in the hydrogen spectrum as also the intensities of the spectral lines. What is more, the existence of certain stationary orbits has no theoretical basis. It is difficult to understand why the accelerated electron should not emit radiation in certain orbits. The theory also arbitrarily used two concepts—the particle (photon) nature to explain the emission and absorption of radiation and the wave nature to explain the propagation of radiation.

Attempts were made to revise this simple theory to make it more compatible with experimental observations and results. The principal modification was to assume that electrons revolve in elliptical orbits, and extra quantum numbers were assigned to limit the eccentricity of each orbit. These modifications, due to Wilson and Sommerfeld, though partially successful, were completely superseded in 1925 by the quantum mechanical model.

SOLVED EXAMPLES

EXAMPLE 1 **The energy of an electron in an excited hydrogen atom is –3.4 eV. What is its angular momentum? Given, $h = 6.626176 \times 10^{-34}$ J s.**

Solution The energy of an electron in the nth orbit of the hydrogen atom is

$$E_n = -\frac{13.6}{n^2}\ \text{eV}.$$

Inserting the value of E_n,

$$-3.4\ \text{eV} = -\frac{13.6}{n^2}\ \text{eV} \Rightarrow n = 2.$$

According to the Bohr quantization rule, the angular momentum of the revolving electron is

$$mvr = \frac{nh}{2\pi} = \frac{2 \times 6.626176 \times 10^{-34}}{2 \times 3.14}\ \text{J s} = 2.1102 \times 10^{-34}\ \text{J s}.$$

EXAMPLE 2 **The wavelength of the first line of the Lyman series for hydrogen is identical to that of the second line of the Balmer series for some hydrogen-like ion *X*. Calculate the energy of the first four levels of *X*. Also, find its ionization potential. Given that the ground state binding energy of the hydrogen atom is 13.6 eV.**

Solution The wavelength of the first line of the Lyman series for hydrogen is

$$\frac{1}{\lambda_1} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3R}{4}.$$

The wavelength of the second line of the Balmer series of X is

$$\frac{1}{\lambda_2} = RZ^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3Z^2R}{16},$$

where Z is the atomic number of X.

It is given that

$$\lambda_1 = \lambda_2 \;\Rightarrow\; Z^2 = 4 \;\Rightarrow\; Z = 2.$$

Hence, X is the singly ionized helium atom. The energy of the nth state of X is

$$E_n = -\frac{13.6Z^2}{n^2}\text{ eV} = -\frac{13.6\times 4}{n^2}\text{ eV} = -\frac{54.4}{n^2}\text{ eV}.$$

Inserting $n = 1, 2, 3, 4$, we get the energies of the first four levels of X as

$$E_1 = -\frac{54.4}{1^2}\text{ eV} = -54.4\text{ eV};\quad E_2 = -\frac{54.4}{2^2}\text{ eV} = -13.6\text{ eV};$$

$$E_3 = -\frac{54.4}{3^2}\text{ eV} = -6.04\text{ eV};\quad E_4 = -\frac{54.4}{4^2}\text{ eV} = -3.4\text{ eV}.$$

EXAMPLE 3 **Suppose that the potential energy of a system comprising an electron and a proton separated by a distance r is given by $-(ke^2)/3r^3$. Use the Bohr theory to obtain the energy levels of such a hypothetical hydrogen atom.**

Solution The potential energy is

$$U = -\frac{ke^2}{3r^3}.$$

The force between the electron and the nucleus is then

$$F = -\frac{\partial U}{\partial r} = -\frac{ke^2}{r^4}.$$

The negative sign shows that the force is attractive. This force supplies the centripetal force necessary for the circular motion of the electron. If v_n be the velocity of the electron,

$$\frac{mv_n^2}{r_n} = \frac{ke^2}{r_n^4}. \qquad (1)$$

The application of the Bohr quantization rule gives

$$mv_n r_n = \frac{nh}{2\pi}. \qquad (2)$$

$$\Rightarrow \qquad v_n = \frac{nh}{2\pi m r_n}. \qquad (3)$$

Using Equation 3, Equation 1 gives

$$r_n = \frac{4\pi^2 mke^2}{n^2h^2}. \qquad (4)$$

The kinetic energy of the electron in the nth orbit is

$$E_k = \frac{1}{2}mv_n^2 = \frac{ke^2}{2r_n^3},$$

where we have used Equation 1.

