

**Section-I**

***Phyiscal and  
General Chemistry***

## Atomic Structure

### 1.1. ELECTRONIC STRUCTURE OF ATOM

Rutherford atomic model laid the foundation of the electronic structure of atom. The term ‘electronic structure’ means (i) number of electrons in the atom, (ii) distribution of electrons in the space around the nucleus *i.e.* the arrangement of electrons in the extra-nuclear part and (iii) the relative energy levels of these distributions. Rutherford recognised that electrons revolve around the heavy positively charged nucleus in orbits. This model is analogous to solar system where nucleus may be compared to the sun and the electrons to the planets.

#### Introduction to Atomic Structure

The founder of “atomic theory” **John Dalton** (1767-1844), an English scientist, postulated his theory as :

- (a) Matter is composed of atoms which cannot be subdivided.
- (b) Atom is the smallest particle of matter that takes part in a chemical reaction.
- (c) Atoms of the same element have similar properties like mass, volume and chemical reactivity.
- (d) Atoms combine in a definite proportion to form molecules.

However, modern researches have conclusively proved that atom is no longer an indivisible particle. Out of the thirty five particles which exist in an atom, electron, proton and neutron are the three fundamental particles of atom. Although the atom is extremely small, it has a definite complicated structure. The arrangement of these constituent particles in atom is called the **atomic structure**.

#### Rutherford model of an atom

According to Rutherford, every atom has two parts (i) nucleus, and (ii) extra-nuclear part.

(i) **Nucleus.** Nucleus is a small positively charged part of the atom consisting of protons and neutrons, collectively called as **nucleons**. Nucleus has a diameter of the order of  $10^{-14}$  to  $10^{-16}$  m and is situated at the center of the atom. It carries almost the entire mass of the atom.

(ii) **Extra-nuclear part.** In this part of the atom, the electrons revolve at a very high speed in a fixed path called **orbits** or **shells**. This extra-nuclear part provides volume to an atom called **atomic volume**.

**1.1.1. Drawbacks of Rutherford model.** According to **Clark Maxwell**, a charged particle moving under the influence of attractive force continuously loses energy in the form of electromagnetic radiations. Bohr argued that the electron (a charged body) moving around the nucleus in an orbit must emit radiations and gradually lose energy. As a result of this, motion of electron should slow down

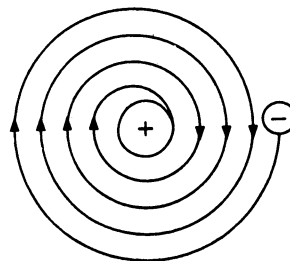


Fig. 1.1. Gradual decrease in the radius of orbit.

and hence it should not be able to withstand the attraction of the nucleus. Consequently, the orbit would become smaller and the electron moves closer and closer to the nucleus following a spiral path as shown in Fig. 1.1.

Finally, the electron would fall into the nucleus and atom would collapse. Since atom is quite stable and such a collapse of the atom does not take place, there must be some drawbacks in the Rutherford's model of an atom.

**Nature and characteristics of light :** Newton regarded light as a stream of particles called corpuscles of light. This concept successfully explained the phenomena of reflection and refraction but could not explain the phenomena of diffraction and interference. Therefore, Newton's corpuscular theory was discarded and replaced by wave theory proposed by Huygens. Wave theory of light has successfully explained the phenomena of interference and diffraction.

**1.1.2. Electromagnetic radiations.** Clark Maxwell (1864) observed that an alternating current of high frequency is capable of radiating continuous energy in the form of waves. He termed these

waves as **electromagnetic waves or electromagnetic radiations**. These are so named because these waves have electric and magnetic properties. Ordinary light rays, infrared rays, ultraviolet rays, X-rays,  $\gamma$ -rays, etc. are also regarded as electromagnetic waves because similar waves can be produced by moving a charged body in the magnetic field. Electromagnetic waves do not require any medium for their propagation. Thus, the electromagnetic radiations have following important characteristics.

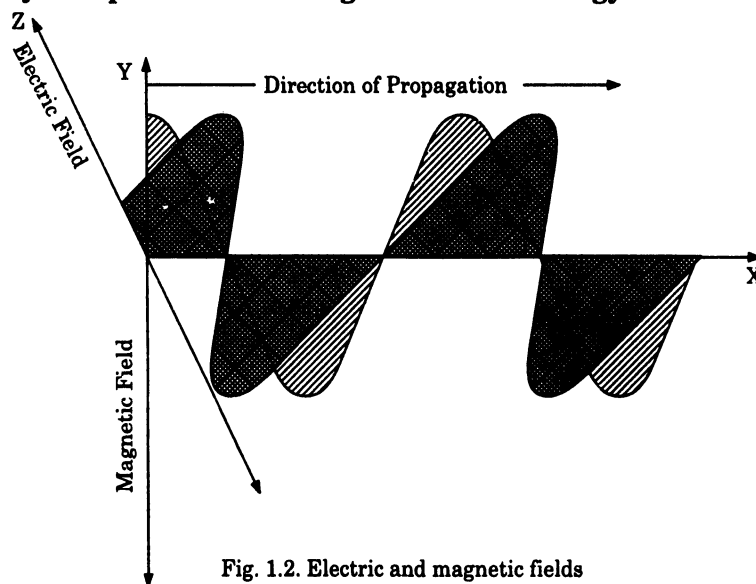


Fig. 1.2. Electric and magnetic fields associated with an electromagnetic wave.

- (i) The electromagnetic waves consist of electric and magnetic fields oscillating perpendicular to each other and both are perpendicular to the direction of propagation of radiation.
- (ii) These waves do not require any medium for propagation.
- (iii) All electromagnetic waves travel with the same speed. (i.e.  $3.0 \times 10^8 \text{ m sec}^{-1}$  or speed of light)

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. All waves have five characteristics by which they can be recognised, viz., wave length, frequency, velocity, wave number and amplitude.

**1. Wave length ( $\lambda$ ) :** It is the distance between two neighbouring crests or troughs of the wave as shown in Fig. 1.3. It is denoted by Greek letter **lambda** ( $\lambda$ ) and is measured in Angstrom ( $\text{\AA}$ ) or nanometer (nm).

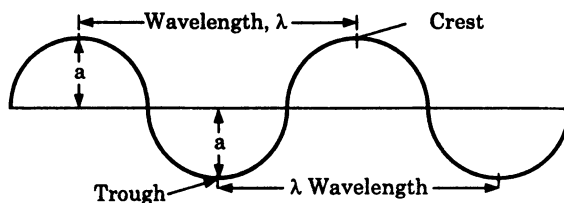


Fig. 1.3

$$1 \text{ \AA} = 10^{-10} \text{ m or } 10^{-8} \text{ cm}$$

$$1 \text{ nm} = 10^{-9} \text{ m or } 10^{-7} \text{ cm.}$$

Besides these two generally used units of wavelength, sometimes following units are also used.

$$1 \text{ pm (picometer)} = 10^{-12} \text{ m or } 10^{-10} \text{ cm.}$$

$$1 \text{ \mu (micron)} = 10^{-6} \text{ m}$$

$$1 \text{ m\mu (millimicron)} = 10^{-9} \text{ m}$$

**2. Frequency ( $\nu$ )** : It is defined as the number of waves which pass through a given point in one second. It is denoted by Greek letter **nu** ( $\nu$ ) and is expressed in units of **cycles per second (cps)** or **Hertz (Hz)**.

$$1 \text{ cps} = 1 \text{ Hz.}$$

**3. Velocity ( $c$ )**. The distance travelled by a wave in one second is called velocity of the wave. It is denoted by letter  $c$ . It is related to frequency and wavelength of the wave by the expression

$$c = \nu \times \lambda \text{ or } \nu = c/\lambda$$

Velocity of all electromagnetic radiations in space or in vacuum is same and is equal to  $3 \times 10^8 \text{ m/s}$  or  $3 \times 10^{10} \text{ cm/s}$ .

**4. Wave number ( $\bar{\nu}$ )** : It is defined as the number of wave lengths per centimeter. It is equal to the inverse of wavelength expressed in centimeters. It is denoted by  $\bar{\nu}$  (**nu bar**) and its unit is  $\text{cm}^{-1}$ . Thus,

$$\text{Wave number, } \bar{\nu} = \frac{1}{\text{Wave length } (\lambda)} \quad \text{i.e. } \bar{\nu} = \frac{1}{\lambda}$$

$$\therefore \text{Frequency, } \nu = \frac{c}{\lambda} = c\bar{\nu}$$

**5. Amplitude ( $a$ )** : It represents the height of the crest or depth of the trough of a wave. It is denoted by the letter ' $a$ ' as shown in Fig 1.3 and determines the intensity or brightness of radiation.

**Relationship between velocity, wave length and frequency of a wave** : These three important characteristics of a particular wave are related as

$$\text{Velocity} = \text{Wavelength} \times \text{frequency}$$

i.e.

$$c = \lambda \times \nu$$

Since all electromagnetic waves have the same velocity (i.e.  $c = 3.0 \times 10^8 \text{ m sec}^{-1}$ ). Thus, the various waves differ from one another in their wavelength or frequency. Hence for a wave of short wavelength the frequency is higher while a wave with long wave length has low frequency.

**Example 1.1.** Calculate the frequency and wave number of yellow radiations having a wave length of 560 nm.

**Solution.** (a) Frequency of yellow radiation,  $\nu = \frac{c}{\lambda}$

$$\text{Given} \quad c = 3.0 \times 10^8 \text{ m/sec. } \lambda = 560 \text{ nm} = 560 \times 10^{-9} \text{ m} = 560 \times 10^{-7} \text{ cm}$$

$$\therefore \nu = \frac{3 \times 10^8 \text{ m/sec}}{560 \times 10^{-9} \text{ m}} = 5.36 \times 10^{14} \text{ cycles/sec}$$

$$(b) \quad \text{Wave number, } \bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{1}{560 \times 10^{-7} \text{ cm}} = 17857 \text{ cm.}$$

**Example 1.2.** Calculate the wave number of lines having the frequency of  $5 \times 10^{16}$  cycles/sec.

**Solution.** Given  $c = 3.0 \times 10^8$  m/sec.  
 $\nu = 5.0 \times 10^{16}$  cycles/sec.

Wave number,  $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$

$$\therefore \bar{\nu} = \frac{5 \times 10^{16} \text{ cycles/sec}}{3 \times 10^8 \text{ m/sec}} = 1.66 \times 10^8 \text{ cycles m}^{-1}$$

**Example 1.3.** Calculate the wavelength, frequency and wave number of a light wave whose time period is  $2.4 \times 10^{-10}$  s.

**Solution.** We know that the time period,  $T$ , is the time for complete one cycle i.e.

$$T = \frac{1}{\nu} \quad \text{or} \quad \nu = \frac{1}{T} = \frac{1}{2.4 \times 10^{-10} \text{ s}} = 4.16 \times 10^9 \text{ sec}^{-1}.$$

Now  $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m/sec}}{4.16 \times 10^9 \text{ sec}^{-1}} = 7.2 \times 10^{-2} \text{ m}.$

and  $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{7.2 \times 10^{-2} \text{ m}} = 13.88 \text{ m}^{-1}.$

**Example 1.4.** Calculate the wave length of radiowave associated with frequency of  $1.6 \times 10^8$  KHz.

**Solution.**  $\nu = 1.6 \times 10^8 \text{ kHz} = 1.6 \times 10^8 \times 10^3 \text{ Hz} = 1.6 \times 10^{11} \text{ Hz}$   
 $c = 3.0 \times 10^8 \text{ m sec}^{-1}$   
 $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{1.6 \times 10^{11} \text{ Hz}} = 1.875 \times 10^{-2} \text{ m}$

## 1.2. ELECTROMAGNETIC SPECTRUM

It is defined as the arrangement of various types of electromagnetic radiations in terms of increasing (or decreasing) wave lengths (or frequency). The complete range of electromagnetic waves is called electromagnetic spectrum. The wavelengths of various waves increases in the following order.

**Cosmic rays <  $\gamma$ -rays < X-rays < UV rays < Visible < IR rays < Micro waves > Radio waves**

**Limitations of electromagnetic wave theory.** As already discussed, electromagnetic wave theory successfully explained the properties of light such as interference and diffraction but it could not explain the phenomena of **photo electric effect** and **black body radiations**. Max Planck (1900) put forward a theory known as quantum theory of radiation to explain these phenomena.

### Planck's Quantum Theory

In order to explain the phenomena of photoelectric effect and black body radiations, **Max Planck** postulated quantum theory of radiations, which was further extended by **Einstein** (1905). The main features of Planck's quantum theory are :

(i) The radiant energy is not emitted or absorbed continuously but discontinuously in the form of **small packets of energy called quantum**. For light the quantum of energy is termed as **photon**.

(ii) The energy associated with each quantum is directly proportional to the frequency of the radiation i.e.

$$E \propto \nu \text{ or } E = h\nu$$

...(i)

where  $h$  is called Planck's constant.

Numerically,  $h = 6.62 \times 10^{-34}$  Joules sec or  $6.62 \times 10^{-27}$  erg sec.

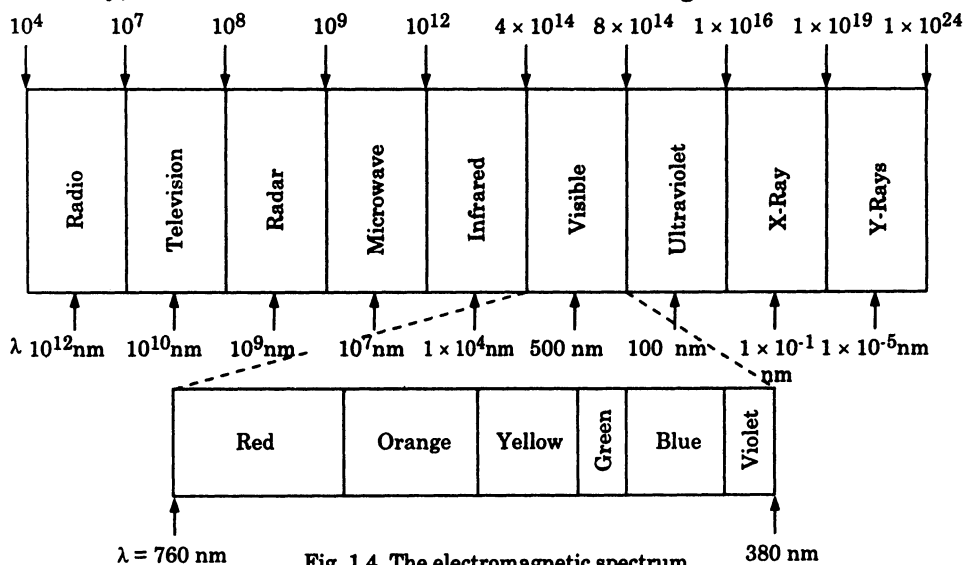


Fig. 1.4. The electromagnetic spectrum.

(iii) The total amount of energy emitted or absorbed by a body will be some whole number multiple of quantum by an integer  $n$  i.e.

$$E = n h \nu$$

where  $n$  is an integer e.g.,  $n = 1, 2, 3, \dots$ , etc.

This implies that a body can emit or absorb energy equal to  $h\nu$ ,  $2h\nu$ ,  $3h\nu$ ,  $4h\nu$ , .... etc. but not in fractions i.e.  $0.5 h\nu$ ,  $1.2 h\nu$ . Further we know that

$$\nu = \frac{c}{\lambda}$$

$$\therefore \text{Equation (i) becomes } E = \frac{hc}{\lambda}$$

This equation represents that a wave of higher frequency or lower wave length will be more energetic and *vice versa*, e.g., violet light of high frequency has more energy while the red light of low frequency is associated with less energy.

**Example 1.5.** Determine the energy of 1 mole photons of radiation whose frequency is  $5.5 \times 10^{10} \text{ sec}^{-1}$ .

**Solution.** We know,  $E = h\nu$

$$h = 6.62 \times 10^{-34} \text{ J sec.}$$

$$\nu = 5.5 \times 10^{10} \text{ sec}^{-1}.$$

$$\therefore E = 6.62 \times 10^{-34} \text{ J sec} \times 5.5 \times 10^{10} \text{ sec}^{-1} = 3.64 \times 10^{-23} \text{ J/photon}$$

$$\text{Energy of one mole of photon} = 6.02 \times 10^{23} \times 3.64 \times 10^{-23} \text{ J/photon} = 21.9 \text{ J}$$

**Example 1.6.** The yellow line in the spectrum of sodium vapour lamp has a wave length of 590 nm. What minimum accelerating potential is needed to excite this line in an electron tube containing sodium vapour?

$$\text{Solution. } E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \text{ J sec} \times 3.0 \times 10^8 \text{ ms}^{-1}}{590 \times 10^{-9} \text{ m}} = 0.0337 \times 10^{-17} \text{ J}$$

$$= \frac{0.0337 \times 10^{-17} \text{ J}}{1.602 \times 10^{-19} \text{ J/eV}} = \mathbf{2.10 \text{ eV.}} \quad [\because 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}]$$

**Example 1.7.** Which has higher energy, a photon of red light with  $\lambda = 7600 \text{ \AA}$  or a photon of green light with  $\lambda = 5200 \text{ \AA}$ ?

**Solution.**  $E = \frac{hc}{\lambda}$

$$E_{\text{Red}} = \frac{6.62 \times 10^{-34} \text{ J sec} \times 3.0 \times 10^8 \text{ m sec}^{-1}}{7600 \times 10^{-10} \text{ m}} = \mathbf{2.6 \times 10^{-19} \text{ J}}$$

$$E_{\text{green}} = \frac{6.62 \times 10^{-34} \text{ J sec} \times 3.0 \times 10^8 \text{ m sec}^{-1}}{5200 \times 10^{-10} \text{ m}} = \mathbf{3.8 \times 10^{-19} \text{ J}}$$

$\therefore$  Green light has higher energy.

