

4. Structure of Atom



Can you recall?

- What is the smallest unit of matter ?
- What is the difference between molecules of an element and those of a compound ?
- Does an atom have any internal structure or is it indivisible ?
- Which particle was identified by J. J. Thomson in the cathode ray tube experiment ?
- Which part of an atom was discovered by Ernest Rutherford from the experiment of scattering of α -particles by gold foil ?

4.1 Subatomic particles : Dalton's atomic theory was able to explain the laws of chemical combination successfully. However, it failed to explain some properties of matter. For example, it could not explain why substances like glass or ebonite when rubbed with silk or fur, generate electricity. Discovery of subatomic particles in late nineteenth and early twentieth century set a blow to Dalton's atomic model of hard sphere. Three important subatomic particles which are of concern to were found. Chemistry are proton, electron and neutron. Proton and neutron are present in the atomic nucleus and together are called nucleons. Electrons are present in the extranuclear part of an atom. The properties of electron, proton and neutron are summarised in Table 4.1

Table 4.1 : Properties of subatomic particles

| Name | Symbol | Absolute charge/C | Relative charge | Symbol for charge | Mass/kg | Mass/u | Approximate mass/u |
|----------|--------|---------------------------|-----------------|-------------------|---------------------------|---------|--------------------|
| Electron | e^- | -1.6022×10^{-19} | -1 | $-e$ | 9.10938×10^{-31} | 0.00054 | 0u |
| Proton | p | $+1.6022 \times 10^{-19}$ | +1 | $+e$ | 1.6726×10^{-27} | 1.00727 | 1 u |
| Neutron | n | 0 | 0 | | 1.67493×10^{-27} | 1.00867 | 1 u |

4.1.1 Discovery of electron : In the year 1897, **J. J. Thomson** investigated the cathode rays and found that the cathode rays are a stream of very small, negatively charged particles which are 1837 times lighter than a hydrogen atom and are present in all atoms. Later these particles were named as electrons.

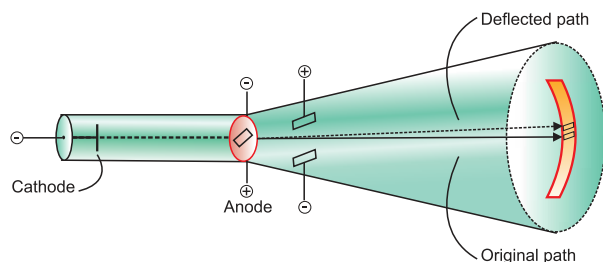


Fig. 4.1 : Cathode ray tube experiment

4.1.2 Discovery of proton : In the year 1911, **Ernest Rutherford** found in the experiment of scattering of α -particles by thin gold foil (see Fig. 4.2) that a few α -particles bounce back. From this he inferred the presence of massive and positively charged nucleus inside the atom. Following the discovery of nucleus in an atom, Rutherford found (1919) that fast moving α -particles transmuted nitrogen into oxygen with simultaneous liberation of hydrogen.



He further showed that other elements could also be transmuted, but hydrogen was always emitted.

On this basis Rutherford proposed that the hydrogen nucleus must be contained inside nuclei of all the elements. Hence, the hydrogen nucleus was renamed as **proton**.

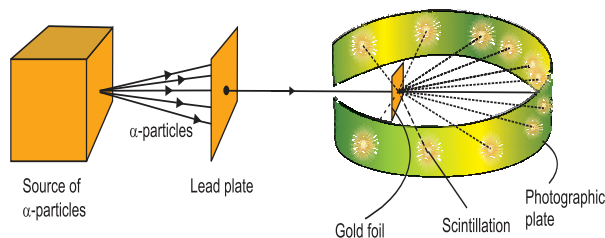


Fig. 4.2 : Rutherford's scattering experiment

4.1.3 Discovery of neutron : Existence of an electrically neutral and massive particle in the nucleus was predicted by Ernest Rutherford in 1920 to account for the disparity in atomic number and atomic mass of an element. In the year 1932, **James Chadwick** measured velocity of protons knocked out from paraffin by an unidentified radiation from beryllium. (See Fig. 4.3). From that he determined the mass of the particles of the unidentified neutral radiation which came out to be almost the same as that of a proton. He named this particle as '**neutron**' which was predicted by Rutherford earlier.

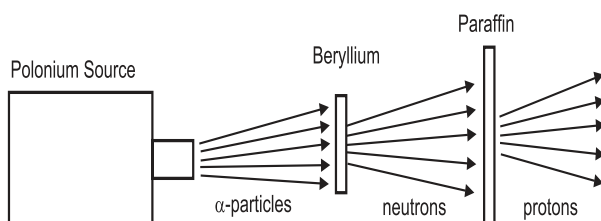


Fig. 4.3 : Discovery of neutron

4.2 Atomic number and atomic mass number

The number of protons in the nucleus is chemical identity of an element. This number is called as atomic number (Z) of the element. The positive charge on the nucleus is due to the protons present in it ($+Ze$). Atom being electrically neutral, it contains the same number of extranuclear electrons in it as its atomic number. Therefore the total electronic charge on an atom is $-Ze$. Thus in any atom,

$$\text{Atomic number } (Z) = \text{Number of protons} \\ = \text{Number of electrons}$$

As can be seen from Table 4.1, mass of an electron is negligibly small compared to that of the nucleons. As a result the mass of an atom can be considered to be concentrated in its nucleus. The approximate mass of one proton or one neutron is 1u. Therefore approximate atomic mass in daltons is numerically equal to the number of nucleons in the atom. The number of neutrons in the nucleus is designated by the symbol N ; and the total number of protons and neutrons, that is nucleons, in an atom is called its atomic mass number (A).

$$\text{Mass number } (A) = \text{Number of protons } (Z) \\ + \text{Number of Neutrons } (N)$$

$$\text{Therefore } A = Z + N \quad N = A - Z$$

The composition of any atom is represented by element symbol (X) with the atomic mass number (A) as superscript on left and atomic number (Z) as subscript its :



The atom or nucleus having a unique composition as specified by A_ZX is called a **nuclide**.

Problem 4.1: Find out the number of protons, electrons and neutrons in the nuclide ${}^{40}_{18}\text{Ar}$

Solution : In case of the nuclide ${}^{40}_{18}\text{Ar}$,

$$A = 40 \text{ and } Z = 18$$

$$\begin{aligned} \text{Number of protons} &= \text{number of} \\ \text{electrons} &= Z = 18 \text{ and number of} \\ \text{neutrons } N &= A - Z \end{aligned}$$

$$= 40 - 18 = 22$$

4.3 Isotopes, isobars and isotones

: Similarities in composition of nuclides results in three types of relationships.

i. Isotopes : Some elements exist as single natural nuclide. For example ${}^{19}_9\text{F}$.