The potential energy of the electron is

$$E_p = U = -\frac{ke^2}{3r_n^3}.$$

The total energy of the electron in the nth orbit is, therefore,

$$E = E_k + E_p = \frac{ke^2}{2r_n^3} + \left(-\frac{ke^2}{3r_n^3}\right) = \frac{ke^2}{2r_n^3} - \frac{ke^2}{3r_n^3} = \frac{ke^2}{6r_n^3} = \left(\frac{h^6}{384\pi^6 m^3 k^2 e^4}\right)n^6.$$

EXAMPLE 4 **In a head-on collision of an α-particle with a gold nucleus ($Z = 79$), the distance of closest approach is 39.5×10^{-15} m. Calculate the energy of the α-particle.**

Solution The distance of closest approach, r_0, is given by

$$r_0 = \frac{1}{4\pi\epsilon_0}\left(\frac{2Ze^2}{E}\right) \Rightarrow E = \frac{1}{4\pi\epsilon_0}\left(\frac{2Ze^2}{r_0}\right).$$

Thus, $\frac{E_{max}}{E_{min}} = \frac{13.6 \text{ eV}}{13.6 \times \frac{3}{4} \text{ eV}} = \frac{4}{3}$

$$\Rightarrow \quad \frac{h\nu_{max}}{h\nu_{min}} = \frac{4}{3} \Rightarrow \frac{\nu_{max}}{\nu_{min}} = \frac{4}{3}.$$

EXAMPLE 6 **Calculate the angular momentum of an electron in the hydrogen atom when the energy is –1.51 eV.**

Solution The energy of an electron in the nth orbit of the hydrogen atom is

$$E = -\frac{13.6}{n^2} \text{ eV}.$$

Substituting $E = -1.51$ eV in the preceding equation,

$$-1.51 = -\frac{13.6}{n^2} \Rightarrow n^2 = \frac{13.6}{1.51} = 9.00 \Rightarrow n = 3.$$

The angular momentum of the electron in the nth orbit is given by

$$L = \frac{nh}{2\pi}.$$

Substituting $n = 3$ in the preceding equation,

$$L = \frac{3h}{2\pi}.$$

EXAMPLE 7 **A doubly ionized lithium atom is like a hydrogen atom with an atomic number $Z = 3$. Find the wavelength of radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit. The ionization energy of the hydrogen atom is 13.6 eV.** **[IIT]**

Solution The energy of the nth orbit of a hydrogen-like atom is

$$E_n = -13.6\left(\frac{Z^2}{n^2}\right).$$

The energies of an electron in the first and third Bohr orbit of Li^{2+} is

$$E_1 = -13.6\left(\frac{3^2}{1^2}\right) \text{eV} = -122.4 \text{ eV}; \quad E_3 = -13.6\left(\frac{3^2}{3^2}\right) \text{eV} = -13.6 \text{ eV}.$$

Thus, the energy required to transfer an electron from the first orbit to the third orbit is

$$\Delta E = E_3 - E_1 = -13.6 \text{ eV} - (-122.4 \text{ eV}) = 108.8 \text{ eV}.$$

If this energy were supplied by photons of frequency $\nu (= c/\lambda)$,

$$\Delta E = h\nu = \frac{hc}{\lambda} = 108.8 \text{ eV} \Rightarrow \lambda = \frac{hc}{108.8 \text{ eV}} = \frac{12400 \text{ eV Å}}{108.8 \text{ eV}} = 113.97 \text{ Å}.$$

EXAMPLE 9 **The electron in a hydrogen atom makes a transition $n_1 \to n_2$ where n_1 and n_2 are the principal quantum numbers. Assume the Bohr model to be valid. The time period of the electron in the initial state is eight times that in the final state. What are the possible values of n_1 and n_2?** **[IIT]**

Solution The time period of an electron in a Bohr orbit of principal quantum number n is

$$T = \left(\frac{2\epsilon_0^2 h^3}{\pi m Z^2 e^4}\right) n^3 \Rightarrow T \propto n^3 \Rightarrow \frac{T_1}{T_2} = \frac{n_1^3}{n_2^3}.$$

Given, $T_1 = 8T_2$. Using this in the preceding equation,

$$\frac{8T_2}{T_2} = \frac{n_1^3}{n_2^3} \Rightarrow n_1 = 2n_2.$$

Thus, the possible values of n_1 and n_2 are

$$n_1 = 2, n_2 = 1; \quad n_1 = 4, n_2 = 2; \quad n_1 = 6, n_2 = 3; \text{ and so on.}$$