**Example 1.8.** Electromagnetic radiation of wave length  $242 \text{ nm}$  is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in  $\text{KJ mol}^{-1}$ . (Roorkee Entrance 1989, 92)

**Solution.**  $\lambda = 242 \text{ nm} = 242 \times 10^{-9} \text{ m}$

$$h = 6.62 \times 10^{-34} \text{ J sec.}$$

$$c = 3.0 \times 10^8 \text{ m sec}^{-1}$$

Now,  $E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \text{ J sec} \times 3.0 \times 10^8 \text{ m sec}^{-1}}{242 \times 10^{-9} \text{ m}} = \mathbf{0.082 \times 10^{-17} \text{ J}}$

$\therefore$  Energy for ionisation of electrons from one mole of sodium atom

$$= 0.082 \times 10^{-17} \text{ J} \times 6.02 \times 10^{23} \text{ mole}^{-1}$$

$$= 494.5 \times 10^3 \text{ J mole}^{-1} = \mathbf{494.5 \text{ kJ}}$$

**Example 1.9.** Find the number of quanta of radiations of frequency  $4.75 \times 10^{13} \text{ sec}^{-1}$ , required to melt  $100 \text{ g}$  of ice. The energy required to melt  $1 \text{ g}$  of ice is  $350 \text{ J}$ .

**Solution.**  $E = h\nu = 6.62 \times 10^{-34} \text{ J sec} \times 4.75 \times 10^{13} \text{ sec}^{-1}$   
 $= 31.445 \times 10^{-21} \text{ J}$

Energy required to melt  $100 \text{ g}$  ice  $= 350 \text{ J} \times 100 = 35000 \text{ J}$

$\therefore$  Number of quanta of energy  $= \frac{35000 \text{ J}}{31.445 \times 10^{-21} \text{ J}} = \mathbf{11.13 \times 10^{23}}$

### 1.3. STUDY OF SOLAR AND ATOMIC SPECTRA

We know that if the rays of white light from the sun is passed through a prism or a grating, it splits into a series of coloured bands called spectrum (a rainbow of colours). These radiations of different colours differ in wave lengths or frequencies. The instrument used to separate and analyse the seven colours of spectrum is known as **spectrograph** or **spectroscope**. Depending upon the source of radiation (*i.e.* sun, a bulb, a metal salt, hydrogen gas etc), the spectra are broadly classified into two groups namely (i) Emission spectra and (ii) Absorption spectra.

(i) **Emission spectra.** When the radiation emitted from sun, a bulb or a glowing body is passed through a

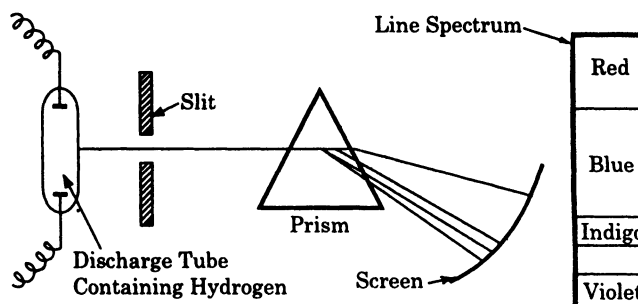


Fig. 1.5. The emission spectrum of hydrogen atom.

prism and the resulting rays are recorded on the photographic plate, the spectrum obtained is called **emission spectra**. Thus, the spectrum obtained from a light coming directly from a source when examined with a spectroscopic, it is known as emission spectra. Emission spectra are of three types.

(a) **Continuous spectra.** A continuous spectrum is one in which all wave lengths of radiations are so inter mixed that there is no line of separation between two colours *e.g.*, the seven colours of the spectrum are violet, indigo, blue, green, yellow, orange, red. These colours are so continuous that each one of them merges into the next. Such spectrum is called **continuous spectrum**.

(b) **Line spectra.** A line spectrum is that spectrum in which only certain wave lengths or bright coloured lines appear on a dark background. This type of spectrum is observed when some volatile salt (*e.g.*, sodium chloride) is heated in a bunsen flame or electric discharge is passed through mercury vapour lamp. This spectra has some isolated coloured lines on the photographic plate separated from each other by dark spaces *i.e.* no continuous spectrum is

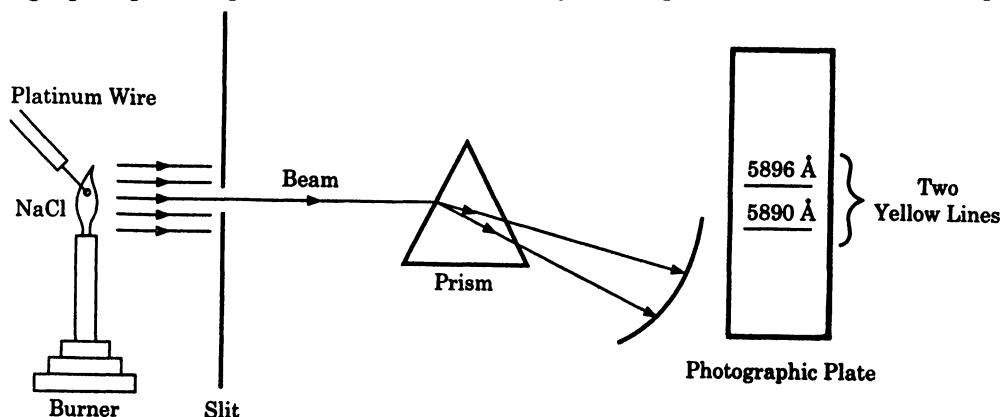


Fig 1.6. Line spectrum produced from a volatile salt placed in a flame.

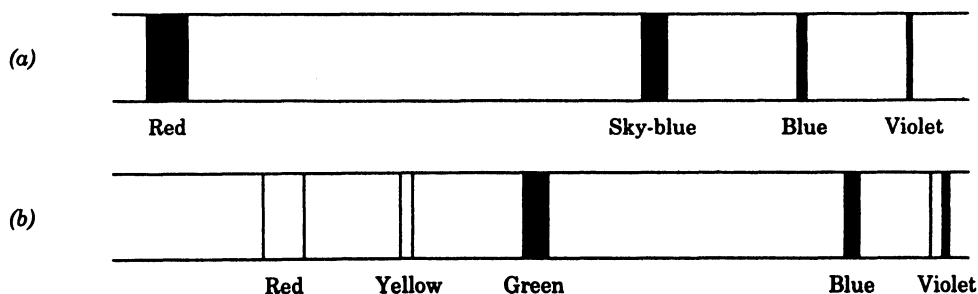


Fig 1.7. Line spectrum of hydrogen (a) and mercury (b).

noticed. Each element gives its own characteristic spectrum which differs from spectrum of the other element. Therefore, the line spectrum is also described as **finger print** of a particular metal. For example, sodium vapour gives two yellow lines corresponding to wave lengths 5890 and 5896 Å. Likewise, mercury vapour lamp produces eight to ten lines from red to violet in its spectrum.

(c) **Band spectrum.** When electric discharge is passed through oxygen, nitrogen or carbon dioxide, the coloured bands of light are observed on a dark background. One end of each band is sharp and bright and the lines are

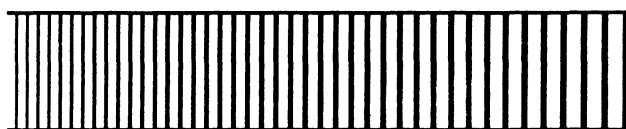


Fig. 1.8. Band spectrum.



closer while towards the other end brightness gradually decreases and the spacing between lines increases as shown in Fig 1.8.

(ii) **Absorption spectrum.** When a gas, solid or transparent liquid is placed in the path of bright light emitted from any source and then analysed by the spectroscopy, dark lines are observed in the spectrum. For example, when light from filament of electric bulb is passed through sodium vapours, two dark lines appear in the spectrum shown in the Fig. 1.9. These dark lines appear at the same place where two yellow lines appeared in the emission spectrum of sodium. This is because the sodium vapours absorb the same wavelength which it emits. This type of spectrum is called **absorption spectrum**.

Like emission spectra, the absorption spectra can also be continuous, line or band spectra.

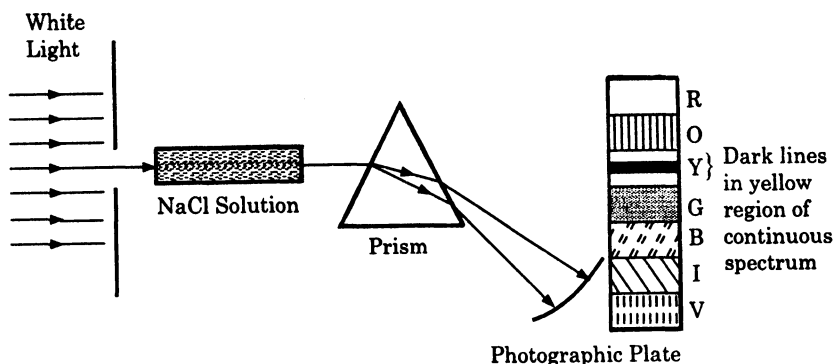


Fig 1.9. Production of absorption spectrum.

### Differences between emission and absorption spectra

The characteristic differences between emission and absorption spectra are compiled below.

	<i>Emission spectrum</i>	<i>Absorption spectrum</i>
1.	Emission spectrum is obtained when radiations emitted by the glowing substance in its excited state are analysed in a spectroscopy.	Absorption spectra is obtained when white bright light is allowed to pass through the substance in gaseous or in solution state. The transmitted rays are analysed by a spectroscopy.
2.	It consists of bright coloured lines separated by dark spaces.	It consists of dark lines against the coloured background.

**1.3.1. Atomic Spectrum of Hydrogen.** The atomic spectrum of hydrogen atom has been studied quite in detail by various scientists during the development of atomic structure. The spectrum of hydrogen atom can be obtained when radiations emitted by hydrogen gas at low pressure are taken in a discharge tube and examined by a spectroscopy, the line spectrum so obtained is called the **atomic spectrum of hydrogen**.

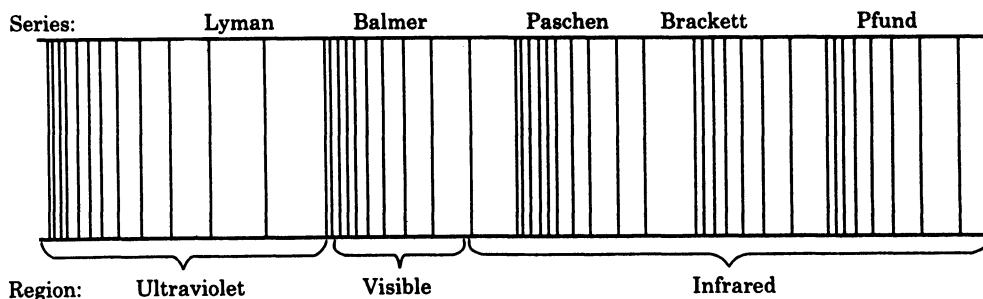


Fig. 1.10. Atomic spectrum of hydrogen.

The spectrum consists of a large number of sharp lines each corresponding to a particular wavelength (or frequency) of light emitted by hydrogen atom. These lines, which are present in ultraviolet, visible and infrared region, are grouped together into different series named after their discoverer as shown in Fig. 1.10. The lines in the emission spectrum of hydrogen are grouped into the following five series.

- |                          |                     |
|--------------------------|---------------------|
| (i) Lyman series .....   | Ultra violet region |
| (ii) Balmer series ..... | Visible region      |
| (iii) Paschen series     | Infrared region     |
| (iv) Brackett series     |                     |
| (v) Pfund series         |                     |

The spectral lines observed by **Balmer** in the visible part of the spectrum are called as  $H_\alpha, H_\beta, H_\gamma, H_\delta, \dots$ , etc. The brightness and spacing of these lines decrease regularly in going from one end to the other.

**J.J. Balmer** (1885) developed a relationship between the different wave lengths of all these lines. The relationship is :

$$\frac{1}{\lambda} = \bar{\nu} = R \left[ \frac{1}{2^2} - \frac{1}{n^2} \right]$$

where  $R$  is a constant called Rydberg's constant and its value is  $109677 \text{ cm}^{-1}$ .

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

Later on, **Rydberg** gave a more general expression which can be applied to all the series of the hydrogen spectrum. This expression is called **Rydberg formula**.

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

where  $n_2 > n_1$ . For a particular series  $n_1$  is constant i.e.

	$n_1$	$n_2$
For Lyman series	1	2, 3, 4, ....
For Balmer series	2	3, 4, 5, ....
For Paschen series	3	4, 5, 6, ....
For Brackett series	4	5, 6, 7, ....
For Pfund series	5	6, 7, 8, ....

**Example 1.10.** In a hydrogen atom, an electron jumps from third orbit to the first orbit. Find out the frequency and wavelength of the spectral line. (Roorkee Entrance 1989)

**Solution.** We know,  $R = 109677 \text{ cm}^{-1} = 1.09677 \times 10^7 \text{ m}^{-1}$  and  $n_1 = 1$  and  $n_2 = 3$

On substituting the given data in the equation  $\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \left[ \frac{1}{1^2} - \frac{1}{3^2} \right] \text{ cycles sec}^{-1} = 0.97490 \times 10^7$$

$$\therefore \lambda = \frac{1}{0.97490 \times 10^7} = 1.0254 \times 10^{-7} \text{ m} = 1025.4 \times 10^{-10} \text{ m} = \mathbf{1025.4 \text{ \AA}}$$

$$\text{Now } \nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{1.0254 \times 10^{-7} \text{ m}} = \mathbf{2.9257 \times 10^{15} \text{ sec}^{-1}}$$

**Example 1.11.** Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity ( $\infty$ ) to stationary state of the hydrogen atom.  $R = 1.09677 \times 10^7 \text{ m}^{-1}$ ,  $h = 6.62 \times 10^{-34} \text{ J sec}$ , and  $c = 3 \times 10^8 \text{ m sec}^{-1}$ . (Roorkee Entrance 1988)

**Solution.** We know that

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = 1.09677 \times 10^7 \text{ m}^{-1} \left[ \frac{1}{1^2} - \frac{1}{\infty^2} \right] = 1.09677 \times 10^7 \text{ m}^{-1}$$

or  $\lambda = 9.11 \times 10^{-8} \text{ m}$

Now  $E = h\nu = h \frac{c}{\lambda}$

$$= \frac{6.62 \times 10^{-34} \text{ J sec} \times 3.0 \times 10^8 \text{ m sec}^{-1}}{9.11 \times 10^{-8} \text{ m}}$$

$$= 2.180 \times 10^{-18} \text{ J or } 218.0 \times 10^{-20} \text{ J} = 218.0 \times 10^{-23} \text{ kJ}$$

**Example 1.12.** Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of the lowest energy in the visible region of its atomic spectrum ( $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ ,  $c = 3 \times 10^8 \text{ ms}^{-1}$  and  $h = 6.62 \times 10^{-34} \text{ Js}$ ) (Roorkee Entrance 1993)

**Solution.** Spectral line in the visible region corresponds to the Balmer series i.e.  $n_2 = 2$  and  $n_1 = 3$  (for lowest energy)

$$\therefore \frac{1}{\lambda} = 1.1 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 1.1 \times 10^7 \left( \frac{1}{4} - \frac{1}{9} \right) = 1.1 \times 10^7 \times \frac{5}{36}$$

or  $\lambda = \frac{36}{1.1 \times 10^7 \times 5} = 6.55 \times 10^{-7} \text{ m}$

Now we know that

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{6.62 \times 10^{-34} \text{ J sec} \times 3 \times 10^8 \text{ m sec}^{-1}}{6.55 \times 10^{-7} \text{ m}} = 3.03 \times 10^{-19} \text{ J}$$

$\therefore$  Energy corresponding to 1 g atom of hydrogen

$$= 3.0 \times 10^{-19} \text{ J} \times 6.02 \times 10^{23} = 18.25 \times 10^4 = 182.5 \text{ kJ}$$

**Example 1.13.** The electron energy in hydrogen atom is given by  $E = (-21.7 \times 10^2)/n^2$  ergs. Calculate the energy required to remove an electron completely from the  $n = 2$  orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? (IIT JEE 1984)

**Solution.** Energy of an electron in the  $n$ th orbit of hydrogen is given by

$$E = -21.7 \times 10^{-12} \times \frac{1}{n^2} \text{ ergs}$$

$$\therefore \Delta E = -21.7 \times 10^{-12} \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right)$$

$$= -21.7 \times 10^{-12} \times \frac{1}{4} = -5.42 \times 10^{-12} \text{ ergs}$$

Now  $\Delta E = h\nu = \frac{hc}{\lambda}$

$$(\because \nu = \frac{c}{\lambda})$$

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

$$\begin{aligned}\text{Substituting the values, we get } \lambda &= \frac{6.62 \times 10^{-27} \text{ ergs} \times 3 \times 10^8 \text{ m}}{5.42 \times 10^{-12} \text{ ergs}} \\ &= 3.67 \times 10^{-7} \text{ m} = 3.67 \times 10^{-5} \text{ cm}\end{aligned}$$

**Example 1.14.** What transition in the hydrogen spectrum would have the same wave length as the Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$  spectrum ? (IIT JEE 1993)

**Solution.** For  $\text{He}^+$  ion, we have  $\frac{1}{\lambda} = Z^2 R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$= (2)^2 R \left[ \frac{1}{(2)^2} - \frac{1}{(4)^2} \right] = \frac{R \times 3}{4} \quad \dots(i)$$

Now for hydrogen atom  $\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots(ii)$

Equating equations (i) and (ii), we get

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Obviously,  $n_1 = 1$  and  $n_2 = 2$

$\therefore$  The transition  $n_2 = 2$  to  $n_1 = 1$  in hydrogen atom will have the same wave length as the transition,  $n_2 = 4$  to  $n_1 = 2$  in  $\text{He}^+$  species.