However, many elements exist naturally as mixture of two or more types of atoms or nuclides. These individual nuclides are called isotopes of that element.

All the isotopes of an element have the same number of protons but different number of neutrons in their nuclei. As the proton number is the atomic number, all the isotopes of an element have the same position in the modern periodic table which exhibit similar chemical properties. All the natural isotopes of an element coexist and a definite natural abundance. Table 4.2 shows various features of the three common isotopes of carbon.

ii. Isobars : The atoms of different elements having the same mass number but different atomic numbers are called isobars. Isobars are different elements. They have different chemical properties and occupy different positions in modern periodic table. Table 4.3 shows an illustration of isobars.

Problem 4.2 : The two natural isotopes of chlorine viz. $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$ exist in relative abundance of 3:1. Find out the average atomic mass of chlorine.

Solution: From the relative abundance 3:1, it is understood that out of 4 chlorine atoms, 3 atoms have mass 35 and 1 has mass 37.

Therefore, the average atomic mass of chlorine

$$= \frac{3 \times 35 + 1 \times 37}{4} = 35.5$$

\therefore Atomic mass of chlorine = 35.5

Table 4.2 : Isotopes of carbon

| Symbol | Atomic Number Z | Atomic mass Number A | Neutron Number $N = A - Z$ | % Abundance | Stability |
|---------------------------|----------------------|---------------------------|----------------------------------|----------------|-------------|
| $^{12}_6\text{C}$ or C-12 | 6 | 12 | 6 | 98.9 % | Stable |
| $^{13}_6\text{C}$ or C-13 | 6 | 13 | 7 | 1.1 % | Stable |
| $^{14}_6\text{C}$ or C-14 | 6 | 14 | 8 | < 0.00017 % | Radioactive |

Table 4.3 : Isobars

| Isobars | Atomic No. Z | Mass No. A | Number of protons Z | No. of neutrons N |
|-------------------|----------------|--------------|-----------------------|---------------------|
| $^{14}_6\text{C}$ | 6 | 14 | 6 | 8 |
| $^{14}_7\text{N}$ | 7 | 14 | 7 | 7 |

Problem 4.3 : Three elements Q, R and T have mass number 40. Their atoms contain 22, 21 and 20 neutrons, respectively. Represent their atomic composition with appropriate symbol.

Solution : $A = Z + N \quad \therefore Z = A - N$

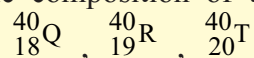
For the given three elements $A = 40$. Values of their atomic numbers Z , are obtained from the given values of neutron numbers, N , using the above expression.

for Q : $Z = A - N = 40 - 22 = 18$

for R : $Z = A - N = 40 - 21 = 19$

for T : $Z = A - N = 40 - 20 = 20$

\therefore The atomic composition of the three elements is written as follows :



iii. **Isotones** : The atoms of different elements having same number of neutrons in their nuclei are called isotones. Table 4.4 shows examples of isotones.

Table 4.4 : Isotones

| Isotones | Atomic number Z | Mass number A | Number of Neutrons $N = A - Z$ |
|---------------------|-------------------|-----------------|--------------------------------|
| ${}^{11}_5\text{B}$ | 5 | 11 | 6 |
| ${}^{12}_6\text{C}$ | 6 | 12 | 6 |

We will consider some more aspects of nuclides in the Chapter 13.

4.4 Drawbacks of Rutherford atomic model

i. Let us now go back to the point of time when Rutherford put forth his nuclear model of atom. It is akin to a miniature of the solar system, the nucleus playing the role of the massive sun and the electrons are lighter planets. Electrons in this model could not be stationary as the electrostatic force of attraction exerted would pull them towards itself, and this would form a miniature version of Thomson's atomic model. However, the electrons revolving about the nucleus, as described by Rutherford, also pose a problem. Electrons in the Rutherford model are negatively charged particles in orbital motion. Such orbital motion is an accelerated motion accompanied by a continuous change in the velocity of electron as noticed from the continuously changing direction. According to the electromagnetic theory of Maxwell, accelerated charged particles would emit electromagnetic radiation. An electron in an orbit would emit radiation, equivalent energy possessed by the radiation associated with the electronic motion. The orbit would, therefore, shrink continuously. **Thus, an electron orbiting about the nucleus would follow a spiral path to the nucleus.** It can be seen that the Rutherford atomic model has an intrinsic instability of atom. However, real atoms are stable.

ii. The second serious drawback of the Rutherford model is that it **does not describe the distribution of electrons** around the nucleus **and their energies**. The drawbacks of the Rutherford model were overcome in the Bohr atomic model.

4.5 Developments leading to the Bohr's atomic model

At the time when different models of atomic structure were being put forth, some results obtained from the studies of **interactions of radiation with matter** required to be correlated to atomic structure. Niels Bohr utilized these results to get over the drawbacks of Rutherford atomic model. These results were : (1) wave particle duality of electromagnetic radiation and (2) line emission spectra of hydrogen.

4.5.1 Wave particle duality of electromagnetic radiation : A dilemma was posed by electromagnetic radiation in the world of science. Phenomena such as **diffraction and interference of light** could be explained by treating light as electromagnetic wave. On the other hand, the **black-body radiation or photoelectric effect** could not be explained by wave nature of light, and only accounted for by considering particle nature of light. The only way to resolve the dilemma was to accept that light has dual behaviour. When light interacts with matter it behaves as a stream of **particles** called **photons**, when light propagates, it behaves as an **electromagnetic wave**.

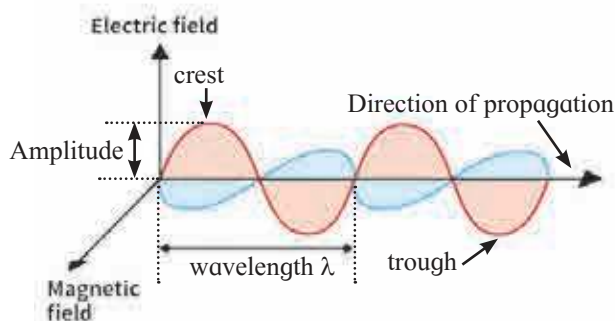


Fig 4.4 : Electromagnetic wave

a. Characteristics of electromagnetic wave

Figure 4.4 shows a schematic representation of an electromagnetic wave. Various parameters used to describe the different types of electromagnetic radiation are wavelength, frequency, wavenumber, amplitude, and velocity.

i. Wavelength (λ) : The distance between two consecutive crests or troughs is called wavelength. It is represented by the symbol λ which is a greek letter (lambda). The SI unit for wavelength is metre (m).

ii. Frequency (ν) : The number of waves that pass a given point in one second is called frequency. It is represented by the greek letter nu, (ν). The SI unit of frequency is Hertz (H_2 or s^{-1}).

iii. Wavenumber ($\bar{\nu}$) : Wavenumber is the number of wavelengths per unit length. Wavenumber is represented by the symbol (nu bar) ($\bar{\nu}$). The commonly used unit for wavenumber is reciprocal centimeter (cm^{-1}), while the SI unit is m^{-1} . Wavenumber is related to the wavelength by an expression $\bar{\nu} = \frac{1}{\lambda}$

iv. Amplitude (A): Amplitude of a wave is the height of the crest. Square of the amplitude denotes the intensity of the radiation.