POINT TO REMEMBER

- An atom is electrically neutral. Therefore, it contains an equal number of positive and negative charges.
- Thomson visualized the atom as a positively charged sphere that has a uniform charge distribution, with the negatively charged electrons embedded in it. His model is also known as the watermelon model or the plum-pudding model.
- The Thomson model was successful in explaining processes like chemical reactions and radioactive disintegration, but failed to explain the origin of the spectral lines of hydrogen and other atoms that were experimentally observed, as also the large-angle scattering of α-particles from thin metal foils, as observed by Rutherford.
- In the Rutherford model, all the positive charge and the entire mass of the atom is concentrated in a very small region at the centre of the atom, called the nucleus, with the electrons revolving around it in different orbits.
- The Rutherford model failed to explain the stability of the atom and the characteristic line spectra of the atoms of different elements.
- The distance of closest approach is the closest that two charged particles can get to each other in a collision.
- The impact parameter is the perpendicular distance of the velocity vector of the α-particle, before it is deflected from the centre of the scattering nucleus.
- In the Bohr model, an electron can revolve round the nucleus without emitting radiation only in those orbits in which its angular momentum is an integral multiple of $\hbar$ or $h/2\pi$. These orbits are known as stationary orbits. The radii of stationary orbits are proportional to n^2.
- In each stationary orbit, an electron has a definite value of energy, which is inversely proportional to n^2. An electron can jump from one stationary orbit to another. When an electron jumps from an orbit of higher energy to an orbit of lower energy, it emits radiation.
- The energy required to take an atom from its ground state to an excited state is known as the excitation energy of that excited state.

Objective Questions

I. Choose the correct option.

1. In the Bohr model of the hydrogen atom,
   (a) the radius of the nth orbit is proportional to n^2
   (b) the total energy of the electron in the nth orbit is inversely proportional to n
   (c) the radius of the nth orbit is proportional to $1/n$.
   (d) the radius of the nth orbit is proportional to $1/\sqrt{n}$.

2. If the energy required to remove one of the electrons from a neutral helium atom is 24.6 eV, the energy (in eV) required to remove both the electrons from a neutral helium atom is [IIT]
   (a) 38.2 (b) 40.2
   (c) 51.8 (d) 79.0

3. The ratio of the frequencies of the long wavelength limits of the Lyman and Balmer series of hydrogen is
   (a) 27 : 5 (b) 5 : 27
   (c) 4 : 1 (d) 1 : 4

4. The ratio of the minimum wavelength and the maximum wavelength in the Balmer series is
   (a) 5 : 9 (b) 5 : 36
   (c) 1 : 4 (d) 3 : 4

5. During which of the following transitions light of the lowest frequency is emitted?
   (a) $n = 1$ to $n = 2$ (b) $n = 2$ to $n = 6$
   (c) $n = 2$ to $n = 1$ (d) $n = 6$ to $n = 2$

6. The transitions of electrons from $n = 4, 5, 6, \ldots$ to $n = 3$ correspond to the [CET]
   (a) Lyman series (b) Balmer series
   (c) Paschen series (d) none of these

7. Which of the following has discrete values according to the Bohr theory? [CET]
   (a) Kinetic energy
   (b) Potential energy
   (c) Linear momentum
   (d) Angular momentum

8. For an electron in the Bohr model,
   (a) kinetic enrgy > potential energy
   (b) kinetic energy < potential energy
   (c) kinetic energy = potential energy
   (d) none of these

9. The electron in a hydrogen atom makes a transition from an excited state to the ground state. Which of the following statements is true? [IIT]
   (a) Its kinetic energy increases and its potential and total energies decrease.

(b) Its kinetic energy decreases, potential energy increases and total energy remains the same.
(c) Its kinetic and total energies decrease and its potential energy increases.
(d) Its kinetic, potential and total energies decrease.

10. As per the Bohr model, the minimum energy (in eV) required to remove an electron from the ground state of the doubly ionized Li atom (Z = 3) is [IIT]
(a) 1.51 (b) 13.6
(c) 40.8 (d) 122.4

11. An α-particle of energy 5 MeV is scattered through 180° by a fixed uranium nucleus. The distance of closest approach is of the order of [AIEEE]
(a) 1 Å (b) 10^{-10} cm
(c) 10^{-12} cm (d) 10^{-15} cm