#### 1.4. BOHR'S MODEL OF THE ATOM

**Neil Bohr** (1913) proposed a new model of the atom which not only explained the origin of hydrogen spectrum and photoelectric effect but also led to an entirely new concept of atomic structure. His new theory of atomic structure is based upon the quantum theory of radiation. The main postulates on which Bohr's model of atom is based are described below.

(i) **An atom consists of a dense positively charged nucleus situated at the center surrounded by electrons. The electrons revolve around the nucleus in certain selected circular paths, called orbits without emitting any energy.** This orbital path without loss of energy follows the Newtonian law *i.e.* the force of attraction between the nucleus and an electron is equal to the centrifugal force of the moving electron.

(ii) Only those orbits are permitted in which the angular momentum ( $mur$ ) of the electron is an integral multiple of  $h/2\pi$  (where  $h$  is Planck's constant).

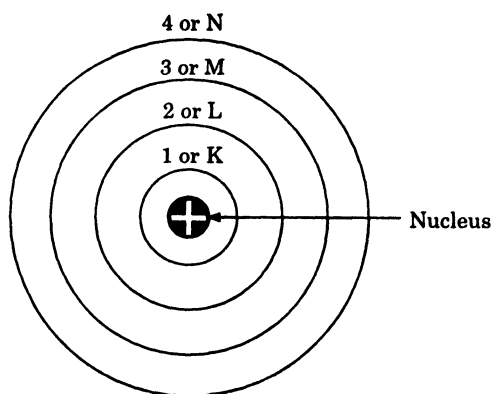
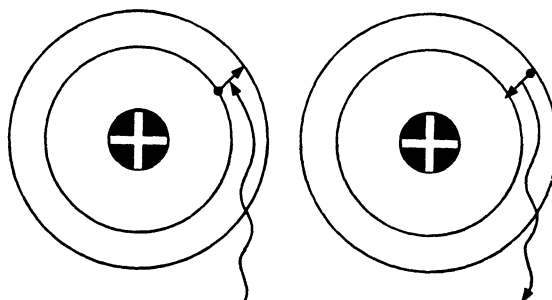


Fig. 1.11. Circular orbits or energy levels in an atom



(a) Energy absorbed  
=  $E_2 - E_1$

(b) Energy emitted  
=  $E_2 - E_1$

Fig. 1.12. Energy change in an electron jump.

$$mur = n \frac{h}{2\pi}$$

where  $m$  = mass of electron

$u$  = velocity of the electron

$n$  = number of orbit in which electron is present *i.e.*  $n = 1, 2, 3, \dots$

$r$  = radius of the orbit.

(iii) The electrons revolve only in those orbits which have fixed value of energy. Thus electrons in an atom can have only definite or discrete values of energy. This postulate introduces the concept of quantization of angular momentum.

(iv) As long as the electron remains in a particular orbit, it neither loses or gains energy. This means that electron is associated with a definite amount of energy. Therefore, these orbits are commonly known as stationary state of electron or permitted **energy level**. The different energy levels are numbered as 1, 2, 3, 4, ..., etc. starting from the nucleus or K, L, M, N, ... etc. Greater the distance of energy level from the nucleus, more is the energy associated with it.

(v) When energy is supplied to an electron, it may jump instantaneously from a lower energy level (say K) to a higher energy level (say L, M, N, ..., etc.) by absorbing one or more quanta of energy.

The new state of the electron is called the **excited state**. Similarly, in the reverse process, the excited electron jumps down instantaneously to a lower energy level by emitting one or more quanta of energy. The quantum of energy absorbed or emitted is equal to the difference in the energies of the two concerned levels *i.e.*

$$E_2 - E_1 = \Delta E = h\nu$$

or

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

where  $E_1$  and  $E_2$  are energies of the electron in the first and second energy levels.

$\nu$  = Frequency of radiations absorbed or emitted.

This shows that the energy of the electron does not change continuously but changes abruptly as the electron jumps from one energy level to another and not in any value of its own. This postulate explains the observation that atomic spectra are discontinuous.

#### 1.4.1. Successes of Bohr's Model. The main features of the Bohr's model are :

(i) **It explains the stability of an atom.** According to Bohr's theory, an electron revolving in a particular orbit does not lose energy as long as it stays in that orbit. Therefore, the earlier objection to Rutherford's model of continuously losing energy and falling into the nucleus, is resolved.

(ii) **It helped in calculating the energy of an electron in a particular orbit of hydrogen.**

On the basis of postulates of Bohr's model, a mathematical expression is derived for the energy of an electron moving in a particular orbit of hydrogen atom. The expression for energy of an electron in the  $n$ th orbit of hydrogen is

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

where,  $k$  = Coulomb's law constant  $m$  = Mass of the electron  
 $e$  = Charge on the electron  $h$  = Planck's constant  
 $Z$  = Atomic number of the element.

Substituting the values of constants,

$$\begin{array}{lll} \pi = 3.14 & m = 9.1 \times 10^{-31} \text{ kg} & k = 9 \times 10^9 \text{ Nm}^2/\text{C}^2 \\ h = 6.62 \times 10^{-34} \text{ J sec}^{-1} & e = 1.6 \times 10^{-19} \text{ C} & Z = 1 \text{ (for hydrogen)} \end{array}$$

$$E_n = -\frac{21.79 \times 10^{-19}}{n^2} \text{ J/atom} = -\frac{1312}{n^2} \text{ kJ/mole}$$

Hence, for each value of  $n$  there exists different energy levels for the electron. Substituting the values for  $n = 1, 2, 3, 4, \dots$ , etc. in the above relation, the energy of electron in various energy levels of hydrogen atom has been calculated as given in Table 1.1

**Table 1.1. Energy of Electron in a Hydrogen Atom in Different Energy Levels**

Energy level ( $n$ )	$E$ (Joules /atom)	$E$ (eV /atom)	$E$ (kJ /mole)
1	$-21.79 \times 10^{-19}$	-13.6	-1312
2	$-5.42 \times 10^{-19}$	-3.4	-328
3	$-2.41 \times 10^{-19}$	-1.51	-145.7
4	$-1.36 \times 10^{-19}$	-0.85	-82.0
5	$-0.87 \times 10^{-19}$	-0.544	-52.5
$\infty$	0	0	0

**Energy expression for hydrogen like ions.** Hydrogen like ions are those ions which contain only one electron. For example,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , ... etc. The energy of the electron in  $n$ th orbit for hydrogen like ions is given by the expression

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

where  $Z$  (atomic number) is not equal to 1 but have values 2, 3, 4, ... etc. Thus for  $\text{He}^+$  and  $\text{Li}^{2+}$ , the energy expression can be written as below.

For  $\text{He}^+$  ( $Z = 2$ )

$$\therefore E_n = -\frac{2k^2 \pi^2 (2)^2 m e^4}{n^2 h^2} = -\frac{4 \times 1312}{n^2} \text{ kJ mol}^{-1}$$

For  $\text{Li}^{2+}$  ( $Z = 3$ )

$$\therefore E_n = -\frac{2k^2 \pi^2 (3)^2 m e^4}{n^2 h^2} = -\frac{9 \times 1312}{n^2} \text{ kJ mol}^{-1}$$

For a particular atom the relationship of energy of  $n$ th orbit ( $E_n$ ) with that of first orbit ( $E_1$ ) is given by the expression

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

and the energy of the electron of a species (say  $\text{He}^+$  or  $\text{Li}^{2+}$ ) in  $n$ th orbit compared to hydrogen in the same orbit is given as

$$E_n (\text{Li}^{2+}) = \frac{E_n (\text{H}) \times Z^2}{n^2}$$

### Reason for negative value of electronic energy

When the electron is at infinite distance from the nucleus, there is no force of attraction between electron and the nucleus. This state of the system is assumed to be zero energy state. When the electron moves towards the nucleus, it experiences some force of attraction by the nucleus and thus energy is released. [Since we know energy is given out when species of

opposite charges come closer to each other], therefore, the value of energy becomes less than zero or negative. Furthermore, as the electron comes more and more closer to the nucleus, the force of attraction increases and it results in more decrease in energy *i.e.* its value becomes more and more negative.

**Bohr theory and concept of quantisation.** The important difference of Bohr's model of the structure of atom from that of Rutherford is that the energy of the electron in an atom is quantised *i.e.* the energy of the electron in a particular orbit is fixed and given by the expression.

$$\text{Energy of the electron of hydrogen atom} = -\frac{1312}{n^2} \text{ kJ mol}^{-1}$$

Where  $n$  is an integer (1, 2, 3, ...) and refers to energy level or orbit.

The electron from one energy level moves to another energy level only on gaining or losing a definite value of energy. This led to the concept of **quantisation**. **The term quantisation means that energy of the electron can not vary continuously to have arbitrary values but changes only discontinuously to acquire some specific values.**

This concept can further be illustrated by comparing the energy levels in Bohr's model with steps of a ladder. Let us label the steps of the ladder as 1, 2, 3, 4, ... from the bottom. A person can have his position only on the steps *i.e.* 1 or 2 or 3 or 4 ... but not in between *i.e.* the energy of the person changes **discontinuously** or energy of the person is quantised. Likewise, the electron jumps from one energy level to another energy level discontinuously rather than continuously.

(iii) **It explains the line spectrum of hydrogen.** According to Bohr's theory, an electron continues to revolve in a particular orbit without emitting or absorbing energy. This state of the electron is called **ground state** or **normal state**.

However, when atom absorb energy, the electron jumps from the ground state to the higher energy level *i.e.* **excited state**. As the life time of electron in the excited state is short, it loses part or whole of the acquired energy and returns to some lower energy level or to the ground state in one or more jumps. During each jump, energy is emitted in the form of a photon of light of a certain frequency or wavelength.

We know, the frequency ( $\nu$ ) of the photon of light emitted depends upon the energy difference of the two energy levels *i.e.*

$$E_2 - E_1 = h\nu \quad \text{or} \quad \nu = \frac{E_2 - E_1}{h}$$

where  $E_2$  and  $E_1$  are the energies in the higher and lower energy levels respectively.

Further, the frequency is related to wavelength ( $\lambda$ ) as  $\nu = c/\lambda$  where  $c$  is the velocity of light. We have

$$\nu = \frac{c}{\lambda} = \frac{E_2 - E_1}{h} \quad \text{or} \quad \lambda = \frac{hc}{E_2 - E_1}$$

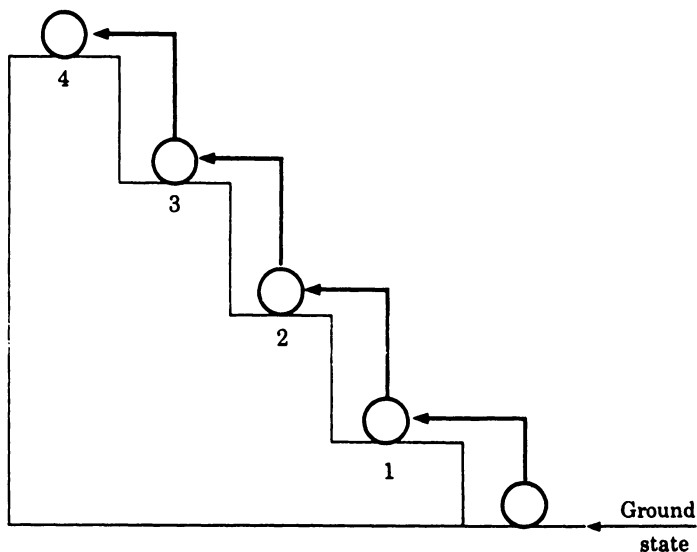


Fig. 1.13. Quantised energy.

Thus, lines appear in the spectrum corresponding to the frequency (or wavelength) of each photon emitted. Thus Bohr's theory explains the line spectrum of hydrogen and hydrogen like species (e.g.,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , etc.).

**Example 1.15.** Calculate the frequency of the light ray emitted, when an electron drops from a higher to a lower energy level of an atom. The difference between the energies is  $35.64 \times 10^{-13}$  ergs ( $h = 6.62 \times 10^{-27}$  erg sec.). (WB Engg. Entrance 1990)

**Solution.** We know,  $E_2 - E_1 = h\nu$

$$\begin{aligned} \therefore \nu &= \frac{E_2 - E_1}{h} = \frac{\Delta E}{h} \\ &= \frac{35.64 \times 10^{-13} \text{ erg}}{6.62 \times 10^{-27} \text{ erg sec.}} = 5.38 \times 10^{14} \text{ sec}^{-1}. \end{aligned}$$

**Example 1.16.** The electron energy in hydrogen atom is given by  $E = \frac{-21.7 \times 10^{-12}}{n^2}$  ergs.

Calculate the energy required to remove an electron completely from the  $n = 2$  orbit. What is the longest wave length of light that can be used to cause this transition ?

**Solution.** The energy of electron in  $n$ th orbit is given by

$$\begin{aligned} E_n &= -\frac{21.7 \times 10^{-12}}{n^2} \text{ ergs} \\ E_2 &= -\frac{21.7 \times 10^{-12}}{2^2} \text{ ergs} = -5.42 \times 10^{-12} \text{ ergs} \end{aligned}$$

Now

$$\Delta E = E_\infty - E_2 = 5.42 \times 10^{-12} \text{ ergs}$$

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

$$\begin{aligned} \therefore \lambda &= \frac{hc}{\Delta E} = \frac{(6.62 \times 10^{-34} \text{ ergs sec}) (3 \times 10^8 \text{ ms}^{-1})}{5.42 \times 10^{-12} \text{ ergs}} \\ &= 3667 \times 10^{-10} \text{ m} = 3667 \text{ \AA}. \end{aligned}$$

(iv) **Simultaneous appearance of a large number of lines in the spectrum of hydrogen.**

In spite of the fact that hydrogen atom has only one electron, its atomic spectrum is observed to have a large number of lines. These spectral lines have been grouped into five series namely (i) Lyman series, (ii) Balmer series, (iii) Paschen series, (iv) Brackett series and (v) Pfund series. The explanation to this observation may be as follows

A sample of hydrogen gas actually has a large number of molecules (1 mole =  $6.02 \times 10^{23}$  molecules). When energy is supplied to such a sample of hydrogen gas by passing electric discharge, the molecules split into atoms and the electron in the different hydrogen atoms absorb different amount of energy. Thus the electrons in hydrogen atoms are excited to different energy levels. For example, electrons in some atoms are excited to L shell, while some are excited to M, N, O, P, ... etc., energy levels. Since the life time of the electrons in the excited state is very short, they return to some lower energy level or even to the ground state in one or more jumps. The various possibilities of return of these excited

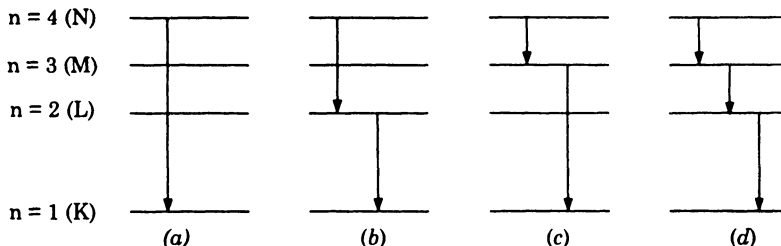


Fig. 1.14. Different routes to the ground state from  $n = 4$  to  $n = 1$ .



electrons to lower energy levels are shown in Fig. 1.14.

Since each jump to lower energy level corresponds to different frequency (or wave length), they result in large number of lines in the emission spectrum of hydrogen.

The group of lines which arise due to transitions from higher energy levels to first energy level are named **Lyman series**. Similarly the group of lines obtained due to transition from higher energy levels to second, third, fourth and fifth energy levels are named as **Balmer**, **Paschen**, **Brackett** and **Pfund** series respectively.

Name of the series	Energy level of excited electron	Lower energy level of electron	Region of the spectrum
Lyman series	$n = 2, 3, 4, 5, \dots$	$n = 1$	U. V. region)
Balmer series	$n = 3, 4, 5, 6, \dots$	$n = 2$	(Visible region)
Paschen series	$n = 4, 5, 6, 7, \dots$	$n = 3$	IR region
Brackett series	$n = 5, 6, 7, 8, \dots$	$n = 4$	IR region
Pfund series	$n = 6, 7, 8, 9, \dots$	$n = 5$	IR region

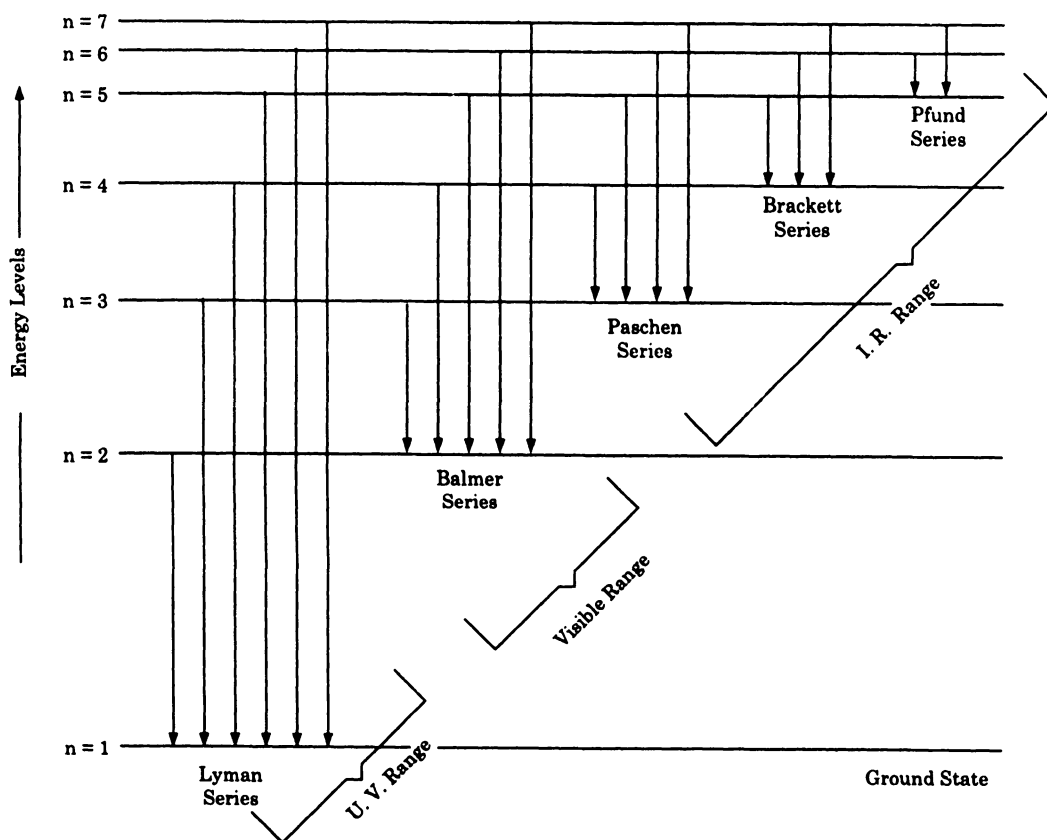


Fig. 1.15. Energy level diagram of hydrogen spectrum.