Problem 4.4 : Visible light has wavelengths ranging from 400 nm (violet) to 750 nm (red). Express these wavelengths in terms of frequency (Hz).

(1 nm = 10^{-9} m)

Solution : $c = \nu\lambda \quad \therefore \nu = \frac{c}{\lambda}$

\therefore frequency of violet light =

$$\frac{3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.50 \times 10^{14} \text{ Hz}$$

and frequency of red light =

$$\frac{3 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.00 \times 10^{14} \text{ Hz}$$

Different regions of electromagnetic radiation have different values of frequency or wavelengths. Thus the radiofrequency region is around 10^6 Hz, microwave region is around 10^{10} Hz, infrared region is around 10^{13} Hz, ultraviolet region is around 10^{16} Hz.

In vacuum, the speed of all the types of electromagnetic radiation is the same, which is $3.0 \times 10^8 \text{ m s}^{-1}$ ($2.997925 \times 10^8 \text{ m s}^{-1}$ to be precise). This is called speed of light, and is denoted by the symbol 'c'.

The parameters wavelength (λ), frequency (ν) and the speed of light (c) are related by the expression : $c = \nu \lambda$

b. Particle nature of electromagnetic radiation : In the year 1900, Max Plank put forth his quantum theory to explain black-body radiation. According to this theory, the energy of electromagnetic radiation depends upon the frequency and not the amplitude. Plank gave the name '**quantum**' to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of one quantum of radiation is proportional to its frequency (ν) and given by

$$E = h\nu \quad \text{..... (4.1)}$$

The proportionality constant 'h' is called **Plank's Constant**. Later its value was found out to be $6.626 \times 10^{-34} \text{ J s}$.

In the year 1905, Albert Einstein explained the photoelectric effect using Plank's quantum theory. In doing so he considered **electromagnetic radiation as a stream of photons of energy $h\nu$** . A photon has zero rest mass.

4.5.2 Line emission spectrum of hydrogen :

When a substance is irradiated with light it absorbs energy. Atoms, molecules or ions, which have absorbed radiation are said to be '**excited**'. Heating can also result in an excited state. When an excited species gives away the absorbed energy in the form of radiation, the process is called emission of radiation. The recorded spectrum of this emitted radiation is called '**emission spectrum**'.

Problem 4.5 : Parameters of blue and red light are 400 nm and 750 nm respectively. Which of the two is of higher energy ?

Solution : 400 nm and 750 nm are the wave lengths of blue and red light, respectively. Energy of radiation is given by the expression $E = h\nu$ and ν , the frequency, of radiation is related to the wavelength by the expression.

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

Therefore, shorter the wavelength, λ , larger the frequency, ν , and higher the energy, E . Thus, blue light which has shorter λ (400nm) than red light (750nm) has higher energy.

Of all the elements, hydrogen has the simplest emission spectrum.



Do you know ?

Fluorescent tube, sodium vapor lamp, neon sign, halogen lamp are all examples of atomic emission.

When electric discharge is passed through gaseous hydrogen, it emits radiation. Hydrogen emission spectrum was studied by five scientists in late nineteenth century. They recorded the hydrogen emission spectra in different regions of electromagnetic radiation. The spectra were not continuous and comprised of a series of lines corresponding to different frequencies (see Fig. 4.5)

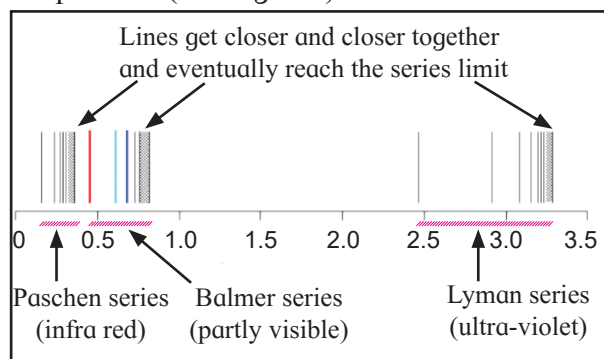


Fig. 4.5 : Emission line spectrum of hydrogen

In the year 1885 Balmer expressed the wavenumbers of the emission lines in the visible region of electromagnetic radiation by the formula

$$\bar{\nu} = 109677 \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \text{ cm}^{-1}, \quad \dots\dots (4.2)$$

where $n = 3, 4, 5, \dots\dots$

The lines described by this formula are called Balmer series. J. Rydberg found that all the five series of lines could be described by the following general expression.

$$\nu = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}, \quad \dots\dots (4.3)$$

where $n_1 = 1, 2, 3, \dots\dots\dots$

$n_2 = [n_1+1], [n_1+2], [n_1+3], \dots\dots\dots$

The value $109,677 \text{ cm}^{-1}$ is called Rydberg constant for hydrogen ' R_H '. Table 4.5 shows the distinctive features of these five series.

Table 4.5 : Series of emission spectral lines for hydrogen

| Series | n_1 | n_2 | Spectral region |
|---------|-------|-----------|-----------------|
| Lyman | 1 | 2,3,..... | Ultraviolet |
| Balmer | 2 | 3,4,..... | Visible |
| Paschen | 3 | 4,5,..... | Infrared |
| Bracket | 4 | 5,6,..... | Infrared |
| Pfund | 5 | 6,7,..... | Infrared |

4.6 Bohr's model for hydrogen atom : Niels Bohr (1913) put forth his postulates about the atomic model for hydrogen. While doing so he used the quantum theory, wave particle duality of electromagnetic radiation and the emission line spectra of hydrogen.

4.6.1 Postulates of Bohr atomic theory

Bohr's model of hydrogen atom is based on the following postulates.

1. The electron in the hydrogen atom can move around the nucleus in one of the many possible circular paths of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus in an increasing order of energy.

2. The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state if and when the required amount of energy is absorbed by the electron. Energy is emitted when electron moves from a higher stationary state to a lower one. The energy change does not take place in a continuous manner.

