



11082CH02

## UNIT 2

# STRUCTURE OF ATOM

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## Objectives

After studying this unit you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity; and
- write the electronic configurations of atoms.

*The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements.*

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word '*a-tomio*' which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit 1). Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton.

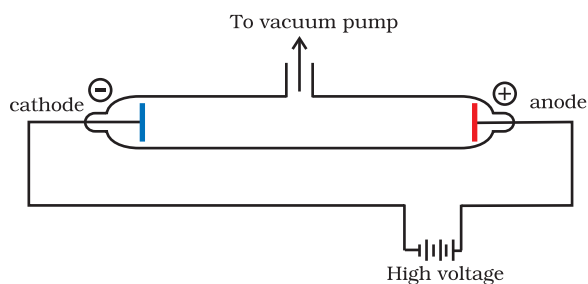
## 2.1 DISCOVERY OF SUB-ATOMIC PARTICLES

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : “Like charges repel each other and unlike charges attract each other”.

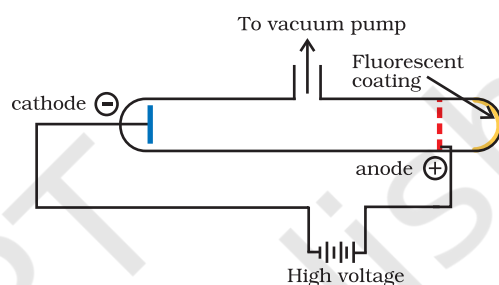
### 2.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in class XII. These results suggested the particulate nature of electricity.

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating [Fig. 2.1(b)].



**Fig. 2.1(a)** A cathode ray discharge tube



**Fig. 2.1(b)** A cathode ray discharge tube with perforated anode

The results of these experiments are summarised below.

- (i) The cathode rays start from cathode and move towards the anode.
- (ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.
- (iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2).
- (iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons**.
- (v) The characteristics of cathode rays (electrons) do not depend upon the

material of electrodes and the nature of the gas present in the cathode ray tube.

*Thus, we can conclude that electrons are basic constituent of all the atoms.*

### 2.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge ( $e$ ) to the mass of electron ( $m_e$ ) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

- (i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.
- (ii) the mass of the particle — lighter the particle, greater the deflection.

- (iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of  $e/m_e$  as:

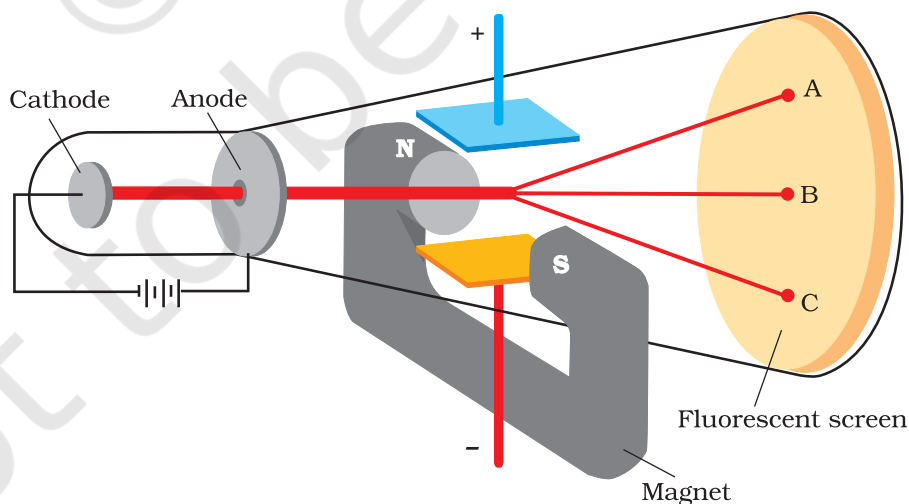
$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1} \quad (2.1)$$

Where  $m_e$  is the mass of the electron in kg and  $e$  is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is  $-e$ .

### 2.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be  $-1.6 \times 10^{-19} \text{ C}$ . The present accepted value of electrical charge is  $-1.602176 \times 10^{-19} \text{ C}$ . The mass of the electron ( $m_e$ ) was determined by combining these results with Thomson's value of  $e/m_e$  ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19} \text{ C}}{1.758820 \times 10^{11} \text{ C kg}^{-1}} = 9.1094 \times 10^{-31} \text{ kg} \quad (2.2)$$



**Fig. 2.2** The apparatus to determine the charge to the mass ratio of electron

### 2.3.3 Evidence for the quantized\* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at  $7.50 \times 10^{14}$  Hz to red at  $4 \times 10^{14}$  Hz. Such a spectrum is called **continuous spectrum**. Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

#### Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **“excited”**. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission

spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 2.10 page 45).