(v) **It helps in calculation of radius of Bohr's orbit.** The radius of various orbits in Bohr's model of atom have been determined on the basis of Bohr's postulates. The expression for radius of  $n$ th orbit is :

$$r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2 k}$$

where  $r_n$  = Radius of the  $n$ th orbit

$h$  = Planck's constant ( $6.62 \times 10^{-34}$  J sec $^{-1}$ )

$m$  = Mass of the electron ( $9.1 \times 10^{-31}$  kg)

$Z$  = Atomic number of element

$e$  = Charge on the electron ( $1.6 \times 10^{-19}$  C)

$k$  = Coloumbs law constant ( $9 \times 10^9$  Nm $^2$ /C $^2$ )

This equation enabled Bohr to calculate the radii of various orbits which the electron of the hydrogen atom is permitted to occupy. Evidently, greater value of  $n$  corresponds to bigger radius.

The radius of the smallest orbit for the hydrogen atom (*i.e.*  $n = 1$  and  $Z = 1$ ) is

$$r_0 = \frac{h^2}{4\pi^2 m e^2 k}$$

Now substituting the values of  $\pi$ ,  $h$ ,  $m$ ,  $e$  and  $k$  we get

$$\begin{aligned} r_0 &= \frac{(6.62 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9} \\ &= 5.29 \times 10^{-11} \text{ m} = \mathbf{0.529 \text{ \AA}} \end{aligned}$$

Therefore, radius of the  $n$ th orbit for the hydrogen atom may be written as

$$r_n = \mathbf{0.529 \times n^2 \text{ \AA}}$$

Likewise, relationship of radius of  $n$ th orbit of an atom to  $n$ th orbit of hydrogen atom is given as

$$r_n (\text{Li}^{2+}) = \frac{r_n (\text{H}) n^2}{Z}$$

(vi) **Calculation of velocity of electron in Bohr's orbit.** Velocity of the revolving electron in  $n$ th orbit is given by the expression

$$v_n = \frac{2\pi k Z e^2}{nh} \quad \dots(i)$$

where  $k$  = Coulombs law constant       $Z$  = Atomic number of element

$e$  = Charge on the electron       $h$  = Planck's constant

$\therefore$  Velocity of electron in  $n$ th orbit with respect to the electron in first orbit is given as

$$v_n = \frac{v_1}{n}$$

**Relationship between energy, radius and velocity of an electron in  $n$ th orbit.**

We know, 
$$E_n = -\frac{2k^2\pi^2 m e^4 Z^2}{n^2 h^2} \quad \dots(i)$$

$$v_n = \frac{2\pi k Z e^2}{nh} \quad \dots(ii)$$

$$r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2 k} \quad \dots(iii)$$

Multiplying (i) with (iii) we get

$$E_n = -\frac{Z e^2}{2r_n}$$

Similarly, multiplying (ii) and (iii)

$$v_n = \frac{nh}{2\pi mr_n}$$

Dividing (i) by square of (ii)

$$E_n = -\frac{m}{2} (v_n)^2$$

**Example 1.17.** The energy associated with the first orbit in the hydrogen atom is  $-21.79 \times 10^{-12}$  ergs/atom. Determine the energy associated with the fourth orbit.

**Solution.** We know  $E_n = \frac{E_1}{n^2}$

$$E_4 = \frac{-21.79 \times 10^{-12} \text{ ergs/atom}}{4^2} = -1.36 \times 10^{-12} \text{ ergs/atom}$$

**Example 1.18.** Calculate the energy of an electron in the second Bohr orbit of an excited  $\text{Li}^{2+}$ . The energy of electron in the first Bohr orbit of hydrogen atom is  $-2.179 \times 10^{-18}$  J/atom.

**Solution.** We know the expression

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

$$E_2 = \frac{-2.179 \times 10^{-18} \text{ J/atom} \times (3)^2}{(2)^2} = -4.903 \times 10^{-18} \text{ J/atom.}$$

**Example 1.19.** Calculate the radius of Bohr's fifth orbit of hydrogen atom [ $r_1 = 0.53 \text{ \AA}$ ].

**Solution.**

$$r_n = n^2 r_1$$

$\therefore$

$$r_5 = 5^2 \times 0.53 \text{ \AA} = 13.25 \text{ \AA.}$$

**Example 1.20.** Calculate the energy and velocity of the electron in first orbit of hydrogen atom. Radius of first orbit for hydrogen atom is  $0.53 \text{ \AA}$ .

**Solution.**  $E_n = -\frac{Ze^2}{2r_n}$

or

$$E_1 = -\frac{1 \times (4.803 \times 10^{-10} \text{ esu})^2}{2 \times (0.53 \times 10^{-8})} = -21.79 \times 10^{-12} \text{ ergs/atom}$$

Velocity,

$$v = \frac{nh}{2\pi mr}$$

$\therefore$

$$v_1 = \frac{1 \times 6.62 \times 10^{-27} \text{ ergs}}{2 \times 3.14 \times (9.1 \times 10^{-28} \text{ g}) (0.53 \times 10^{-8} \text{ cm})}$$

$$= 2.188 \times 10^8 \text{ cm s}^{-1} = 2.188 \times 10^6 \text{ ms}^{-1}$$

**Example 1.21.** The ionization energy of hydrogen atom is  $13.6 \text{ eV}$ . What will be the ionization energy of  $\text{He}^+$  and  $\text{Li}^{2+}$  ions? (Roorkee Entrance 1986)

**Solution.**  $\text{He}^+$  and  $\text{Li}^{2+}$  are hydrogen like species i.e. the electron is ionised from first orbit

$$\therefore \text{Ionization energy of } \text{He}^+ = \frac{Z^2 E_H}{n^2} = \frac{4 \times 13.6}{1^2} = 54.4 \text{ eV}$$

$$\text{Ionization energy of } \text{Li}^{2+} = \frac{9 \times 13.6}{1^2} = 122.4 \text{ eV}$$

#### 1.4.2. Limitations of Bohr's Theory

- (i) **Its inability to explain line spectra of multielectron atom.** Bohr's atomic model theory explained successfully the line spectrum of species having only one electron

*e.g.*, H atom,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , etc. However, it failed to explain the line spectra of atoms having more than one electron.

- (ii) **Its inability to explain the presence of multiple spectral lines.** According to Bohr's concept, only one spectral line is developed between any two given energy levels. However, if a powerful spectroscope is used, certain single lines are found to split into a number of very closely related lines. The presence of these lines could not be explained on the basis of Bohr's theory.
- (iii) **Its inability to explain the splitting of spectral lines in magnetic field. [Zeeman effect].** When the atom emitting radiation is placed in a strong magnetic field, it is noticed that each spectral line further splits into a number of lines. This phenomenon is known as **Zeeman effect**. Bohr's model could not explain this splitting.
- (iv) **Its inability to explain the splitting of spectral lines in electrical field [Stark effect].**
- (v) **Its inability to explain the three dimensional shape of the atom.** According to Bohr's model of atom, the electrons revolve around the nucleus in a definite path in one plane. It has suggested a flat model of the atom which is contrary to the present three dimensional shape of the atom.
- (vi) **Its inability to explain the deBroglie's concept of dual nature of matter.** Bohr regarded electron as a discrete particle but the electron is observed to behave not only as particle but also as wave.
- (vii) **Its inability to explain Heisenberg uncertainty principle.** According to Bohr's concept the electron in an atom is located at a definite distance from the nucleus and revolves with a definite velocity around it. This assumption is against **Heisenberg uncertainty principle** according to which "it is impossible to determine simultaneously both the position and velocity of an electron or moving microscopic particle with absolute accuracy."

The above stated shortcomings lead to the presumption that **radiations possess dual nature**, *i.e.* particle nature as well as the wave nature.

### 1.5. DUAL NATURE OF MATTER AND RADIATIONS

According to quantum theory, proposed by Max Planck (1900) and subsequently applied by Albert Einstein (1905), the electromagnetic radiations propagating in space as waves *e.g.*, visible light, is believed to consist of discrete packets (quanta) of energy photons. The relationship of energy of photon with the frequency of radiation is given as

$$E = h \nu \quad \text{[Planck's relationship]}$$

where  $E$  is the quantum of energy and  $h$  is Planck constant. Radiations are thus emitted or absorbed only in terms of photons *i.e.* quanta of energy. Substituting  $\nu = c/\lambda$ , the energy could be correlated with wavelength  $\lambda$ .

$$E = hc/\lambda \quad \text{where } c \text{ is velocity of light radiations.}$$

Einstein further suggested that light has a dual behaviour. It can act as a wave as well as a particle. Phenomena like photoelectric effect, reflection and refraction of light can be explained on the basis of particle nature of light, while the common phenomena of interference and diffraction can be explained by wave theory of light. These experiments prove beyond doubt that quantum theory as well as wave theory of light proceed side by side and dual nature is a fundamental feature of light.

**Photoelectric effect : J.J. Thomson** (1896) observed that certain rays (cathode rays) were emitted out when light of certain frequency falls on the metal surface. These observations were further elaborated by **Einstein** in his **theory of photoelectric effect**. He defined **photoelectric effect as a phenomenon in which electrons are ejected out from the surface of the metal when irradiated with a light of sufficiently high frequency**. The ejected electrons are termed as **photoelectrons**. Metals with low ionization energy such as K, Rb, Cs and Na etc. show photoelectric effect. He assumed that the light that is falling on the metal plate consists of photons with energy  $h\nu$ . Further when the light is absorbed by the metal all the energy of photon is converted into energy of a photoelectron. Photoelectrons (negatively charged) are then ejected out from the metal plate and the metal plate becomes positively charged. Diagram of photoelectric cell is shown in Fig. 1.16. Out of the total absorbed energy of electron, part of the energy is utilized for ionization of electron from the metal surface, while the remaining energy is kinetic energy of the photoelectron.

The famous Einstein photoelectric equation is

$$h\nu = E_i + \frac{1}{2} mc^2$$

where  $E_i$  is ionization energy and  $m$  and  $c$  represent mass and velocity of ionizing electron respectively. The significance of this equation is that the electrons are ejected out from the metal surface only when electromagnetic radiations of certain definite frequency or higher frequency fall on it. Such frequency of radiation is called **threshold frequency**.

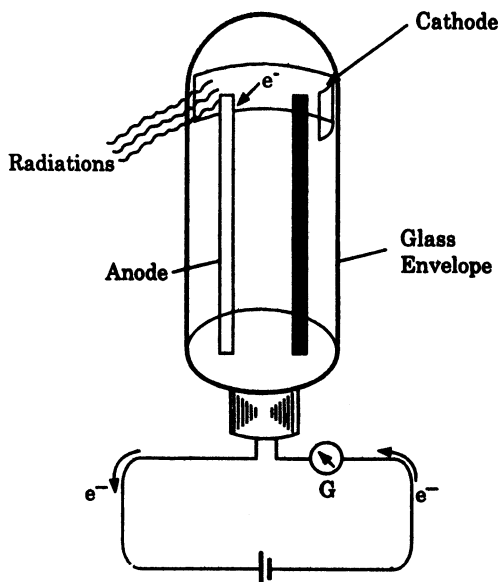


Fig. 1.16. Photoelectric cell.

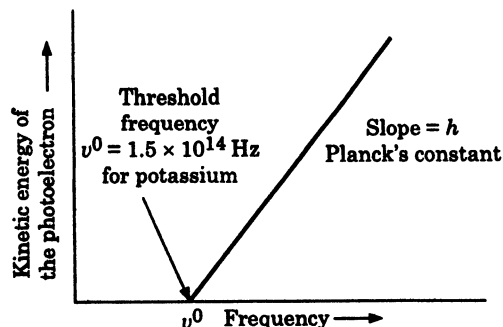


Fig. 1.17. The kinetic energy of the photoelectron increases with increase in frequency of radiation.

**Threshold frequency.** It is defined as the **minimum frequency of light (or electromagnetic radiation) that can just remove electrons from the surface of the metal and is represented by  $\nu^0$** . Light of frequency less than  $\nu^0$  cannot cause the emission of electrons from the metal surface while the light with higher frequency is able to remove the electrons from the metal and give it some kinetic energy. Therefore, **the minimum energy required to remove an electron from the metal surface is termed as escape energy ( $E_i$ )**. It is also known as

work function ( $\phi$ ) of the metal. The work function or escape energy is related to its threshold frequency ( $\nu^0$ ) by the equation

$$E_i = h\nu^0$$

Substituting this value in Einstein photoelectric equation, it takes the form

$$h\nu = h\nu^0 + \text{K.E.}$$

or

$$\text{K.E.} = h\nu - h\nu^0 = h(\nu - \nu^0)$$

Hence, kinetic energy gained by electron could successfully be calculated by knowing threshold frequency and the frequency of radiant energy.

### 1.6. THE DE-BROGLIE'S EQUATION (WAVE PARTICLE DUALITY)

Louis de-Broglie (1924) introduced his concept of “**particle waves**” and stated that **if light can display particle-wave duality, then matter which physically appears particle like should display wave properties**. According to him both light and matter obeys the deBroglie's equation.

$$\lambda = \frac{h}{mc} \quad \text{or} \quad \lambda = \frac{h}{p}$$

where  $\lambda$  is wavelength of the wave,  $h$  is Planck constant,  $m$  is mass,  $c$  its velocity and  $p$  is momentum of the particle respectively.

de-Broglie's equation for an electron is derived as follows.

$$E = h\nu \text{ (Planck's relation for energy of radiation)}$$

$$E = mc^2 \text{ (Einstein relation for motion of particle)}$$

Combining the two equations,  $h\nu = mc^2$

Substituting  $\nu = c/\lambda$ , the equation is written as

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

or

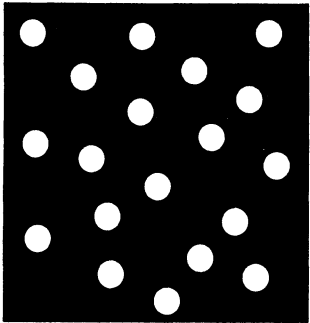
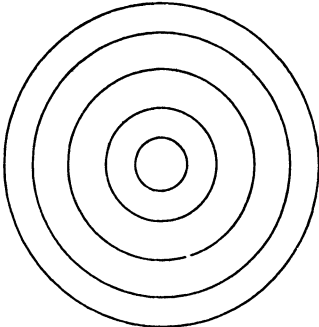
$$\lambda = \frac{h}{mc}; \quad \lambda = \frac{h}{p} \quad [\because p = mc]$$

#### Basic Differences between Wave and Particle

Particle	Wave
(i) Particle is a small quantity of matter.	(i) A wave is “to and fro” wave motion
(ii) A particle is localised in space and its position is definite.	(ii) It is delocalised in space and spread out as wave originating from the centre.
(iii) Two or more particles in space retain their identity and do not interfere with each other.	(iii) Two or more waves when present in the same region or space interfere with each other. The resulting new wave may have smaller or higher amplitude.

#### Experimental proof of de-Broglie's equation

The wave particle nature of electron has been supported by the undermentioned experiments.

Particle nature of electrons	Wave nature of electrons
<p>Particle nature of electrons is shown by <b>Scintillation experiment</b>. When an electron strikes a screen coated with ZnS, it produces bright spots of light against black background. Each striking electron produces one scintillation, which is highly localised as shown in Fig. 1.18 and does not spread on the plate like a wave.</p> <p style="text-align: center;">Bright Spot</p>  <p style="text-align: center;">Fig. 1.18. Particle nature of electrons observed by scintillation experiment</p>	<p>Wave character of electrons is verified by experiments of Davisson and Germer. They showed that when a beam of electrons emitted from tungsten filament is subjected to strong electric field, it enhances the speed of electrons. When these accelerated electrons are allowed to strike against nickel crystal as grating, concentric dark and bright rings are formed on the screen as shown in Fig. 1.19.</p>  <p style="text-align: center;">Fig. 1.19. Wave nature of electrons. Similar diffraction pattern is shown by X-rays which have wave nature. Therefore, the electrons must also possess wave nature.</p>

### Significance of de-Broglie's relation.

(i) As defined, the wavelength associated with an electron or moving object is inversely proportional to the momentum of the particle.

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda = \frac{h}{p}$$

where  $h$  is Planck constant.

If  $c$  is velocity of particle of mass  $m$  then momentum,  $p = m c$

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

(ii) The wavelength is inversely proportional to mass, i.e.  $\lambda \propto \frac{1}{m}$ . So **greater the mass of the moving particle, shorter is the wavelength of the matter wave associated with it**. Sometimes wavelengths become too small to be measured experimentally and the moving body appears only as particle in nature. The lighter particles have longer and experimentally measurable wavelengths.