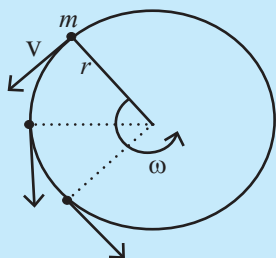
Angular Momentum :

Angular momentum is a product of moment of inertia (I) and angular velocity (ω) omega

Angular momentum = $I \times \omega$; but

$I = m r^2$ and $\omega = v/r$

\therefore Angular momentum = $mr^2 \times v/r = mvr$



3. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE is given by the following expression

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \dots\dots (4.4)$$

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

4. The angular momentum of an electron in a given stationary state can be expressed as

$$mvr = n \times \frac{h}{2\pi} \text{ where } n = 1, 2, 3 \dots\dots (4.5)$$

Thus, an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. Thus only certain fixed orbits are allowed here.

4.6.2 Results of Bohr's theory : Bohr's theory is used to derive the energies of orbits, that is, the stationary states, in hydrogen atom. The results of Bohr's theory for hydrogen atom are summarized here.

a. The stationary states for electron are numbered $n = 1, 2, 3, \dots\dots$. These integers are known as **principal quantum numbers**.

b. The radii of the stationary states are

$$r_n = n^2 a_0,$$

where $a_0 = 52.9$ pm (picometer). Thus, the radius of the first stationary state, called the Bohr radius is 52.9 pm.

c. The most important property associated with the electron is the energy of its stationary state. It is given by the expression.

$$E_1 = -R_H (1/n^2), \text{ where } n = 1, 2, 3, \dots\dots (4.6)$$

R_H is the Rydberg constant for hydrogen and its value in joules is 2.18×10^{-18} J

The lowest energy state is called the **ground state**. Energy of the ground $1/1^2$ state is

$$E_1 = -2.18 \times 10^{-18} \cdot 1/1^2 = -2.18 \times 10^{-18} \text{ J}$$

Energy of the stationary state corresponding to $n = 2$ is

$$E_2 = -2.18 \times 10^{-18} (1/(2)^2) = -0.545 \times 10^{-18} \text{ J}$$



Just think

What does the negative sign of electron energy convey ?

A free electron at rest is an electron that is at infinity from the nucleus and does not experience any electrostatic force of attraction towards the nucleus and therefore, it is assigned the energy value of zero.

The negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. Mathematically this corresponds to setting ' n ' equal to infinity in the equation so that $E_\infty = 0$. As the electron gets close to the nucleus, ' n ' decreases E_n becomes large in absolute value and more and more negative. Thus stationary states with smaller values of ' n ' have large and negative energy. The negative sign corresponds to attractive force between the electron and nucleus.



Do you know ?

The Bohr's theory is applicable to hydrogen atom and hydrogen-like species which contain only one extranuclear electron.

Problem 4.6 :

How many electrons are present in ${}^2_1\text{H}$, ${}_2\text{He}$ and He^\oplus ? Which of these are hydrogen like species?

Solution : Hydrogen-like species contain only one electron.

${}^2_1\text{H}$ number of protons = 1

= number of electrons

${}_2\text{He}$: number of protons = 2

= number of electrons

He^\oplus : (number of electron in He)-1

= (number of electron in He^\oplus)

= (2 - 1) = 1

Thus ${}^2_1\text{H}$ and He^\oplus are hydrogen-like species.

d. Bohr theory can be applied to hydrogen like species. For example He^\oplus , $\text{Li}^{2\oplus}$, $\text{Be}^{3\oplus}$ and so on. Energies of the stationary states associated with these species are given by :

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J} \quad \text{..... (4.7)}$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{ pm}, \quad \text{..... (4.8)}$$

where Z is the atomic number. From the above expression it can be seen that the energy decreases (becomes more negative) and radius becomes smaller as the value of Z increases.

e. Velocities of electrons can also be calculated from the Bohr theory. Qualitatively it is found that the magnitude of velocity of an electron increases with increase of Z and decreases with increase in the principal quantum number n .

Problem 4.7 :

Calculate the radius and energy associated with the first orbit of He^\oplus .

Solution : He^\oplus is a hydrogen-like species having the nuclear charge $Z = 2$ and for the first orbit $n = 1$ radius of first orbit of He^\oplus

$$r_1 = \frac{52.9(n^2)}{Z} = \frac{52.9 \times 1^2}{2}$$

Energy of first orbit of He^\oplus

$$\begin{aligned} E_n &= -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J} \\ &= -2.18 \times 10^{-18} \left(\frac{2^2}{1^2} \right) \\ &= -8.72 \times 10^{-18} \text{ J} \end{aligned}$$

4.6.3 Explanation of the line spectrum of hydrogen using Bohr theory :

The line emission spectrum (Fig. 4.5) obtained from atomic hydrogen can be explained quantitatively using Bohr theory. According to second postulate of Bohr theory, radiation is emitted when electron moves from an outer orbit of higher principal quantum number (n_i) to an inner orbit of lower principal quantum number (n_f). The energy difference (ΔE) between the initial and final orbit of the electronic transition corresponds to the energy of the emitted radiation. From the third postulate of Bohr theory ΔE can be expressed as

$$\Delta E = E_i - E_f \quad \text{..... (4.9)}$$

According to the results derived from Bohr theory the energy E of an orbit is related to its principal quantum number ' n ' by the Eq. (4.6).

$$E = -R_H \left(\frac{1}{n^2} \right) \quad \text{..... (4.6)}$$

Combining these two Eq. (4.9) and Eq. (4.6) we get:

$$\Delta E = \left[-\frac{R_H}{n_i^2} \right] - \left[-\frac{R_H}{n_f^2} \right] = R_H \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

Substituting the value of R_H in joules we get

$$\Delta E = 2.18 \times 10^{-18} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{ J} \quad \text{.....(4.10)}$$

This expression can be rewritten in terms of wavenumber of the emitted radiation in the following steps.

We know: $(\Delta E) \text{ J} = (h) \text{ J s} \times (\nu) \text{ Hz} \dots (4.1)$

and by definition

$$(\bar{\nu}) \text{ cm}^{-1} = \frac{(\nu) \text{ Hz}}{(c) \text{ cm s}^{-1}} \quad \text{.....(4.11)}$$

combining these Eq. (4.10), Eq. (4.1) and Eq. (4.11) we get

$$\begin{aligned} \therefore (\bar{\nu}) \text{ cm}^{-1} &= \frac{(\Delta E)}{(h) \text{ Js}} \times \frac{1}{(c) \text{ cms}^{-1}} \\ &= \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34} \times 3 \times 10^{10}} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{ cm}^{-1} \\ \therefore (\bar{\nu}) \text{ cm}^{-1} &= 109677 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{ cm}^{-1} \end{aligned}$$

This appears like the Rydberg Eq. (4.3), where $n_f = n_1$ and $n_i = n_2$.