**Line emission spectra** are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

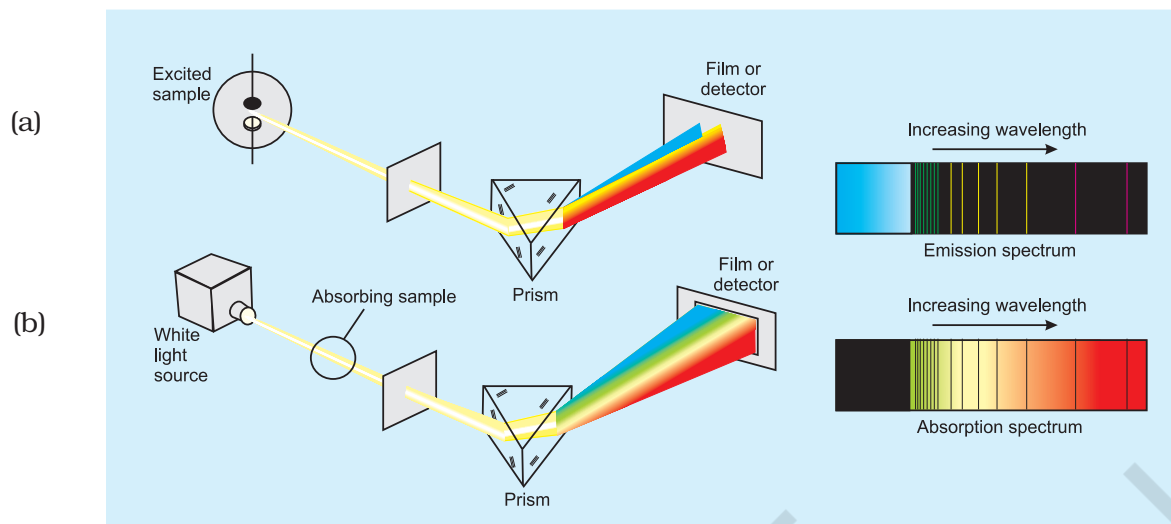
Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

#### Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the  $H_2$  molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of *discrete frequencies*. The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if

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\* The restriction of any property to discrete values is called quantization.



**Fig. 2.10 (a) Atomic emission.** The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption.** When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

spectral lines are expressed in terms of wavenumber ( $\bar{\nu}$ ), then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{\nu} = 109,677 \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \text{ cm}^{-1} \quad (2.8)$$

where  $n$  is an integer equal to or greater than 3 (i.e.,  $n = 3, 4, 5, \dots$ )

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{\nu} = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \quad (2.9)$$

where  $n_1 = 1, 2, \dots$

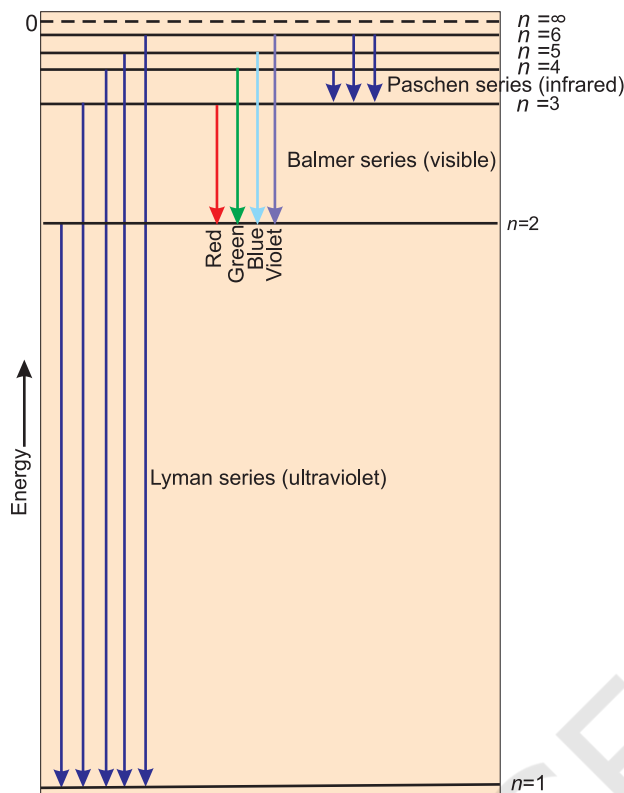
$n_2 = n_1 + 1, n_1 + 2, \dots$

The value  $109,677 \text{ cm}^{-1}$  is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to  $n_1 = 1, 2, 3, 4, 5$  are known as Lyman, Balmer, Paschen, Brackett and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig 2.11 (page, 46) shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes

**Table 2.3 The Spectral Lines for Atomic Hydrogen**

Series	$n_1$	$n_2$	Spectral Region
Lyman	1	2, 3, ...	Ultraviolet
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	Infrared
Brackett	4	5, 6, ...	Infrared
Pfund	5	6, 7, ...	Infrared



**Fig. 2.11** Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)

more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

## 2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to

rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

- The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

### Angular Momentum

Just as linear momentum is the product of mass ( $m$ ) and linear velocity ( $v$ ), angular momentum is the product of moment of inertia ( $I$ ) and angular velocity ( $\omega$ ). For an electron of mass  $m_e$ , moving in a circular path of radius  $r$  around the nucleus,

$$\text{angular momentum} = I \times \omega$$

Since  $I = m_e r^2$ , and  $\omega = v/r$  where  $v$  is the linear velocity,

$$\therefore \text{angular momentum} = m_e r^2 \times v/r = m_e v r$$

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by  $\Delta E$ , is given by:

$$v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \quad (2.10)$$

Where  $E_1$  and  $E_2$  are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

- The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots \quad (2.11)$$