(iii) The wavelength associated with a moving object is inversely proportional to its velocity, i.e.  $\lambda$  changes with velocity.

**Hence higher the speed of the moving particle, shorter is its wavelength and vice versa.**

**Example 1.22.** Calculate the momentum of a particle which has a wave length of  $2 \text{ \AA}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ].

**Solution.** We know that,  $\lambda = \frac{h}{p}$  or  $p = \frac{h}{\lambda}$

$$\lambda = 2 \text{ \AA} = 2 \times 10^{-10} \text{ m} \quad ; \quad h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\therefore p = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{2 \times 10^{-10} \text{ m}} = 3.3 \times 10^{-24} \text{ kg m s}^{-1}$$

**Example 1.23.** Calculate the wavelength associated with a body of mass 1 mg moving with a velocity of  $10 \text{ m sec}^{-1}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ].

**Solution.**

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

where

$$m = 1 \text{ mg} = 1 \times 10^{-6} \text{ kg}, \quad c = 10 \text{ m sec}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\therefore \lambda = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{1 \times 10^{-6} \text{ kg} \times 10 \text{ ms}^{-1}} = 6.6 \times 10^{-29} \text{ m}$$

**Example 1.24.** A beam of electrons has a wavelength of  $100 \text{ \AA}$ . Find out the velocity of this beam.

**Solution.**

$$\lambda = 100 \text{ \AA} = 100 \times 10^{-10} \text{ m} = 10^{-8} \text{ m}$$

$$\lambda = \frac{h}{mc} \quad \text{or} \quad c = \frac{h}{m \times \lambda}$$

$$c = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 10^{-8} \text{ m}} = 7.253 \times 10^4 \text{ ms}^{-1}$$

**Example 1.25.** An electron is moving with a kinetic energy of  $4.55 \times 10^{-25} \text{ J}$ . Calculate wavelength and frequency of the particle wave [ $m = 9.1 \times 10^{-31} \text{ kg}$ ;  $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ].

**Solution.** Kinetic energy,

$$E = \frac{1}{2} mc^2 \quad \text{or} \quad c^2 = \frac{2E}{m}$$

$$\therefore c^2 = \frac{2 \times 4.55 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \quad [\because \text{J} = \text{kg m}^2 \text{ s}^{-2}]$$

$$= 10^6 \text{ m}^2 \text{ s}^{-2}$$

$$\text{or} \quad c = \sqrt{10^6} = 10^3 \text{ m s}^{-1}$$

$$\text{Now} \quad \lambda = \frac{h}{mc} = \frac{6.66 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 10^3 \text{ m s}^{-1}} = 7.318 \times 10^{-7} \text{ m}$$

$$v = \frac{c}{\lambda} = \frac{10^3 \text{ ms}^{-1}}{7.318 \times 10^{-7} \text{ m}} = 1.366 \times 10^9 \text{ s}^{-1}$$

**Example 1.26.** Iodine molecule dissociates into atoms by absorption of light of wavelength  $5000 \text{ \AA}$ . If each quantum is absorbed by one molecule of iodine, how much energy would be needed to dissociate one mole of iodine by this process ? [ $h = 6.6 \times 10^{-34} \text{ Js}$ ,  $c = 3 \times 10^8 \text{ ms}^{-1}$ ,  $N_A = 6 \times 10^{23} \text{ molecules}$ ].

**Solution.** 1 mole of iodine =  $6 \times 10^{23}$  molecules of iodine.

Since 1 quantum of energy is used to dissociate 1 molecule of iodine, total energy required for 1 mole of iodine is

$$E_{\text{Total}} = N_A \times \frac{hc}{\lambda}$$



$$E_{Total} = \frac{6 \times 10^{23} \times 6.6 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{5000 \times 10^{-10} \text{ m}} = 23.76 \times 10^4 \text{ J/mole}$$

$$= 237.6 \text{ kJ/mole} = \mathbf{56.79 \text{ kcal/mole}} \quad [\because 4.184 \text{ J} = 1 \text{ cal}]$$

### 1.7. HEISENBERG UNCERTAINTY PRINCIPLE

One of the important consequences of the dual nature of an electron is the uncertainty principle given by **Werner Heisenberg** (1927). This principle is an important feature of wave mechanics and discusses the relationship between the position and momentum of a moving particle.

**Heisenberg's uncertainty principle states that it is impossible to determine simultaneously the exact velocity (or momentum) and the exact position of a moving microscopic particle (e.g., electron).**

Accordingly, both momentum and position of a particle cannot be determined exactly at any instant. This implies that if momentum is measured very accurately, the measurement of position becomes less precise and *vice versa*.

If  $\Delta p$  ( $\Delta mv$ ) is the uncertainty in measurement of momentum and  $\Delta x$  as the uncertainty in determination of position, then according to Heisenberg principle the product of these two quantities is greater than or equal to  $h/4\pi$  where  $h$  is Planck's constant

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

$$\Delta mv \times \Delta x \geq \frac{h}{4\pi}$$

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

**Explanatory proof of Heisenberg uncertainty principle.** A particle is visible only when it reflects light or any other radiation from its surface. In order to locate the position of a revolving electron, one has to use bright light and super microscope. Bright light of very small wavelength or high energy when strikes an electron and the latter becomes visible, then energy of light is transferred to the electron. This results in change of momentum of electron. Thus the position of the electron though ascertained but its momentum changes drastically. However, if radiations of large wavelength or low energy is employed then the position of electron can't be determined with accuracy though its momentum is not altered. Therefore, it may be concluded that **it is not possible to determine simultaneously both the position and momentum of a small moving particle with absolute accuracy.**

**Example 1.27.** Calculate the uncertainty in position of an electron if uncertainty in velocity is  $5.7 \times 10^5 \text{ ms}^{-1}$ . [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$  and  $m = 9.1 \times 10^{-31} \text{ kg}$ ]

**Solution.** Formula :  $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

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

$$\therefore \Delta x \geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.143 \times 9.1 \times 10^{-31} \text{ kg} \times 5.7 \times 10^5 \text{ ms}^{-1}}$$

$$\geq \mathbf{1.012 \times 10^{-10} \text{ m}}$$

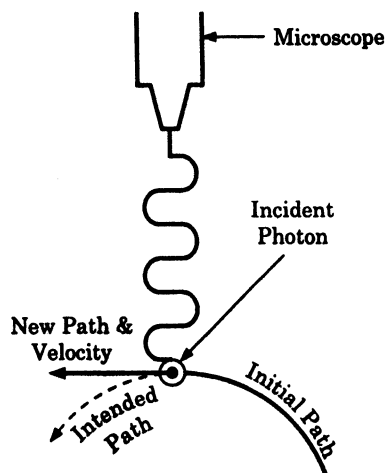


Fig. 1.20. The uncertainty principle.

**Example 1.28.** Calculate the uncertainty in the velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of  $1 \text{ \AA}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ].

**Solution.**  $\Delta x \times m \Delta v \geq \frac{h}{4\pi}$

or  $\Delta v \geq \frac{h}{4\pi m \Delta x}$

Given  $\Delta x = 1 \text{ \AA} = 10^{-10} \text{ m}$

$$m = 150 \text{ g} = \frac{150}{1000} = \frac{3}{20} \text{ kg}$$

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\begin{aligned} \therefore \Delta v &\geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1} \times 20}{4 \times 3.143 \times 10^{-10} \times 3} \\ &\geq 3.5000 \times 10^{-24} \text{ ms}^{-1} \end{aligned}$$

**Example 1.29.** Calculate the product of uncertainties of displacement and velocity of a moving electron having a mass of  $9.1 \times 10^{-28} \text{ g}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ].

**Solution.**  $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

$$m = 9.1 \times 10^{-28} \text{ g} = 9.1 \times 10^{-31} \text{ kg}$$

$$\therefore \Delta x \times \Delta v \geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 4 \times 3.143}$$

$$\Delta x \times \Delta v \geq 5.768 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

**Example 1.30.** Calculate the uncertainty in the velocity of a wagon of mass 1000 kg, whose position while in motion is known to an accuracy of  $\pm 10 \text{ m}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ].

**Solution.**  $\Delta v \times \Delta x \geq \frac{h}{4\pi m}$

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

$$\begin{aligned} \therefore &\geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.143 \times 1000 \text{ kg} \times 10 \text{ m}} \\ &\geq 0.5249 \times 10^{-38} \text{ ms}^{-1} \end{aligned}$$

**Example 1.31.** Calculate the uncertainty in the velocity of an electron, if the uncertainty in its position is  $1.0 \times 10^{-10} \text{ m}$  [ $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ ;  $m = 9.1 \times 10^{-31} \text{ kg}$ ].

**Solution.**  $\Delta v \geq \frac{h}{4\pi m \Delta x}$

$$\therefore \Delta v \geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.143 \times 9.1 \times 10^{-31} \text{ kg} \times 10^{-10} \text{ m}}$$

or  $\geq 5.768 \times 10^5 \text{ ms}^{-1}$

### Probability Picture of Electrons

Keeping in view the wave character of an electron and the uncertainty to determine precisely the position and momentum of an electron **Schrodinger** (1927) gave a mathematical expression known as **Schrodinger wave equation**. His theory is based on quantum mechanical model of atom in which the **concept of probability** of finding the electron at any position around the nucleus at any instant of time is considered. In order to understand the concept of **electron probability**, let us take a set of pictures of hydrogen atom each with only one

electron. If the electron in each picture is represented by a small dot at that instant and if all the pictures are superimposed over each other then the final picture will look like the one given in Fig 1.21.

Since most of the dots lie at a certain distance from the nucleus on all sides, the probability of finding an electron is maximum in the region. **The region of space around the nucleus within which the probability of finding the electron of a given energy is maximum**

**(nearly 90-95%) is called the atomic orbital.** This means that there is no sharp boundary for an orbital. However, this region is imaginary and separated from the region of minimum probability

of electron called **nodal plane**. Thus, for pictorial clarity and for the convenience of representation, a boundary surface is drawn to enclose a certain volume of space around the nucleus which encloses the maximum number of electrons of a given energy. Such electron cloud model of atom separated by imaginary boundaries is shown in Fig. 1.22.

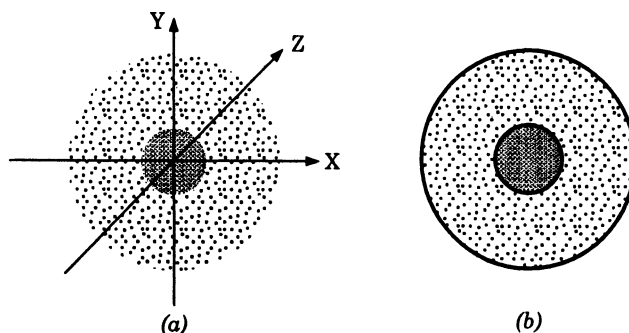


Fig. 1.21 (a) Electron cloud picture of the hydrogen atom. (b) Boundary surface for maximum probability density.

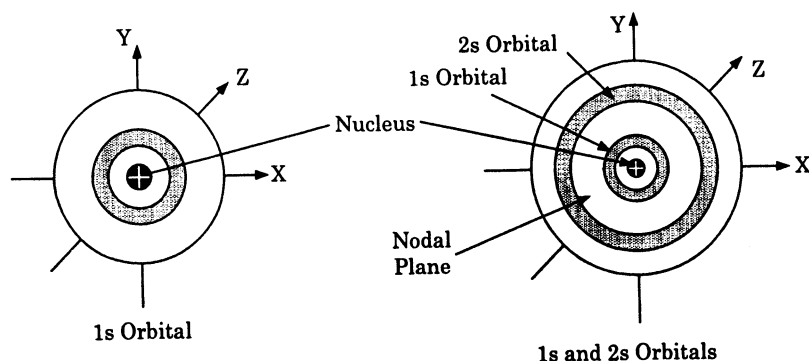


Fig. 1.22. Shapes of s-orbitals.

### Difference between Orbit and Orbital

Following are some important points which differentiate an orbital from an orbit.

	Orbital	Orbit
1.	An orbital is the region around the nucleus within which the probability of finding an electron is maximum.	An orbit is a circular path around the nucleus in which the electron revolves.
2.	It represents the three dimensional motion of an electron around the nucleus.	It represents the planar motion of an electron around the nucleus.
3.	Different orbitals have different shapes. Except s-orbital, all other orbitals are directional. (i) s-Orbitals are spherically symmetrical (ii) p-Orbitals are dumbbell in shape directing in x, y, and z axis respectively.	All orbits are circular in shape and do not have any directional characteristics.
4.	The maximum number of electrons in an orbital is <b>two</b> .	The maximum number of electrons in any orbit is $2n^2$ where $n$ represents the number of orbit.

### Schrodinger Wave Equation

As a result of great mathematical calculations on the subject and the concept of **wave mechanical model of atom**, Ervin Schrodinger (1926) described the behaviour of the electron in an atom by an equation called **Schrodinger wave equation**.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8 \pi^2 m}{h^2} (E - V) \psi = 0$$

where  $x, y$  and  $z$  are the three space coordinates

$h$  is Planck's constant

$m$  is the mass of the electron

$E$  is the total energy and  $V$  represents the potential energy of the electron.

$\psi$  represents the amplitude of the wave and is termed as **wave function**; while

$\frac{\partial^2 \psi}{\partial x^2}$ ,  $\frac{\partial^2 \psi}{\partial y^2}$  and  $\frac{\partial^2 \psi}{\partial z^2}$  represent the second derivatives of  $\psi$  with respect to  $x, y$  and  $z$  axis respectively.

In the Schrodinger wave equation, the  $\psi$  value will have significance only for certain definite values of the total energy  $E$ . The permissible energy values are called as **Eigen values** and the corresponding wave function  $\psi$  is termed as Eigen function. The  $\psi^2$  is a measure of the probability of finding an electron in a given region, i.e. a high value of  $\psi^2$  shows the greater probability of locating the electron at that point. Accordingly, the electrons are regarded as a **diffused cloud rather than a small individual**.

### 1.8. QUANTUM NUMBERS

We have studied that orbital is that area around the nucleus in which the probability of finding the electron is maximum. However, an atom contains a large number of orbitals, which are distinguished from each other by their size, shape and orientation (direction) in space. The parameters by which the orbitals are distinguished can be expressed by a set of numbers known as **quantum numbers**. Thus, **quantum numbers may be defined as set of numbers which display complete information about size, shape and orientation of the orbital**. These are designated as **principal quantum number** ( $n$ ), **azimuthal quantum number** ( $l$ ) and **magnetic quantum number** ( $m$ ). Thus, an orbital is designated by three quantum numbers. The fourth quantum number designated as **spin quantum number** ( $s$ ), represents the spin of electron i.e. rotation of electron about its own axis. Thus, an electron is designated by four quantum numbers  $n, l, m$  and  $s$ . These four quantum numbers are discussed below.

1. **Principal quantum number** ( $n$ ). This is an important quantum number which gives the following information about the electron.

- (i) This refers to the average **distance of the electron from the nucleus** i.e. it relates to the size of the electron cloud.
- (ii) It denotes the energy level to which the electron belongs i.e. the energy of the electron in a particular orbit is given by the equation

$$E_n = - \frac{2\pi^2 Z^2 e^4 m K^2}{n^2 h^2} = - \frac{313.3 Z^2}{n^2} \text{ kcal}$$

For hydrogen atom  $Z = 1$  and  $n = 1$ . Thus the energy of electron in first orbit is

$$E_1 = - \frac{313.3 \times 1^2}{1^2} \text{ kcal} \quad \textbf{K shell,}$$

Similarly, when  $n = 2$  and  $n = 3$ , the energy levels  $E_2$  and  $E_3$  are

$$E_2 = - \frac{313.3 \times 1^2}{2^2} = - 78.33 \text{ kcal} \quad \textbf{L shell}$$

$$E_3 = - \frac{313.3 \times 1^2}{3^2} = - 34.81 \text{ kcal} \quad \textbf{M shell}$$

Thus the energy increases with the increase in the value of  $n$ .

Thus, the various shells in increasing order of energy are designated by the capital letter as given below.

<i>n</i>	1	2	3	4	5	6	7
Shell	K	L	M	N	O	P	Q

- (iii) It gives information about the maximum number of electrons that can be accommodated in any shell. Number of electrons in any shell is given by expression  $2n^2$  where  $n = 1, 2, 3, 4, \dots$  etc.

<i>n</i>	1	2	3	4	5
Number of electrons	2	8	18	32	50

**2. Azimuthal quantum number or angular quantum number (*l*).** This quantum number is denoted by '*l*' and gives the following information about the electron.

- (i) It tells about the number of subshells within a given principal energy shell to which the electron belongs. For a given value of principal quantum number, '*n*', the azimuthal quantum number, '*l*', may have all integral values from 0 to ( $n - 1$ ), each of which represents a different subenergy level or subshell. These subshells are designated by letters *s*, *p*, *d* and *f* for which  $l = 0, 1, 2$  and  $3$  respectively e.g.,

<i>n</i>	1	2	3	4
<i>l</i>	0	0, 1	0, 1, 2	0, 1, 2, 3
Subshell	<i>s</i>	<i>s</i> , <i>p</i>	<i>s</i> , <i>p</i> , <i>d</i>	<i>s</i> , <i>p</i> , <i>d</i> , <i>f</i>
Designation of sub shell	1 <i>s</i>	2 <i>s</i> , 2 <i>p</i>	3 <i>s</i> , 3 <i>p</i> , 3 <i>d</i>	4 <i>s</i> , 4 <i>p</i> , 4 <i>d</i> , 4 <i>f</i>

Thus, the total number of subshells for a given principal shell is equal to the value of *n*.