In other words, Bohr theory successfully accounts for the empirical Rydberg equation for the line emission spectrum of hydrogen. In the Rydberg equation ' n_1 ' and ' n_f ' are integers. Bohr's theory assigns physical meaning to them as principal quantum numbers corresponding to the concentric orbits. The integers in Rydberg equation, stand for the final orbit, n_f of electronic transition and n_i for the initial orbit.

The emission lines comprising the five series thus, are result of electronic transitions from the excited hydrogen atoms.

The Lyman series is the result of moving of electron excited to higher orbits of $n_2 = n_i = 2, 3, 4, \dots$ etc. to lower orbits of $n_1 = n_f = 1$; the Balmer series results from electron from $n_2 = n_i = 3, 4, \dots$ to the lower orbit of $n_1 = n_f = 2$, so on and so forth. The electronic transitions giving rise to different emission line series of atomic hydrogen are shown in Fig. 4.6

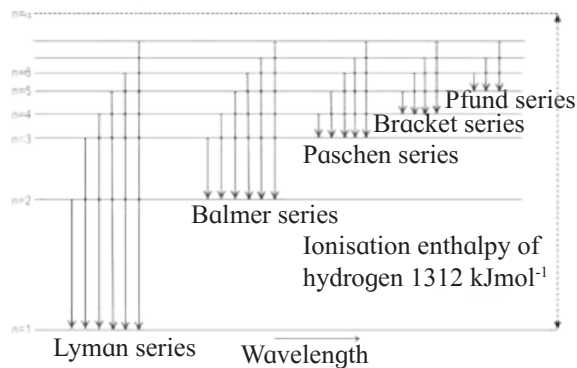


Fig. 4.6 : Electronic transition in the hydrogen spectrum

Problem 4.8 :

What is the wavelength of the photon emitted during the transition from the orbit of $n = 5$ to that of $n = 2$ in hydrogen atom?

Solution: The wavenumber of transition is given by Rydberg expression

$$(\bar{\nu}) = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}$$

Here $n_1 = 2$ and $n_2 = 5$

$$\therefore (\bar{\nu}) = 109677 \left[\frac{1}{2^2} - \frac{1}{5^2} \right]$$

$$= 109677 \left[\frac{1}{4} - \frac{1}{25} \right]$$

$$= 109677 \times \frac{21}{100} = 23032.17 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{23032.17}$$

$$\lambda = \frac{1}{\bar{\nu}} = 4.34 \times 10^{-5} \text{ cm}$$

wavelength of photon

$$\lambda = 4.34 \times 10^{-5} \text{ cm}$$

$$= 4.34 \times 10^{-5} \times 10^7 \text{ nm} = 434 \text{ nm}$$

4.6.4 Limitations of Bohr model

1. Bohr's atomic model failed to account for finer details of the hydrogen atom spectrum observed in sophisticated spectroscopic experiments.
2. Bohr model was unable to explain the spectrum of atoms other than hydrogen.
3. Bohr theory could not explain the splitting of spectral lines in the presence of a magnetic field (Zeeman effect) or electric field (Stark effect).

4. Bohr theory failed to explain the ability of atoms to form molecules by chemical bonds.

It was, therefore, thought that a better theory was needed to explain salient features of atomic structure.

4.6.5 Reasons for failure of the Bohr model

With the limitations of Bohr model for hydrogen atom becoming transparent, attempts were made to develop a better and general model for atom. This was possible because of two important developments took place after the Bohr model was postulated.

These development were :

1. de Broglie's proposal of dual behaviour of matter, and
2. Heisenberg uncertainty principle.

In Bohr model an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. In contrast to this **de Broglie** proposed in **1924** that matter should exhibit **a dual behaviour**, that is, both particle and wave like properties. This means that electron should have momentum, p , a property of particle as well as wavelength, λ , a property of wave. He gave the following relation between λ and p of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

De Broglie's prediction was confirmed by diffraction experiments (a wave property).



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In the year **1927 Werner Heisenberg** stated the uncertainty principle : **“It is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.** In other words the position and momentum of an electron can not be determined with the same certainty. If the certainty of determination of one property of the two is high, it means that the uncertainty

of its determination is low. In that case the uncertainty of determination of the other property is very high.

Mathematically Heisenberg uncertainty principle is expressed as:

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

$$\Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

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

Here Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum. A further implication of the uncertainty principle is that for an electron having certain energy one can only determine its probability at a particular point x around the nucleus. Bohr's model describes concentric orbits as well defined paths of the electron rotating about the nucleus and calculate energy of electron occupying these orbits. Bohr model assumes that both position and momentum, of the electron in hydrogen atom are known exactly at the same time, which is ruled out by the Heisenberg uncertainty principle. No attempt was made to extend the Bohr model to other atoms. A different approach to atomic model which could account for particle duality of matter and consistent with Heisenberg uncertainty principle was required. This became possible with the development of quantum mechanics.

4.7 Quantum mechanical model of atom :

A new branch of science, called **quantum mechanics**, was developed in **1926** by **Werner Heisenberg** and **Erwin Schrodinger** based on uncertainty principle and wave motion, respectively. Quantum mechanics based on the ideas of wave motion will be discussed here. Schrodinger developed the fundamental equation of quantum mechanics which incorporates wave particle duality of matter. The **Schrodinger equation** or **wave equation** is written as

$$\hat{H}\psi = E\psi \quad \text{..... (4.12)}$$

Here \hat{H} is a mathematical operator called Hamiltonian, ψ (psi) is the wave function and E the total energy of the system. Solving Schrodinger equation is beyond the scope of this book. It may, however, be noted that solution of Schrodinger equation gives E and ψ .

4.7.1 Schrodinger equation : When Schrodinger equation is solved for hydrogen atom, the possible values of energy (E) that the electron may have along with the corresponding wave function (ψ) are obtained. As a natural consequence of solving this equation, a set of three quantum numbers characteristic of the quantized energy levels and the corresponding wave functions are obtained. These are : **Principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_l).**

The solution of Schrodinger wave equation led to three quantum numbers and successfully predicted features of hydrogen atom emission spectrum. Splitting of spectral lines in multi-electron atomic emission spectra could not be explained through such model. These were explained by **George Uhlenbeck** and **Samuel Goudsmit (1925)** who proposed the presence of the **fourth quantum number** called **electron spin quantum number, m_s** .

Wave function, ψ , as such does not have any physical meaning. The probability of finding an electron at a point within an atom is proportional to ψ^2 in the neighbourhood of that point (within a tiny volume element) around it.

4.7.2 Atomic orbitals and quantum numbers

Many wave function are possible for an electron, and therefore, many atomic orbitals in an atom. Thus the wave functions or atomic orbitals form the basis of the quantum mechanical electronic structure of an atom. Various orbitals in an atom differ in size, shape and orientation with respect to the nucleus depending upon the value of ψ^2 . Each orbital is designated by three quantum numbers labelled as n , l and m_l , and each electron being assigned with four quantum numbers, viz, n , l , m_l and m_s .