12. In which of the transitions depicted in Figure 2-Q1 will the photon have the greatest energy? [AIEEE]

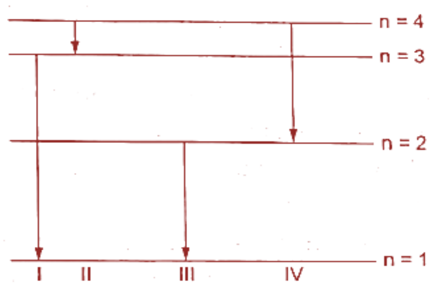


Fig. 2-Q1

(a) I (b) II
(c) III (d) IV

13. The energy of an electron in the lowest orbit ($n = 1$) in the hydrogen atom is –13.6 eV. How much energy would be required to ionize a hydrogen atom which is already in the first excited state?
(a) 3.4 eV (b) 10.2 eV
(c) 13.6 eV (d) 1.9 eV

II. Fill in the blanks.

1. The Thomson atomic model is also known as the ....
2. The central core of an atom containing positive charge is called the ....
3. Most of the space in an atom is ....
4. ...... correctly explained the spectrum of the hydrogen atom.
5. The radius of the nth orbit in a hydrogen atom is proportional to ....
6. The energy of the nth orbit in a hydrogen atom is proportional to ....
7. The value of the Rydberg constant is ....
8. 1 rydberg = ... eV.
9. An electron can revolve in only that orbit in which its angular momentum is an integral multiple of ....
10. When an electron makes a transition from a higher-order orbit to a lower-order orbit, energy is ....
11. When an electron makes a transition from a lower-order orbit to a higher-orbit, energy is ....

Very-Short-Answer Questions

1. What is the Bohr quantization condition for the angular momentum of an electron in the second orbit? [CBSE]
2. What do you understand by the term 'distance of closest approach'?
3. What is impact parameter?
4. Which series in the hydrogen spectrum lies in the ultraviolet region? [CBSE]
5. Which series of the hydrogen spectrum lies in the visible region of electromagnetic spectrum?[CBSE]
6. What is the ionization energy of the hydrogen atom?
7. What does the negative energy of the electron in the hydrogen atom signify?
8. Write the expression for the Rydberg constant. What is its value?
9. What is the Bohr radius?
10. The wavelengths of some of the spectral lines in the hydrogen spectrum are 9546 Å, 6463 Å and 1216 Å. Which of these belong to the Lyman series? [CBSE]
11. Figure 2-Q2 shows the stationary orbits of the hydrogen atom. Mark the transitions representing the Balmer and Lyman series. [CBSE]

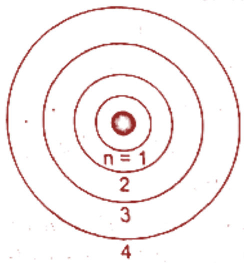


Fig. 2-Q2

Short-Answer Questions

1. State the postulates of the Bohr theory of the hydrogen atom. [CBSE]
2. Calculate the radius of the smallest orbit of the hydrogen atom. [CBSE]
3. Derive an expression for the energy of an electron in any orbit of hydrogen. [CBSE]
4. What were the observations made by Rutherford in the experiment on the scattering of α-particles?
5. Derive an expression for the distance of closest approach in Rutherford's α-particle scattering experiment.
6. Draw a labelled diagram of the Geiger–Marsden experiment on the scattering of α-particles. How is the size of the nucleus estimated in this experiment? [CBSE]

Long-Answer Questions

1. Describe the Rutherford atomic model. What are its drawbacks? [CBSE]
2. Give an account of the structure of an atom according to Bohr.
3. Give an account of the Bohr theory of the hydrogen atom and explain the energy level diagram of the hydrogen atom.
4. How does the Bohr theory account for the observed spectrum of hydrogen? What are the limitations of this theory?
5. State the Bohr postulate for the permitted orbits of the electron in a hydrogen atom. Use this postulate to prove that the circumference of the nth permitted orbit can contain exactly n wavelengths of the de Broglie waves associated with the electron in that orbit. [CBSE Sample Paper]