- (ii) It tells for the relative energies of subshells belonging to same shell. The energies of the different subshells present within the same principal shell are in the following order

$$\frac{s < p < d < f}{\text{Increasing energy}}$$

- (iii) The value of *l* refers to the shape of the subshell. For example,

<i>l</i>	Subshell	Shape of subshell
0	<i>s</i>	Spherical
1	<i>p</i>	Dumbbell
2	<i>d</i>	Double dumbbell
3	<i>f</i>	Complex shape.

- (iv) It gives information for the orbital angular momentum, whose value is equal to  $\frac{h}{2\pi} \sqrt{l(l+1)}$

**3. Magnetic quantum number (*m*).** This quantum number describes the behaviour of electron in a magnetic field. This is due to the fact that a revolving electron possesses angular momentum which results in the development of small magnetic field. When this magnetic field interacts with the external magnetic field of the earth, the electron cloud in a given subshell orients itself in a certain preferred region of space around the nucleus. These preferred regions of space taken by the electron cloud are called **orbitals**. Thus, this quantum number provides following information about the electron.

- (i) This quantum number gives the number of permitted orientations of subshells. For example, for a given value of ' $l$ ', the possible values of ' $m$ ' range from  $-l$  through 0 to  $+l$ . This gives a total of  $(2l + 1)$  values of  $m$ . Each value of  $m$  corresponds to one atomic orbital. For example,

For $s$ -subshell	$l = 0$	$m = 0$	<i>i.e.</i> $s$ -subshell has <b>one</b> orbital
For $p$ -subshell	$l = 1$	$m = -1, 0, +1$	<i>i.e.</i> $p$ -subshell has <b>three</b> orbitals
For $d$ -subshell	$l = 2$	$m = -2, -1, 0, +1, +2$	<i>i.e.</i> $d$ -subshell has <b>five</b> orbitals
For $f$ -subshell	$l = 3$	$m = -3, -2, -1, 0, +1, +2, +3$	<i>i.e.</i> $f$ -subshell has <b>seven</b> orbitals

These permitted orientations can be summed up for a given value of principal quantum number,  $n$ , as shown below in Table 1.2

**Table 1.2. Permitted Combinations of  $n$ ,  $l$  and  $m$ .**

$n$	$l$	$m$	Designation of subshell	Number of orbitals	Total number of orbitals
1	0	0	1s	1	1
2	0	0	2s	1	4
	1	-1, 0, +1	2p	3	
3	0	0	3s	1	9
	1	-1, 0, +1	3p	3	
	2	-2, -1, 0, +1, +2	3d	5	

- (ii) It explains successfully the splitting of spectral lines in the magnetic field *i.e.* Zeeman effect.

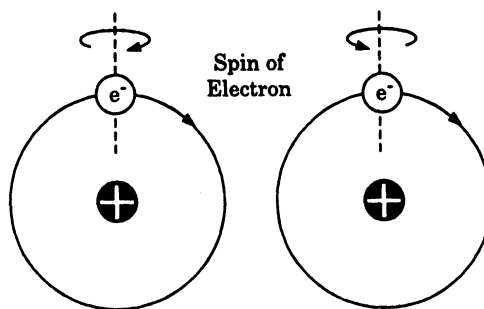
**4. Spin quantum number ( $s$ ):** The above discussed three quantum numbers ( $n$ ,  $l$  and  $m$ ), used to designate an orbital, can be used equally well to label the electron in an orbital. It has actually been observed that the electron in an atom is not only revolving around the nucleus but is also spinning about its own axis. This quantum number accounts for the spinning orientation of the electron.

The electron in an orbital can have only two types of spins *i.e.* in clockwise and anticlockwise direction. Therefore, the spin quantum number can have only two values *i.e.*  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . The two spins of

the electrons in an orbital are usually represented by arrows pointing in the opposite direction *i.e.*  $\uparrow$  and  $\downarrow$  respectively.

The value of spin quantum number is independent of the values of other three quantum numbers.

**1.8.1. Relationship between various quantum numbers.** We have seen that the value of ' $m$ ' is derived from ' $l$ ' and those of ' $l$ ' from ' $n$ '. Therefore, each electron can be identified in terms of four quantum numbers namely  $n$ ,  $l$ ,  $m$  and  $s$  as given in Table 1.3.



**Fig. 1.23. Clockwise and anticlockwise spins of an electron.**

**Table 1.3. Maximum Number of Electrons in K, L, M Shell**

Energy level	Principal quantum number "n"	Total number of energy sublevels and their azimuthal quantum number "l"	Magnetic quantum number "m"	Spin quantum number "s"	Designation of orbital	Total number of electrons
K	1	One : 0	0	$\pm \frac{1}{2}$	1 s	2
L	2	Two : 0 1	0	$\pm \frac{1}{2}$	2 s	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">2</div> <div style="font-size: 3em;">}</div> <div>8</div> </div>
			- 1	$\pm \frac{1}{2}$	2 $p_x$	
			0	$\pm \frac{1}{2}$	2 $p_z$	
			+ 1	$\pm \frac{1}{2}$	2 $p_y$	
M	3	Three : 0 1 2	0	$\pm \frac{1}{2}$	3 s	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">2</div> <div style="font-size: 3em;">}</div> <div>18</div> </div>
			- 1	$\pm \frac{1}{2}$	3 $p_x$	
			0	$\pm \frac{1}{2}$	3 $p_z$	
			+ 1	$\pm \frac{1}{2}$	3 $p_y$	
			- 2	$\pm \frac{1}{2}$	3 $d_{x^2-y^2}$	
			- 1	$\pm \frac{1}{2}$	3 $d_{yz}$	
			0	$\pm \frac{1}{2}$	3 $d_z^2$	
			+ 1	$\pm \frac{1}{2}$	3 $d_{zx}$	
			+ 2	$\pm \frac{1}{2}$	3 $d_{xy}$	

### Orbital Wave Function and Probability Distribution Curves

For presenting the molecular geometry of an orbital, the concept of wave mechanical model provided a better understanding. An orbital wave function  $\psi$  can be written as the product of two functions.

$$\psi = \psi(r) \cdot \psi(\theta, \phi)$$

The square of the wave function ( $\psi^2$ ) gives the probability of finding the electron in a given volume of space.

Here  $\psi(r)$  represents the radial wave function and  $\psi(\theta, \phi)$  denotes the angular part of the wave function as shown in Fig. 1.24.

#### Radial Wave Function $\psi(r)$

The radial part of the wave function **depends on  $n$  and  $l$  values** and gives the distribution of the electrons with respect to its distance from the nucleus, *i.e.* **it relates to the size of the orbital**. The radial wave function may be represented graphically in two ways.

- (i) The radial wave function  $\psi(r)$  is plotted against distance  $r$  from the nucleus as shown for 1s, 2s, 2p, etc. in Fig. 1.25.

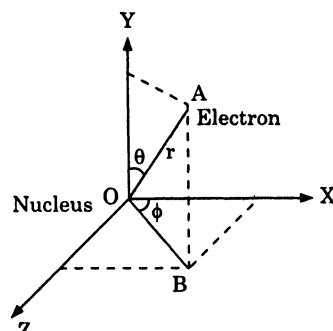


Fig. 1.24. Spherical polar coordinates

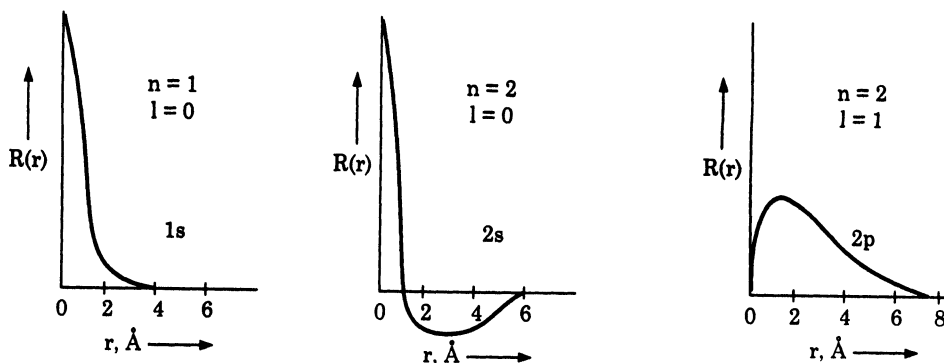
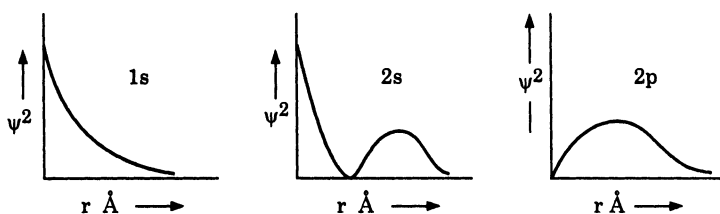


Fig. 1.25. Radial part of the wave function for 1s, 2s, and 2p.

- (ii) A graph between  $\psi_{(r)}^2$  and  $r$  (distance from the nucleus) gives the **probability distribution curve**. Such curves are similar to Fig. 1.25 except that the negative part of the radial distribution becomes positive in  $\psi_{(r)}^2$  curve. Furthermore as shown below in Fig. 1.26, the value of  $\psi_{(r)}^2$  is either positive or zero in distribution curves.

Fig. 1.26. Variation of  $\psi^2$  in 1s, 2s and 2p orbitals.

These probability distribution curves enclose regions of maximum probability, *i.e.* to an extent of 95% or higher.

### Angular wave function $\psi(\theta, \phi)$

The angular part of the wave function **depends on the values of  $l$  and  $m$**  and relates to the **shape of the atomic orbital**. Shape of atomic orbitals depends on the angles  $\theta$  and  $\phi$  determines the geometry of the atom.

The expression for s-orbital has no angular dependence and hence it is spherically symmetrical.

## 1.9. SHAPES OF ATOMIC ORBITALS

An orbital is described as **the region around the nucleus in which the probability of finding the electron of given energy is maximum**. However, a better way to describe the probability of electron is in terms of negative charge cloud. The density of charge cloud is proportional to  $\psi^2$  or probability. Such representation of orbital is called **charge cloud picture of orbital**.

**Shape of s-orbitals.** The spherical electron cloud picture of 1s orbital is shown in Fig. 1.27. The s-orbital of higher energy levels are also spherical in shape but more diffused. Between the orbitals, there is some spherical region around the nucleus where probability of finding the electron is zero or minimum. These regions of zero or minimum electron probability are called **nodes** or **nodal plane**, *e.g.* in 2 s orbital, there is one node. Similarly, for  $n$  s orbital the number of nodes will be  $(n - 1)$ .



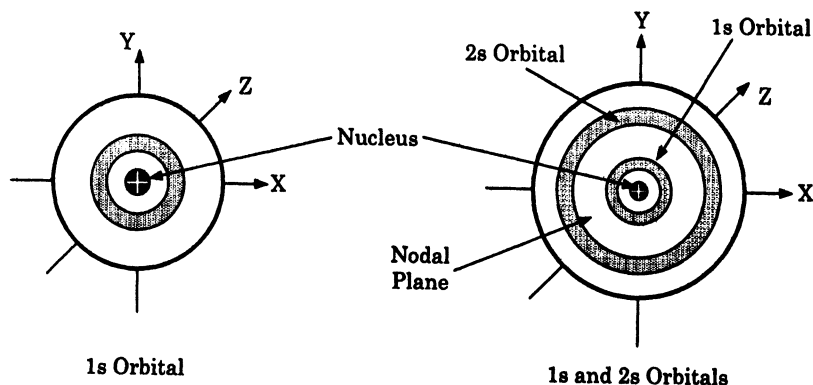
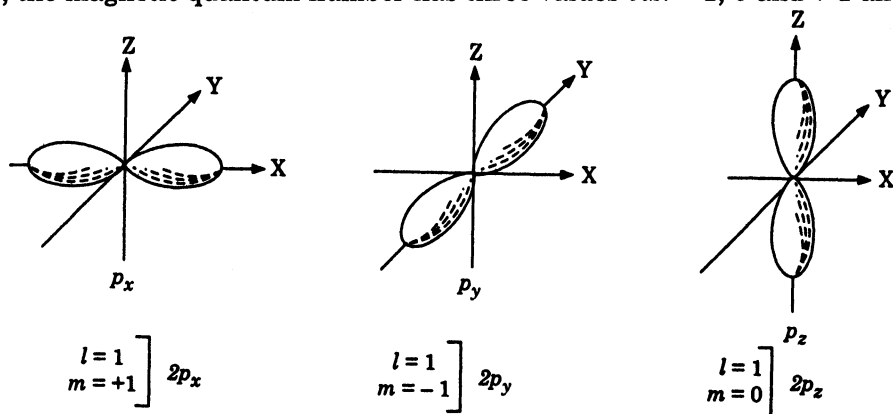


Fig. 1.27. Shape of s-orbitals.

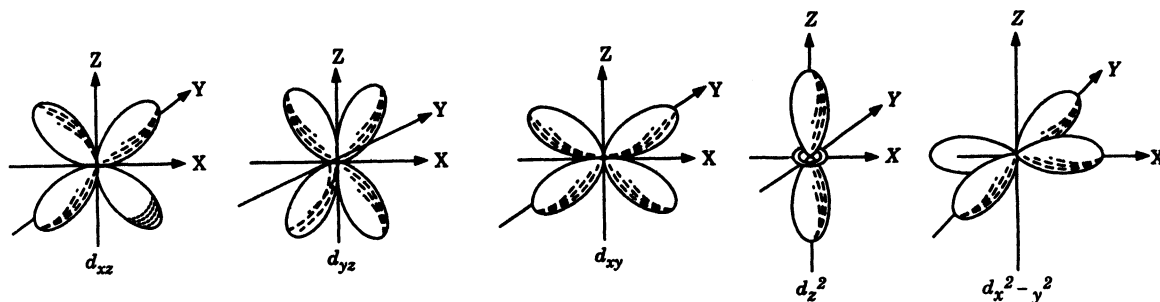
**Shape of  $p$ -orbitals.** The atomic orbital with azimuthal quantum number  $l = 1$  are called  **$p$ -orbitals**. For  $l = 1$ , the magnetic quantum number has three values *viz.*  $-1, 0$  and  $+1$  and correspondingly results in three  $p$ -orbitals. Each  $p$ -orbital has two lobes which are separated by a plane of zero probability (node). These three **dumb-bell** shaped orbitals are orienting along  $x$  axis,  $y$  axis and  $z$ -axis. These are designated as  $p_x$ ,  $p_y$  and  $p_z$  respectively.

Fig. 1.28. Shape of  $2p$  orbitals.

The spatial distribution of these three  $2p$  orbitals are shown in Fig. 1.28.

**Shape of  $d$ -orbitals.** The atomic orbitals with  $l = 2$  are termed as  $d$ -orbitals. For  $l = 2$ ,  $m$  has five values, *i.e.*  $-2, -1, 0, +1, +2$  representing the five orientations of  $d$  orbitals designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_z^2$ ,  $d_{xz}$  and  $d_x^2 - y^2$  respectively. Three of these five orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  are identical in shapes and are directed in between the three mutually perpendicular axis. The other two ( $d_x^2 - y^2$  and  $d_z^2$ ) are pointing along the axis as shown in Fig. 1.29.

Except  $d_z^2$  orbital, all other  $d$ -orbitals are double dumb-bell in shape.

Fig. 1.29. Shape of  $d$ -orbitals.

**1.9.1. Pauli's Exclusion Principle.** This guiding principle, which can be applied to calculate the maximum number of electrons that can be added in each shell and subshell in an atom, was put forward by **Wolfgang Pauli** (1925). According to this principle, **'no two electrons in an atom can have the same set of all the four quantum numbers'**. To illustrate this concept let us take an orbital specified by three quantum numbers  $n$ ,  $l$  and  $m$ . Since an electron in an orbital can have two values of 's' as  $+1/2$  or  $-1/2$ , therefore, the two electrons have different set of four quantum numbers. For example,  $2s$  orbital has  $n = 2$ ,  $l = 0$ ,  $m = 0$  and  $s = +\frac{1}{2}$  or  $-\frac{1}{2}$

Therefore, one  $2s$  electron has quantum numbers as  $n = 2$ ,  $l = 0$ ,  $m = 0$  and  $s = +1/2$  and second electron has quantum numbers as  $n = 2$ ,  $l = 0$ ,  $m = 0$  and  $s = -1/2$ .

So, the Pauli's exclusion principle can be redefined as :

- (i) an orbital cannot have more than two electrons.
- (ii) if orbital has two electrons, these must have opposite spins *i.e.* they exist as paired electrons.

From the aforesaid discussion, we can conclude that

- (i) **s-subshell** (containing only **one orbital**) can have a maximum of **two electrons**.
- (ii) **p-subshell** (containing **three orbitals**) can have a maximum of **six electrons**.
- (iii) **d-subshell** (containing **five orbitals**) can have a maximum of **ten electrons**.
- (iv) **f-subshell** (containing **seven orbitals**) can have a maximum of **fourteen electrons**.

From this knowledge we can calculate the total number of electrons in various shells as shown in table 1.4.