The **principal quantum number 'n'** is a positive integer with values of n being 1, 2, 3, 4, It identifies the shell. Atomic orbitals, having the same value 'n' belong to the same shell. With increase of 'n', the number of allowed orbitals in that shell increases and given by ' n^2 '. A set of orbitals with given value of 'n' constitutes a single shell. Shells are represented by symbols K, L, M, N, so on. Table 4.6 shows 'n' and electronic shell symbol.

Table 4.6 : Allowed orbitals in the first four shells

| Principal quantum number n | Shell symbol | Allowed number of orbitals n^2 | Size of shell |
|---------------------------------|--------------|-------------------------------------|---------------|
| 1 | K | 1 | ↓ increases |
| 2 | L | 4 | |
| 3 | M | 9 | |
| 4 | N | 16 | |

With an increase of 'n', the distance from the nucleus and size of the shell increases and also the energy increases (becoming lesser and lesser negative). In hydrogen-like species the energy of orbital depends only on the value of 'n'. In the case of multi-electron atoms the energy of orbital depends on two quantum numbers 'n' and 'l' as well.

The **azimuthal quantum number, l** , is also called **subsidiary quantum number**. Atomic orbitals with the same value of 'n' but different values of 'l' constitute a subshell belonging to the shell for the given 'n'. The number of subshells in a shell is equal to 'n'. Thus, the third shell contains three subshells (with three different values of 'l'), the second shell contains two subshells and the first shell contains only one subshell. The values of 'l' range from 0 to ($n - 1$). Thus, the K shell (with $n = 1$) contains only one subshell having $l = 0$. The subshells or sub-levels have 'l' to be 0, 1, 2, 3, which are represented by the symbols s, p, d, f,, respectively.

The magnetic orbital quantum number, m_l , gives information about the relative spatial orientation of the orbitals in a given subshell.

For any subshell (defined by ' l ' value) $(2l + 1)$ values of m_l are possible which range through :

$$m_l = -l, -(l-1), -(l-2), \dots, 0, \dots, (l-2), (l-1), l.$$

Thus for the subshell 's' with $l = 0$, the only allowed value of $m_l = 0$. In other words, 's' subshell has only one orbital in it. For the subshell 'p' having $l = 1$, the allowed values of m_l are -1, 0, +1. Thus 'p' subshell contain three orbitals having distinct orientations, and so on.

The sum of orbitals in a constituent subshell gives the total number of orbitals in a concerned shell and is given by n^2 . See Table 4.7

Electron spin quantum number, m_s , specifies the spin state of the electron in an orbital. An electron spins around its axis. This imparts spin angular momentum, to the electron.

The two orientations which the spin angular momentum of an electron can take up give rise to the spin states which can be distinguished from each other by the spin quantum number, m_s , which can be either $+1/2$ or $-1/2$. The two spin states are represented by two arrows, \uparrow (pointing up) and \downarrow (pointing down) and thus have opposite spins. **“An orbital can accomodate maximum two electrons and they must have opposite spins.”**

This is known as **Pauli exclusion principle** which will be dealt with in section 4.7.5

4.7.3 Shapes of atomic orbitals : The probability of finding an electron at a given point in an atom is proportional to square of the wave function ψ^2 at that point. According to Max Born ψ^2 at a point in an atom is the probability density of electron at that point.

Figure 4.7 (a) shows the probability density diagrams of 1s and 2s atomic orbitals. These diagrams appear like a cloud. The electron cloud of 2s orbital shows one node, which is a region with nearly zero probability density and displays the change of sign for its corresponding wavefunction.

Table 4.7 : Distribution of orbitals in shells and subshells

| Shell | Principal quantum number n | Total orbitals in the shell n^2 | Total number of subshells in a shell n | Azimuthal quantum number l | Number of orbitals in the subshell $2l+1$ | Sum of orbitals in all the subshells |
|-------|------------------------------|-----------------------------------|--|-------------------------------|--|--------------------------------------|
| K | $n = 1$ | $1^2 = 1$ | 1 | $l = 0$ | $2 \times 0 + 1 = 1$ | 1 |
| L | $n = 2$ | $2^2 = 4$ | 2 | $l = 0$ $l = 1$ | $2 \times 0 + 1 = 1$ $2 \times 1 + 1 = 3$ | $1 + 3 = 4$ |
| M | $n = 3$ | $3^2 = 9$ | 3 | $l = 0$ $l = 1$ $l = 2$ | $2 \times 0 + 1 = 1$ $2 \times 1 + 1 = 3$ $2 \times 2 + 1 = 5$ | $1 + 3 + 5 = 9$ |

(a) Probability density plots

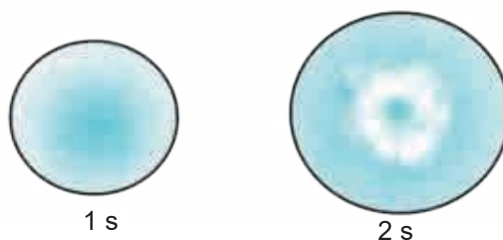


Fig. 4.7 : (a) Shapes of 1s and 2s orbitals

The Table 4.8 shows orbitals in the first four shells with the three quantum numbers for each orbital.

Table 4.8 : Orbital distribution in the first four shells

| Symbol of Shell | Value of Principal quantum number (n) | Number of subshells | Value of Azimuthal Quantum number l | Symbol of subshell | Total Number of orbitals in the subshell $= 2l + 1$ | Values of the magnetic quantum number m_l for the subshell |
|-----------------|---|---------------------|---------------------------------------|--------------------|---|---|
| K | $n = 1$ | 1 | $l = 0$ | 1s | $2 \times 0 + 1 = 1$ | $m_l = 0$ |
| L | $n = 2$ | 2 | $l = 0$ | 2s | $2 \times 0 + 1 = 1$ | $m_l = 0$ |
| | | | $l = 1$ | 2p | $2 \times 1 + 1 = 3$ | $m_l = -1$ $m_l = 0$ $m_l = +1$ |
| M | $n = 3$ | 3 | $l = 0$ | 3s | $2 \times 0 + 1 = 1$ | $m_l = 0$ |
| | | | $l = 1$ | 3p | $2 \times 1 + 1 = 3$ | $m_l = -1$ $m_l = 0$ $m_l = +1$ |
| | | | $l = 2$ | 3d | $2 \times 2 + 1 = 5$ | $m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$ |
| N | $n = 4$ | 4 | $l = 0$ | 4s | $2 \times 0 + 1 = 1$ | $m_l = 0$ |
| | | | $l = 1$ | 4p | $2 \times 1 + 1 = 3$ | $m_l = -1$ $m_l = 0$ $m_l = +1$ |
| | | | $l = 2$ | 4d | $2 \times 2 + 1 = 5$ | $m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$ |
| | | | $l = 3$ | 4f | $2 \times 3 + 1 = 7$ | $m_l = -3$ $m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$ $m_l = +3$ |

Problem 4.9 How many orbitals make the N shell? What is the subshell wise distribution of orbitals in the N shell?