Numerical Problems

1. Find the radius of the first Bohr orbit of the electron in the hydrogen atom. Given, $h = 6.62 \times 10^{-27}$ erg, $m_e = 9.11 \times 10^{-28}$ g, $e = 4.804 \times 10^{-10}$ esu.
2. The first member of the Balmer series of hydrogen has a wavelength of 6563 Å. Calculate the wavelength of the second member. [BIT]
3. Find the ratio of the wavelengths of the first and the second members of the Lyman series of the hydrogen spectrum.
4. The radius of the first orbit of the hydrogen atom is 0.53 Å. What will be the radius of the second orbit of the Li^{++} ion?
5. Calculate the frequency of the photon which can excite an electron to –3.4 eV from –13.6 eV.
6. The energy of an electron in the nth orbit of the hydrogen atom is given by $E_n = -13.6/n^2$ eV. How much energy is required to take an electron from the ground state to the first excited state? [CBSE]
7. Find the wavelength of the first Lyman line when the electron makes a transition from the second orbit to the first. In what region of the electromagnetic spectrum does this line lie?
8. Determine the maximum wavelength that can be absorbed by hydrogen in its ground state.
9. The ground state energy of the hydrogen atom is –13.6 eV. If an electron makes a transition from the energy level –0.85 eV to the energy level –3.4 eV, calculate the wavelength of the spectral line emitted. To which series does this wavelength belong? [CBSE]
10. The ionization energy of the hydrogen atom is –13.6 eV. Calculate the wavelength of the photon which excites a hydrogen atom that is initially in the ground state to the $n = 4$ state. [MNR]
11. A hydrogen-like atom (atomic number Z) is in a higher excited state of quantum number n. The excited atom can make a transition to the first excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV. Alternatively, it can make a transition to the second excited state by successively emitting two photons of energies 4.25 eV and 5.95 eV. Determine the values of n and Z (ionization energy of hydrogen atom = 13.6 eV).
12. What is the angular momentum of an electron in the third orbit of an atom? [CBSE]
13. Show that the speed of an electron in the innermost orbit of the hydrogen atom is 1/137 times the speed of light in vacuum.
14. The energy of an electron in the nth orbit is given by $E_n = -13.6/n^2$ eV. Calculate the energy required to excite an electron from the ground state to the second excited state. [CBSE Sample Paper]
15. The ground-state energy of the hydrogen atom is –13.6 eV. (a) What is the kinetic energy of an electron in the 2nd excited state? (b) What is the potential energy of an electron in the 3rd excited state? (c) If the electron jumps to the ground state from the 3rd excited state, calculate the wavelength of the photon emitted. [CBSE]

16. The energy levels of an element are represented in Figure 2-Q3. Identify the transition which corresponds to the emission of a spectral line of wavelength 102.7 nm. [CBSE]

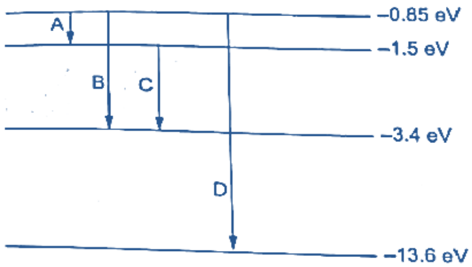


Fig. 2-Q3

17. The energy of an electron in the hydrogen atom may be expressed as

$$E_n = -\frac{13.6 \text{ eV}}{n^2}, n = 1, 2, 3, \ldots .$$

Using this expression show that (a) the electron in the hydrogen atom cannot have an energy of −6.8 eV, and (b) the space between the lines (consecutive energy levels) of the observed spectrum decreases as n increases. [CBSE]

18. The ground-state energy of an atom is 13.6 eV. The photon emitted during the transition of an electron from $n = 3$ to $n = 1$ of this atom is incident on a photosensitive material of unknown work function. If the photoelectrons emitted from the material have a maximum kinetic energy of 9 eV, calculate the threshold wavelength of the material. [CBSE]

ANSWERS

Objective Questions

I. 1. (a) 2. (d) 3. (b) 4. (a)
5. (d) 6. (c) 7. (d) 8. (a)
9. (a) 10. (d) 11. (c) 12. (a)
13. (a)

II. 1. plum-pudding model 2. nucleus
3. empty 4. Bohr 5. n^2 6. $1/n^2$
7. $1.097 \times 10^7 \text{ m}^{-1}$ 8. 13.6
9. $\hbar$ (or $h/2\pi$) 10. emitted
11. absorbed

Numerical Problems

1. 0.5282×10^{-8} cm 2. 4861 Å 3. 32 : 27
4. 0.70 Å 5. 2.47×10^{15} Hz 6. 10.2 eV
7. 122 nm, ultraviolet region 8. 122 nm
9. 4870 Å, Balmer series 10. 974 Å
11. $n = 6$, $Z = 3$ 12. 3.15×10^{-34} J s
14. 12.09 eV 15. (a) 1.51 eV (b) −1.70 eV (c) 970 Å
16. Transition D, energy change = 12.1 eV
18. 4×10^{-7} m