**Table 1.4**

$(n = 1)$ <b>K-shell</b>	$(l = 0)$ <b>1s-subshell</b>	$(m = 0)$ <b>one orbital</b>	<b>2 electrons</b>
$(n = 2)$ <b>L-shell</b>	$(l = 0)$ <b>2s-subshell</b>	$(m = 0)$ <b>one orbital</b>	2 electrons
	$(l = 1)$ <b>2p-subshell</b>	$(m = -1, 0, +1)$ <b>three orbitals</b> <b>4 orbitals</b>	6 electrons <hr/> <b>8 electrons</b>
$(n = 3)$ <b>M-shell</b>	$(l = 0)$ <b>3s-subshell</b>	$(m = 0)$ <b>one orbital</b>	2 electrons
	$(l = 1)$ <b>3p-subshell</b>	$(m = -1, 0, +1)$ <b>three orbitals</b>	6 electrons
	$(l = 2)$ <b>3d-subshell</b>	$(m = -2, -1, 0, +1, +2)$ <b>five orbitals</b> <b>9 orbitals</b>	10 electrons <hr/> <b>18 electrons</b>
$(n = 4)$ <b>N-shell</b>	$(l = 0)$ <b>4s-subshell</b>	$(m = 0)$ <b>one orbital</b>	2 electrons
	$(l = 1)$ <b>4p-subshell</b>	$(m = -1, 0, +1)$ <b>three orbitals</b>	6 electrons
	$(l = 2)$ <b>4d-subshell</b>	$(m = -2, -1, 0, +1, +2)$ <b>five orbitals</b>	10 electrons
	$(l = 3)$ <b>4f-subshell</b>	$(m = -3, -2, -1, 0, +1, +2, +3)$ <b>seven orbitals</b> <b>16 orbitals</b>	14 electrons <hr/> <b>32 electrons</b>

**Example 1.32.** (a) Write all the values of  $l$  and  $m$  for  $n = 3$ .

(b) For  $l = 3$ , write all values of  $m$ .

**Solution.** (a) When  $n = 3$ , the values of  $l$  are 0, 1, 2

$\therefore$  when  $l = 0$   $m = 0$

$l = 1$   $m = -1, 0, +1$

$l = 2$   $m = -2, -1, 0, +1, +2$

(b) For  $l = 3$ , the values of  $m$  are  $-3, -2, -1, 0, +1, +2, +3$ .

**Example 1.33.** What designation will you assign to an orbital having following quantum numbers ?

(a)  $n = 3$ ,  $l = 1$ ,  $m = -1$

(b)  $n = 4$ ,  $l = 2$ ,  $m = +2$

(c)  $n = 5$ ,  $l = 0$ ,  $m = 0$

(d)  $n = 2$ ,  $l = 1$ ,  $m = 0$

**Solution.** (a) Since  $l = 1$  corresponds to  $p$ -orbital and  $m = -1$  shows orientation either in  $x$  or  $y$  axis, this orbital refers to  $3p_x$  or  $3p_y$

(b)  $4d_{xy}$  or  $4d_{x^2-y^2}$  ; (c)  $5s$  ; (d)  $2p_z$

**Example 1.34.** How many orbitals will be present in the subshell when

(a)  $l = 0$ , (b)  $l = 1$ , (c)  $l = 2$ , (d)  $l = 3$

**Solution.** Number of orbitals in any subshell are given by the formula  $(2l + 1)$

Therefore, no. of orbitals when  $l = 0$  are  $(2 \times 0 + 1) = 1$  orbital.

$l = 1$   $(2 \times 1 + 1) = 3$  orbitals

$l = 2$   $(2 \times 2 + 1) = 5$  orbitals

$l = 3$   $(2 \times 3 + 1) = 7$  orbitals

**Example 1.35.** How many electrons in a given atom can have the following quantum numbers ?

(a)  $n = 4$ ,  $l = 1$ , (b)  $n = 2$ ,  $l = 1$ ,  $m = -1$ ,  $s = +\frac{1}{2}$ , (c)  $n = 3$ , (d)  $n = 4$ ,  $l = 2$ ,  $m = 0$ .

**Solution.** (a)  $l = 1$  refers to  $p$ -subshell which has three orbitals ( $p_x$ ,  $p_y$  and  $p_z$ ) each having two electrons. Therefore, total number of electrons are 6.

(b)  $l = 1$  refers to  $p$ -subshell,  $m = -1$  refers to  $p_x$  or  $p_y$  orbital whereas,  $s = +\frac{1}{2}$  indicates for only 1 electron.

(c) For  $n = 3$ ,  $l = 0, 1, 2$

$l = 0$   $m = 0$  2 electrons

$l = 1$   $m = -1, 0, +1$  6 electrons

$l = 2$   $m = -2, -1, 0, +1, +2$  10 electrons

Total electrons 18 electrons

Alternatively, number of electrons for any energy level is given by

$$2n^2 \quad \text{i.e.} \quad 2 \times 3^2 = 18 \text{ electrons}$$

(d)  $l = 2$  means  $d$ -subshell and  $m = 0$  refers to  $d_z^2$  orbital

$\therefore$  Number of electrons are 2.

**Example 1.36.** What subshells are possible when

(a)  $n = 2$

(b)  $n = 3$

(c)  $n = 4$ .

**Solution.** Number of subshells for any energy level is given by  $n^2$ . Therefore, number of subshells are

(a)  $2^2 = 4$

(b)  $3^2 = 9$

(c)  $4^2 = 16$ .

**Example 1.37.** Which of the following set of quantum number are not permitted ?

- (a)  $n = 3, l = 2, m = -1, s = 0$       (b)  $n = 2, l = 2, m = +1, s = -\frac{1}{2}$   
 (c)  $n = 2, l = 0, m = +1, s = -\frac{1}{2}$       (d)  $n = 3, l = 2, m = -2, s = +\frac{1}{2}$ .

**Solution.** (a) This set of quantum number is not permitted as value of  $s$  cannot be zero.

(b) This set of quantum number is not permitted as the value of  $l$  cannot be equal to  $n$ .

(c) This set of quantum number is not permitted as value of  $m$  cannot be greater than  $l$ .

(d) This set of quantum number is permitted.

### 1.10. ENERGY LEVEL DIAGRAMS

Since the principal quantum number  $n$ , representing a shell varies in energy thus the various orbitals in an atom also differ in energy level. A **diagram showing the relative energies of various orbitals in an atom is called energy level diagram.**

**Energy level diagram of hydrogen or hydrogen like species.** A hydrogen atom or hydrogen like species (*e.g.*,  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ....etc.) has only one electron which is present in  $1s$  orbital in ground state. By absorption of energy, this electron may jump to any orbital of higher energy levels. The relative energies of these orbitals have been observed as given in Fig 1.30.

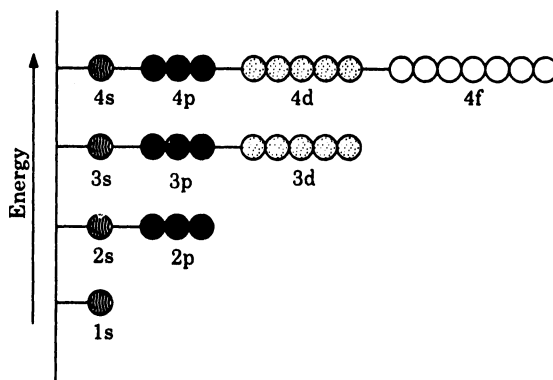


Fig. 1.30. Energies of different orbitals in a hydrogen atom.

This shows that all the orbitals of a given principal energy level *i.e.*  $s$ ,  $p$ ,  $d$  and  $f$  orbitals have same energies at a particular energy level *i.e.*  $2s$  and  $2p$  orbitals have same energy. Likewise,  $3s$ ,  $3p$  and  $3d$  have same energy and so on.

Thus, the energies of various orbitals in hydrogen or hydrogen like species depend on the value of  $n$  and independent of the value of  $l$  (obviously the quantum number  $l$  refers only to the shape of the orbital).

**Energy level diagram of multielectron atoms.** Energies of orbitals having the same value of  $n$  but different values of  $l$  have been observed to be different in case of multielectron atom *i.e.* for  $n = 2$ , the subshell,  $2s$  and  $2p$  have different energies. Likewise,  $3s$ ,  $3p$  and  $3d$  subshells of  $n = 3$  have different energies as shown in Fig. 1.31.

The relative order of energies of various sub-shells in a multielectron atom can be predicted with the help of following **Bohr-Bury's rules** also known as  **$(n + l)$  rules.**

(i) **Rule :** Lower the value of  $(n + l)$  for an orbital, lower is its energy. For example,

(a)  $3s$  orbital has lower energy than  $3p$

For  $3s$  orbital,  $n = 3$  and  $l = 0$ .

$\therefore (n + l) = 3 + 0 = 3$



**Solution.** Applying  $(n + l)$  rule we have,

(a) For  $3d$ ,  $(n + l) = 3 + 2 = 5$

For  $3s$ ,  $(n + l) = 3 + 0 = 3$

$\therefore 3s < 3d$

(b) For  $4f$ ,  $(n + l) = 4 + 3 = 7$

For  $5d$ ,  $(n + l) = 5 + 2 = 7$

Since  $4f$  orbital has lower value of  $n$

$\therefore$  According to Bohr Bury rule (ii)  $4f < 5d$

(c) For  $4d$ ,  $(n + l) = 4 + 2 = 6$

For  $5s$ ,  $(n + l) = 5 + 0 = 5$

$\therefore 5s < 4d$

(d) For  $4p$ ,  $(n + l) = 4 + 1 = 5$

For  $3d$ ,  $(n + l) = 3 + 2 = 5$

Since value of  $n$  is lower for  $3d$  orbital

$\therefore 3d < 4p$

(e) For  $3s$ ,  $(n + l) = 3 + 0 = 3$

For  $3p$ ,  $(n + l) = 3 + 1 = 4$

$\therefore 3s < 3p$

### 1.11. ELECTRONIC CONFIGURATION OF ATOMS

The distribution of electrons of the atom in different orbitals is known as the **ground state electronic configuration of the atom**. The term **ground state** represents the position of electrons in the **lowest energy state** or the **most stable state**. The filling of orbitals in an atom is governed by the following three fundamental rules.

(i) **Aufbau's rule.** According to this rule "**the orbitals are filled progressively in order of their increasing energy beginning with the orbital of lowest energy**". The order of increasing energies of various orbitals based on  $(n + l)$  rule may be compiled as :

1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f
<b>Increasing energy</b>												

This trend of increasing energies of various orbitals may be remembered in the form of diagram represented in Fig. 1.32.

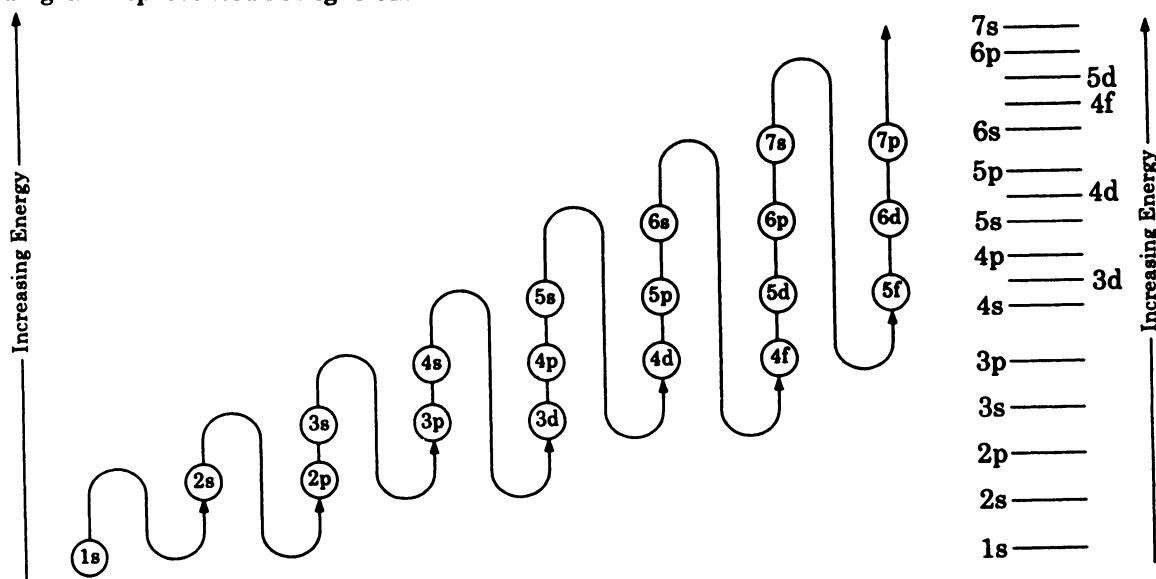


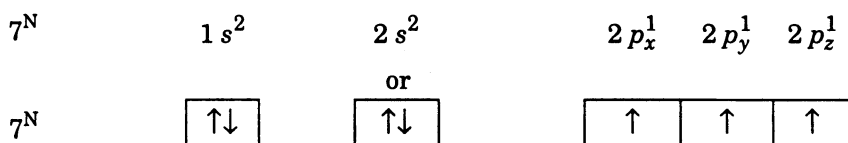
Fig. 1.32. Increasing order of energy of various orbitals.

(ii) **Pauli's exclusion principle.** According to this principle **"no two electrons in an atom can have the same set of all the four quantum numbers"**. In other words,

- (a) an orbital cannot have more than two electrons
- (b) if an orbital has two electrons, they must have opposite spins *i.e.* the two electrons must be paired.

(iii) **Hund's rule of maximum multiplicity.** This rule governs the arrangement of electrons in the orbitals of identical energies *e.g.*, amongst  $p_x, p_y$  and  $p_z$  or amongst  $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$  and  $d_z^2$ . According to this rule, **electron pairing in orbitals of same energy (*i.e.* orbitals of  $p, d$  or  $f$  subshell) shall take place only when all the orbitals of the subshell contain one electron each.**

This implies that two negatively charged electrons in a particular orbital experience greater repulsion and thus the pairing of electrons is avoided as long as it is possible during filling of orbitals of equal energy. Furthermore, the orbitals occupying single electron in parallel spin has higher stability because it corresponds to the state of lower energy. For example, electronic configuration of nitrogen (At. No. 7), applying Hund's rule, has three unpaired electrons in  $2p$  orbitals.



Applying these rules, the electronic configuration of first thirty elements are summarized below in Tables 1.5 and 1.6. From sodium (At. No. 11) to argon (At. No. 18),  $3s$  and  $3p$  orbitals are successively filled. After  $3p$ , the 19th electron in potassium (At No. 19) enters the  $4s$  orbital instead of  $3d$  because of Aufbau's rule.

**Table 1.5. Electronic Configuration of the First 20 Elements**

At. No.	Element	Electronic configuration			
		K	L	M	N
1	H	$1s^1$			
2	He	$1s^2$			
3	Li	$1s^2$	$2s^1$		
4	Be	$1s^2$	$2s^2$		
5	B	$1s^2$	$2s^2 2p_x^1$		
6	C	$1s^2$	$2s^2 2p_x^1 2p_y^1$		
7	N	$1s^2$	$2s^2 2p_x^1 2p_y^1 2p_z^1$		
8	O	$1s^2$	$2s^2 2p_x^2 2p_y^1 2p_z^1$		
9	F	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^1$		
10	Ne	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$		
11	Na	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^1$	
12	Mg	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2$	
13	Al	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1$	
14	Si	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1$	

At. No.	Element	Electronic configuration			
15	P	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1 3p_z^1$	
16	S	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^1 3p_z^1$	
17	Cl	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^1$	
18	Ar	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	
19	K	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	$4s^1$
20	Ca	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^2 3p_z^2$	$4s^2$

The electronic configuration of next ten elements, known as transition elements, are given in Table 1.6. These elements (from scandium to zinc) have atomic numbers 21 to 30 and follow calcium. During filling of electrons in these elements, the electrons are added in the  $3d$  orbitals.

**Table 1.6. Electronic Configuration of Transition Elements**

At. No.	Element	Electronic configuration		
21	Sc		$[Ar] 3d_{xy}^1$	$4s^2$
22	Ti		$[Ar] 3d_{xy}^1 3d_{yz}^1$	$4s^2$
23	V		$[Ar] 3d_{xy}^1 3d_{yz}^1 3d_{xz}^1$	$4s^2$
24	Cr		$[Ar] 3d_{xy}^1 3d_{yz}^1 3d_{xz}^1 3d_{x^2-y^2}^1 3d_z^1$	$4s^1$
25	Mn		$[Ar] 3d_{xy}^1 3d_{yz}^1 3d_{xz}^1 3d_{x^2-y^2}^1 3d_z^1$	$4s^2$
26	Fe		$[Ar] 3d_{xy}^2 3d_{yz}^1 3d_{xz}^1 3d_{x^2-y^2}^1 3d_z^1$	$4s^2$
27	Co		$[Ar] 3d_{xy}^2 3d_{yz}^2 3d_{xz}^1 3d_{x^2-y^2}^1 3d_z^1$	$4s^2$
28	Ni		$[Ar] 3d_{xy}^2 3d_{yz}^2 3d_{xz}^2 3d_{x^2-y^2}^1 3d_z^1$	$4s^2$
29	Cu		$[Ar] 3d_{xy}^2 3d_{yz}^2 3d_{xz}^2 3d_{x^2-y^2}^2 3d_z^2$	$4s^1$
30	Zn		$[Ar] 3d_{xy}^2 3d_{yz}^2 3d_{xz}^2 3d_{x^2-y^2}^2 3d_z^2$	$4s^2$

### Exceptional configurations of Cr and Cu

Elements with atomic numbers 24 and 29 have shown little deviation from Aufbau's rule. Here one electron from  $4s$  orbital shifts to higher energy level  $3d$  orbital. This migration of electron is due to higher stability of half-filled and fully-filled orbitals. The electronic configuration of these elements is given below.

Element	Atomic number	Expected electronic configuration	Observed electronic configuration
Cr	24	$[Ar]^{18} 3d^4 4s^2$	$[Ar]^{18} 3d^5 4s^1$
Cu	29	$[Ar]^{18} 3d^9 4s^2$	$[Ar]^{18} 3d^{10} 4s^1$

### Stability of fully filled and half filled orbitals

The reasons for higher stability of Cr (half-filled orbitals) and Cu (fully-filled orbitals) can be explained as follows.

(i) **Symmetry amongst orbitals.** Orbitals which are either half-filled or fully-filled are more symmetrical and therefore possess lower energy *i.e.* extra stability. Two negatively charged electrons when present in one orbital will have higher electron-electron repulsion. Therefore, higher stability of unpaired electrons in chromium is because of less electron-electron repulsion.