Solution: For N shell principal quantum number $n = 4$ \therefore Total number of orbitals in N shell $= n^2 = 4^2 = 16$ The total number of subshells in N shell $= n = 4$. The four subshells with their azimuthal quantum numbers and the constituent orbital number are as shown below

| Azimuthal quantum number l | Symbol of subshell | number of orbitals $2l + 1$ |
|------------------------------|--------------------|-----------------------------|
| $l = 0$ | s | $(2 \times 0) + 1 = 1$ |
| $l = 1$ | p | $(2 \times 1) + 1 = 3$ |
| $l = 2$ | d | $(2 \times 2) + 1 = 5$ |
| $l = 3$ | f | $(2 \times 3) + 1 = 7$ |

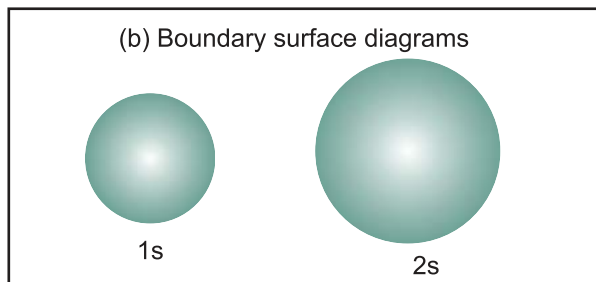


Fig 4.7 (b) : Shapes of 1s and 2s orbitals

Figure 4.7 (b) shows the boundary surface diagram of atomic orbitals 1s and 2s, which are spherical in shape. Here, a boundary surface is drawn in space for an orbital such that the value of probability density ψ^2 is constant and encloses a region where the probability of finding electron is typically more than 90%. Such a boundary surface diagram is a good representation of shape of an orbital.

Problem 4.10 : An atom has two electrons in its 4s orbital. Write the values of the four quantum numbers for each of them.

Solution: For the 4s orbital 4 stands for the principal quantum number n ; s stands for the subshell s having the value of azimuthal quantum number $l = 0$. In the 's' subshell there is only one orbital and has magnetic quantum number $m_l = 0$. The two electrons in this orbital have opposite spins. Thus the four quantum numbers of two electrons in 4s orbital are :

| | n | l | m_l | m_s |
|------------|-----|-----|-------|--------|
| electron 1 | 4 | 0 | 0 | $+1/2$ |
| electron 2 | 4 | 0 | 0 | $-1/2$ |



Do you know ?

The value of ψ^2 at any finite distance from the nucleus is never zero. Therefore a boundary surface enclosing 100% probability density (which occurs only at the infinity) cannot be drawn.

The s orbitals are spherical in shape. Their size increases with increase of n . It means that the electron is located farther away from the nucleus as the principal quantum number n increases.

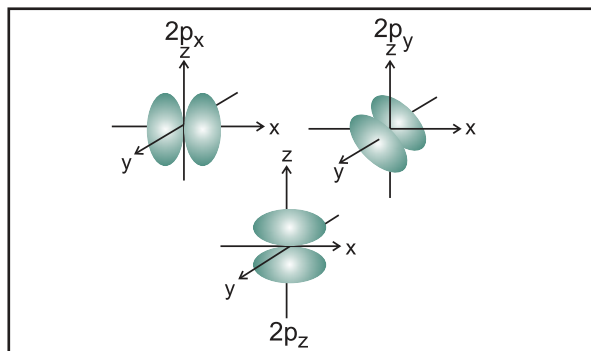


Fig. 4.8 : Shapes of 2p orbitals

Figure 4.8 displays the boundary surface diagram with the nucleus being at the origin, for the three 2p orbitals ($n = 2$ and $l = 1$). It can be seen that each p orbital has two lobes on the two sides of a nodal plane passing through the nucleus. (A nodal plane has ψ^2 very close to zero)

The size and energy of the dumbbell shaped three 2p orbitals are the same. Their orientations in space are, however, different. The lobes of the three 2p orbitals are along the x, y and z axes. Accordingly the corresponding orbitals are designated as $2p_x$, $2p_y$ and $2p_z$. The size and energy of the orbitals in p subshell increase with the increase of principal quantum number.

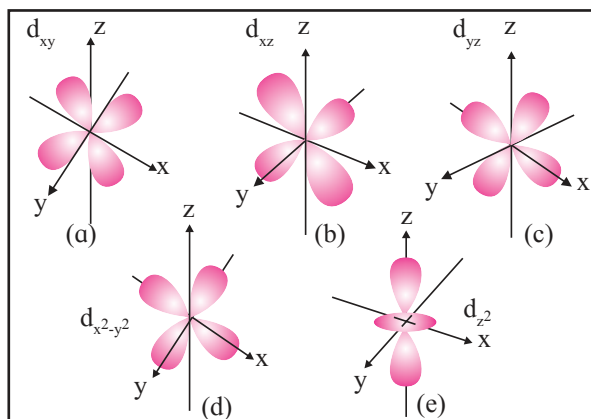


Fig. 4.9 : Shapes of 3d orbitals

There are five orbitals associated with d subshell. Designated by d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . The shapes of the five 3d orbitals are shown in Figure 4.9. In spite of difference in their shapes, the five d orbitals are equivalent in energy. The shapes of 4d, 5d, 6d..... orbitals are similar to those of 3d orbitals, but their respective size and energies are large or they are said to be more diffused.

4.7.4 Energies of orbitals : The energy of an electron in the hydrogen atom or hydrogen-like species is determined by the principal quantum number alone. This is because the only interaction in these species is attraction between the electron and nucleus. An increasing order of energies of orbitals in the hydrogen atom is given by

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots\dots\dots$$

Of course the shapes of the concerned s, p, d, f orbitals are different, as described earlier. The orbitals with the same energy and the corresponding wave functions being different are called **degenerate orbitals**.

Thus, in hydrogen atom 2s and 2p are degenerate orbitals. In multi-electron atoms there is mutual repulsion among the electrons. The energy of an electron in a multi-electron atom, therefore, depends both on the principal quantum number, n , and the azimuthal quantum number, l . The lower the sum $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n + l)$ values then orbital with the lower value of n is of lower energy. This is called the **$(n + l)$ rule**.