(ii) When orbitals are half-filled or fully-filled, the exchange of electrons between orbitals is maximum. Such exchange leads to greater stability of electrons in the orbitals, because low exchange energy results in higher stabilization energy.

Besides stability of half-filled and fully-filled orbitals, some more deviations are observed like **strong nuclear attraction** and **less shielding effect caused by *d* and *f* electrons**, in the electronic configuration of elements with At. No. > 30. However, detailed study of such deviations are not included as it is beyond the scope of this book. The electronic configuration of elements with At. No. > 30 in their ground state is given in Table 1.7.

**Table 1.7. Electronic Configuration of Elements (At. No. > 30) in the Ground State**

Atomic number	Element	Chemical Name	Electronic Configuration
31	Ga	Gallium	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^1$
32	Ge	Germanium	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^2$
33	As	Arsenic	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^3$
34	Se	Selenium	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^4$
35	Br	Bromine	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^5$
36	Kr	Krypton	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^6$
37	Rb	Rubidium	$[\text{Kr}]^{36} 5s^1$
38	Sr	Strontium	$[\text{Kr}]^{36} 5s^2$
39	Y	Yttrium	$[\text{Kr}]^{36} 4d^1 5s^2$
40	Zr	Zirconium	$[\text{Kr}]^{36} 4d^2 5s^2$
*41	Nb	Niobium	$[\text{Kr}]^{36} 4d^4 5s^1$
*42	Mo	Molybdenum	$[\text{Kr}]^{36} 4d^5 5s^1$
43	Te	Technetium	$[\text{Kr}]^{36} 4d^6 5s^2$
*44	Ru	Ruthenium	$[\text{Kr}]^{36} 4d^7 5s^1$
*45	Rh	Rhodium	$[\text{Kr}]^{36} 4d^8 5s^1$
*46	Pd	Palladium	$[\text{Kr}]^{36} 4d^{10} 5s^0$
47	Ag	Silver	$[\text{Kr}]^{36} 4d^{10} 5s^1$
48	Cd	Cadmium	$[\text{Kr}]^{36} 4d^{10} 5s^2$
49	In	Indium	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^1$
50	Sn	Tin	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^2$
51	Sb	Antimony	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^3$
52	Te	Tellurium	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^4$
53	I	Iodine	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^5$
54	Xe	Xenon	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^6$
55	Cs	Cesium	$[\text{Xe}]^{54} 6s^1$
56	Ba	Barium	$[\text{Xe}]^{54} 6s^2$
*57	La	Lanthanum	$[\text{Xe}]^{54} 5d^1 6s^2$
*58	Ce	Cerium	$[\text{Xe}]^{54} 5f^1 5d^1 6s^2$
59	Pr	Praseodymium	$[\text{Xe}]^{54} 5f^3 5d^0 6s^2$
60	Nd	Neodymium	$[\text{Xe}]^{54} 5f^4 6s^2$
61	Pm	Promethium	$[\text{Xe}]^{54} 5f^5 6s^2$
62	Sm	Samarium	$[\text{Xe}]^{54} 5f^6 6s^2$
63	Eu	Europium	$[\text{Xe}]^{54} 5f^7 6s^2$
64	Gd	Gadolinium	$[\text{Xe}]^{54} 5f^7 5d^1 6s^2$
65	Tb	Terbium	$[\text{Xe}]^{54} 5f^9 6s^2$
66	Dy	Dyprosium	$[\text{Xe}]^{54} 5f^{10} 6s^2$
67	Ho	Holmium	$[\text{Xe}]^{54} 5f^{11} 6s^2$

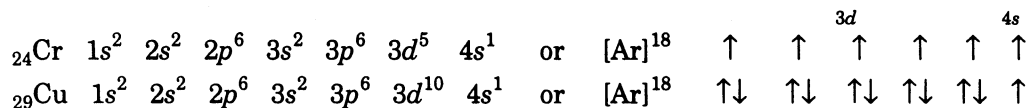
Atomic number	Element	Chemical Name	Electronic Configuration
68	Er	Erbium	$[\text{Xe}]^{54} 5f^{12} 6s^2$
69	Tm	Thulium	$[\text{Xe}]^{54} 5f^{13} 6s^2$
70	Yb	Ytterbium	$[\text{Xe}]^{54} 5f^{14} 6s^2$
71	Lu	Lutetium	$[\text{Xe}]^{54} 5f^{14} 5d^1 6s^2$
72	Hf	Hafnium	$[\text{Xe}]^{54} 5f^{14} 5d^2 6s^2$
73	Ta	Tantalum	$[\text{Xe}]^{54} 5f^{14} 5d^3 6s^2$
74	W	Tungsten	$[\text{Xe}]^{54} 5f^{14} 5d^4 6s^2$
75	Re	Rhenium	$[\text{Xe}]^{54} 5f^{14} 5d^5 6s^2$
76	Os	Osmium	$[\text{Xe}]^{54} 5f^{14} 5d^6 6s^2$
77	Ir	Iridium	$[\text{Xe}]^{54} 5f^{14} 5d^7 6s^2$
78	Pt	Platinum	$[\text{Xe}]^{54} 5f^{14} 5d^8 6s^2$
79	Au	Gold	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^1$
80	Hg	Mercury	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2$
81	Tl	Thallium	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^1$
82	Pb	Lead	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^2$
83	Bi	Bismuth	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^3$
84	Po	Polonium	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^4$
85	At	Astatine	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^5$
86	Rn	Radon	$[\text{Xe}]^{54} 5f^{14} 5d^{10} 6s^2 6p^6$
87	Fr	Francium	$[\text{Rn}]^{86} 7s^1$
88	Ra	Radium	$[\text{Rn}]^{86} 7s^2$
89	Ac	Actinium	$[\text{Rn}]^{86} 6d^1 7s^2$
90	Th	Thorium	$[\text{Rn}]^{86} 5f^2 6d^0 7s^2$
91	Pa	Protactinium	$[\text{Rn}]^{86} 5f^2 6d^1 7s^2$
92	U	Uranium	$[\text{Rn}]^{86} 5f^3 6d^1 7s^2$
93	Np	Neptunium	$[\text{Rn}]^{86} 5f^4 6d^1 7s^2$
94	Pu	Plutonium	$[\text{Rn}]^{86} 5f^6 7s^2$
95	Am	Americium	$[\text{Rn}]^{86} 5f^7 7s^2$
96	Cm	Curium	$[\text{Rn}]^{86} 5f^7 6d^1 7s^2$
97	Bk	Berkelium	$[\text{Rn}]^{86} 5f^9 7s^2$
98	Cf	Californium	$[\text{Rn}]^{86} 5f^{10} 7s^2$
99	Es	Einsteinium	$[\text{Rn}]^{86} 5f^{11} 7s^2$
100	Fm	Fermium	$[\text{Rn}]^{86} 5f^{12} 7s^2$
101	Md	Mendelevium	$[\text{Rn}]^{86} 5f^{13} 7s^2$
102	No	Nobelium	$[\text{Rn}]^{86} 5f^{14} 7s^2$
103	Lr	Lawrencium	$[\text{Rn}]^{86} 5f^{14} 6d^1 7s^2$
104	Rf**	Rutherfordium	$[\text{Rn}]^{86} 5f^{14} 6d^2 7s^2$
105	Ha	Hahnium	$[\text{Rn}]^{86} 5f^{14} 6d^3 7s^2$
106	Unh	Unnithexium	$[\text{Rn}]^{86} 5f^{14} 6d^4 7s^2$
107	Ns	Neilsbohrium	$[\text{Rn}]^{86} 5f^{14} 6d^5 7s^2$
108	Hs	Hassium	$[\text{Rn}]^{86} 5f^{14} 6d^6 7s^2$
109	Mt	Meitnerium	$[\text{Rn}]^{86} 5f^{14} 6d^7 7s^2$
110	Uun	Ununnilium	$[\text{Rn}]^{86} 5f^{14} 6d^8 7s^2$

**Example 1.39.** Why is the electronic configuration  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$  not correct for the ground state of nitrogen atom ?

**Solution.** According to Hund's rule pairing of electrons in  $2p_x$  orbital shall take place when all orbitals of  $2p$  subshell have one electron each.

**Example 1.40.** Write the stable electronic configuration of Cr and Cu elements.

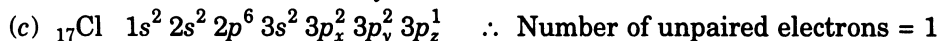
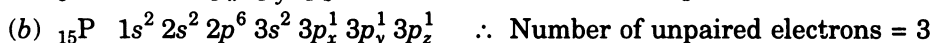
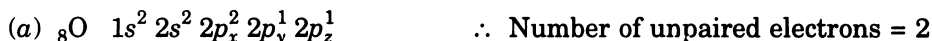
**Solution.**



It is because of greater stability of half-filled and fully-filled orbitals.

**Example 1.41.** Write down the electronic configuration of (a) oxygen, (b) phosphorus and (c) chlorine and also mention the number of unpaired electrons present in each element.

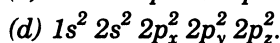
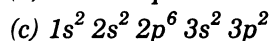
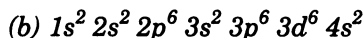
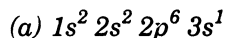
**Solution.**



#### 1.11.1. Rules for determining the group number of element by its electronic configuration

- If the last orbit (shell) has 1 or 2 electrons, then the group number of element is 1 or 2 respectively.
- If the last orbit (shell) has 3 or more electrons then the group number is the sum of electrons in the last shell plus 10.
- If electrons are present in  $(n - 1) d$  orbital (i.e. penultimate shell) in addition to those in  $ns$  shell, then the group number is equal to the total number of electrons in  $ns$  and  $(n - 1) d$  orbitals.

**Example 1.42.** From the following electronic configuration find out the group number of elements in the periodic table.



**Solution.** (a) In this electronic configuration, the last shell has only **one** electron.

Hence it belongs to group number 1.

(b) In this electronic configuration the penultimate shell has **6** electrons and last shell has **2** electrons. Therefore, the element belongs to group number **8**.

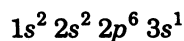
(c) In this electronic configuration, the last shell has **4** electrons. Therefore, the group number is  $4 + 10 = 14$ .

(d) Last shell has **8** electrons. Therefore, group number is  $8 + 10 = 18$ .

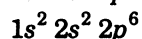
#### 1.11.2. Electronic configuration of cations and anions

(i) For writing the **electronic configuration of cations**, subtract the number of electrons equivalent to the number of positive charges from the atomic number of the element and then write the electrons in appropriate energy orbitals.

e.g., Na (At. No. = 11)

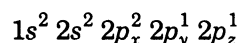


$\text{Na}^+$  (No. of electrons in  $\text{Na}^+ = 11 - 1 = 10$ )

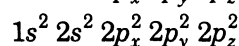


(ii) Electronic configuration of **anions** can be written by **adding number of electrons equivalent to the number of negative charges on the atom to its atomic number**. The electronic configuration of anions can be written as follows e.g., oxygen.

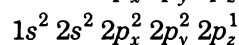
O (At. No. = 8)



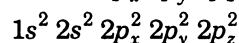
$O^{2-}$  (No. of electrons in  $O^{2-}$  anion =  $8 + 2 = 10$ )



Similarly, F (At. No. = 9)

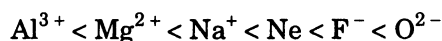


$F^-$  (No. of electrons in  $F^-$  anion) =  $9 + 1 = 10$



**The atom or ions which possess the same number of electrons are termed as isoelectronic species, e.g.,  $Na^+$ ,  $F^-$ ,  $O^{2-}$ , Ne,  $Al^{3+}$  and  $Mg^{2+}$  are isoelectronic species as each ion has ten electrons.**

**Atomic or ionic size of isoelectronic species decrease with the increase of nuclear charge i.e., number of protons present in the nucleus e.g., increasing order of ionic or atomic size is as given below.**

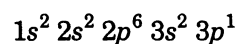


**Example 1.43.** Write the electronic configuration of the following ions.

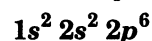
- (a)  $Al^{3+}$       (b)  $Cl^-$       (c)  $Mn^{2+}$       (d)  $Cu^+$

**Solution.**

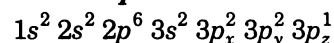
- (a)  $_{13}Al$  (At. No. = 13)



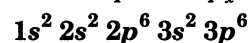
$Al^{3+}$  (No. of electrons =  $13 - 3 = 10$ )



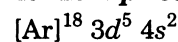
- (b)  $_{17}Cl$  (At. No. = 17)



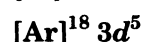
$Cl^-$  (No. of electrons =  $17 + 1 = 18$ )



- (c)  $_{25}Mn$  (At. No. = 25)

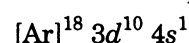


$Mn^{2+}$  (No. of electrons =  $25 - 2 = 23$ )

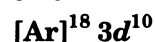


**Note :** Electrons are ionised first from the outermost shell and then from the penultimate shell.

- (d)  $_{29}Cu$  (At. No. = 29)



$Cu^+$  (No. of electrons =  $29 - 1 = 28$ )



**Example 1.44.** If the electronic configuration of elements A and B is



Write the formula of the compound.

**Solution.** Electronic configuration of A indicates that by losing one electron, it can acquire inert gas configuration i.e.  $A^+ = 1s^2$

Similarly, by gaining one electron, element B can attain inert gas configuration i.e.  $B^- = 1s^2 2s^2 2p^6$ .

Thus, the valence or oxidation state of A is + 1 and that of B is - 1 i.e.  $A^+$  and  $B^-$

The neutral compound of A and B will have their charges equal. Hence the formula of compound is **AB**.

### MULTIPLE CHOICE TYPE QUESTIONS

- The nucleus of the atom consists of
  - proton and neutron
  - proton and electron
  - neutron and electron
  - proton, neutron and electron
- The radius of hydrogen atom in the ground state is  $0.53 \text{ \AA}$ . The radius of  $Li^{2+}$  ion (atomic number = 3) in a similar state is
  - $0.17 \text{ \AA}$
  - $1.06 \text{ \AA}$
  - $0.53 \text{ \AA}$
  - $0.265 \text{ \AA}$
- The uncertainty principle was given by
  - Heisenberg
  - de Broglie

- (c) Clark Maxwell (d) Curies
4. The correct ground state electronic configuration of chromium atom (At. No. = 24) is  
 (a)  $[\text{Ar}] 3d^5 4s^1$  (b)  $[\text{Ar}] 3d^4 4s^2$   
 (c)  $[\text{Ar}] 3d^6 4s^0$  (d)  $[\text{Ar}] 4d^5 4s^1$
5. Principal, azimuthal and the magnetic quantum numbers are respectively related to  
 (a) size, shape and orientation (b) shape, size and orientation  
 (c) size, orientation and shape (d) none of the above
6. In a given atom no two electrons can have the same values for all the four quantum numbers. This is called  
 (a) Hund's rule (b) Aufbau principle  
 (c) Uncertainty principle (d) Pauli's exclusion principle
7. For azimuthal quantum number  $l = 3$ , the maximum number of electrons will be  
 (a) 2 (b) 6  
 (c) 0 (d) 14
8. How many unpaired electrons are there in  $\text{Ni}^{2+}$  ?  
 (a) 0 (b) 2  
 (c) 4 (d) 8
9. As per Aufbau principle, the energies of  $3p$ ,  $4d$ ,  $4s$  orbitals are in the order  
 (a)  $3p < 3d < 4s < 4p$  (b)  $3p < 4s < 3d < 4p$   
 (c)  $3d < 3p < 4s < 4p$  (d)  $3d < 3p < 4p < 4s$
10.  $\text{Na}^+$  ion is isoelectronic with  
 (a)  $\text{Li}^+$  (b)  $\text{Mg}^{2+}$   
 (c)  $\text{Ca}^{2+}$  (d)  $\text{Ba}^{2+}$

(CSE Pre. 1997)

### ANSWERS

1. (a)    2. (a)    3. (a)    4. (a)    5. (a)    6. (d)    7. (d)    8. (b)    9. (b)    10. (b)

### OTHER QUESTIONS

- Deduce the possible set of four quantum numbers when  $l = 2$
- Write down the number of electrons, protons and neutrons in the following.  
 ${}_1\text{H}^3$ ,  ${}_7\text{N}^{14}$ ,  ${}_{92}\text{U}^{238}$ ,  ${}_{24}\text{Cr}^{52}$ ,  ${}_{36}\text{Kr}^{84}$
- A neutral atom has 3K, 8L, 8M and 2N electrons. Find out the following from these data.  
 (i) Atomic number (ii) Total number of  $s$  electrons.  
 (iii) Total number of  $p$  electrons (iv) Total number of protons in the nucleus.  
 (v) Valency of the element.
- Write down the electronic configuration of P, Cr, Cu,  $\text{Cl}^-$  and  $\text{Co}^{2+}$
- (a) Given the electronic configuration of the following elements.  
 ${}_{16}\text{S}^{32}$ ,  ${}_{24}\text{Cr}^{52}$ ,  ${}_{29}\text{Cu}^{63}$  and  ${}_{36}\text{Kr}^{84}$   
 (b) Pick up the pairs of isotopes and isobars from the following.  
 ${}_1\text{H}^1$ ,  ${}_7\text{N}^{14}$ ,  ${}_8\text{O}^{16}$ ,  ${}_1\text{H}^2$ ,  ${}_{20}\text{Ca}^{40}$ ,  ${}_8\text{O}^{17}$ ,  ${}_{78}\text{Pt}^{198}$ ,  ${}_{18}\text{Ar}^{40}$ ,  ${}_6\text{C}^{14}$ ,  ${}_{78}\text{Pt}^{192}$
- What are isotopes and isobars ? Differentiate between the two and mention the characteristics of each.
- Why is there no  $2d$  or  $3f$  orbital ?