From the $(n + l)$ rule the increasing order of energy of orbitals in multi-electron atoms can be written as: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s \dots\dots\dots$ (See Table 4.9)

In a multi-electron atom, electrons occupy different orbitals. The lowest total electronic energy corresponds to the most stable, that is, the **ground state of an atom**. The orbital wise distribution of electrons in the ground state can be understood from what is called the **aufbau principle**.

4.7.5 Aufbau principle : ‘Aufbau’ is a German word meaning ‘building up’. The building up of orbital means filling up of orbitals with electrons in the ground state of an atom. The aufbau principle is based on, (i) Increasing order of energies of orbitals, (ii) Pauli’s exclusion principle, and (iii) Hund’s rule of maximum multiplicity.

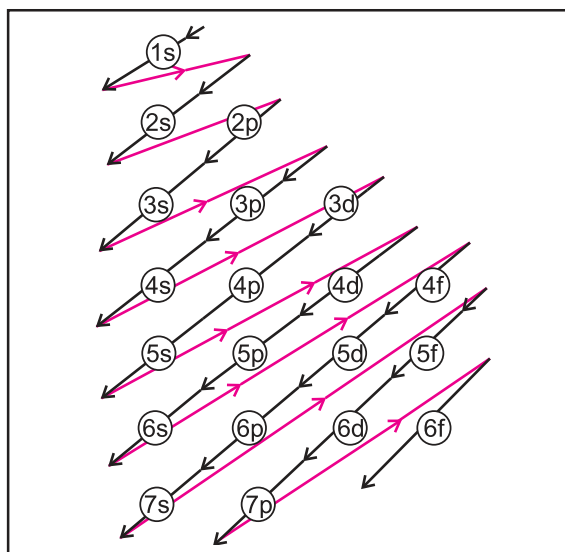


Fig. 4.10 : Increasing order of orbital energy

Table 4.9 : Dependence of orbital energy on $(n + l)$ value

| Orbital Energy | Principal quantum number n | Azimuthal quantum number l | $(n + l)$ |
|----------------|------------------------------|------------------------------|-------------|
| 1s | $n = 1$ | $l = 0$ | $1 + 0 = 1$ |
| 2s | $n = 2$ | $l = 0$ | $2 + 0 = 2$ |
| 2p | $n = 2$ | $l = 1$ | $2 + 1 = 3$ |
| 3s | $n = 3$ | $l = 0$ | $3 + 0 = 3$ |
| 3p | $n = 3$ | $l = 1$ | $3 + 1 = 4$ |
| 4s | $n = 4$ | $l = 0$ | $4 + 0 = 4$ |
| 3d | $n = 3$ | $l = 2$ | $3 + 2 = 5$ |
| 4p | $n = 4$ | $l = 1$ | $4 + 1 = 5$ |

↑ increases ↓

} $n = 2$ (lower)
 } $n = 3$ (higher)
 } $n = 3$ (lower)
 } $n = 4$ (higher)
 } $n = 3$ (lower)
 } $n = 4$ (higher)

i. The increasing order of energies of orbitals

As seen in section 4.7.4, the increasing order of energies of orbitals is decided by the $(n + l)$ value. Electrons in the ground state atom are filled in the orbitals in an increasing order of energy. Fig 4.10 shows a useful method to remember this increasing order of orbital energy.

ii. Pauli exclusion principle : The capacity of an orbital to accommodate electrons is decided by Pauli exclusion principle. **Wolfgang Pauli (1926)** recognized that “**No two electrons in an atom can have the same set of four quantum numbers.**” Another way to state this Pauli exclusion principle is: “**Only two electrons can occupy the same orbital and they must have opposite spins.**” Pauli exclusion principle implies that for an electron belonging to the same orbital, the spin quantum number ‘ m_s ’ must be different since the other three quantum numbers n , l and m_l are the same. There are only two values that ‘ m_s ’ can which are $+1/2$ and $-1/2$. An orbital thus can accommodate only two electrons with opposite spins, so that the fourth quantum number is different for two occupying electrons. These two electrons with opposite spins occupying the same orbital are called an **electron pair**.

This principle is illustrated with helium atom He ($Z = 2$). Its electronic configuration is $1s^2$ as $\uparrow\downarrow$. And two electrons are in $1s$ orbital. The two non - identical combinations of the four quantum numbers of both electrons in helium are given in Table 4.10.

Table 4.10

| Electron | Quantum number | | | | Set of values of four quantum numbers |
|--------------------------|----------------|-----|-------|--------|---------------------------------------|
| | n | l | m_l | m_s | |
| 1 st electron | 1 | 0 | 0 | $+1/2$ | $(1, 0, 0, +1/2)$ |
| 2 nd electron | 1 | 0 | 0 | $-1/2$ | $(1, 0, 0, -1/2)$ |

It implies that two electrons in the same atom have always different set of quantum numbers that means, the set of (n, l, m_l) is the same and the m_s is different.

Since an orbital can accommodate up to two electrons only, the capacity of a shell with the principal quantum number n , to accommodate electrons is given by $2n^2$.

iii. Hund’s rule of maximum multiplicity : Filling of electrons in the orbitals belonging to the same subshell (orbitals of equal energy or degenerate orbitals) follows the Hund’s rule of maximum multiplicity. As per this rule “**Pairing of electrons in the orbitals belonging to the same subshell does not occur unless each orbital belonging to that subshell has got one electron each.**”

Consider, for example, filling of p subshell. The p subshell has three degenerate orbitals. Here pairing of electrons starts when the fourth electron enters the p subshell. The electronic configuration of four electrons occupying p -orbital then will be $\uparrow\downarrow\uparrow\uparrow$ and not as $\uparrow\downarrow\uparrow\downarrow$. It is observed that **half-filled and fully filled set of degenerate orbitals has extra stability.**

4.7.6 Electronic configuration of atoms and its representation : Electronic configuration of an atom is the distribution of its electrons in orbitals. The electronic configuration can be written by applying the aufbau principle. There are two methods of representing electronic configuration:

(i) Orbital notation: $ns^a np^b nd^c \dots\dots\dots$

(ii) Orbital diagram: $\square \square \square \square \square \square \square$

In the **orbital notation method**, a shells is represented by the principal quantum number followed by respective symbol of a subshell and number of electrons occupying that subshell being written as super script on right side of the symbol. In the **orbital diagram method** each orbital in a subshell is represented by a box and the electron represented by an arrow (\uparrow for up spin and \downarrow for low spin) placed in the respective boxes. In this second method all the four quantum numbers of electron are accounted for. Electronic configuration of a few elements is illustrated in Table 4.11.

Table 4.11 : Representation of electronic configuration

| Element symbol | Orbital notation | Orbital diagram |
|-----------------|------------------|---|
| ${}_1\text{H}$ | $1s^1$ | $\begin{array}{ c } \hline \uparrow \\ \hline 1s \end{array}$ |
| ${}_2\text{He}$ | $1s^2$ | $\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s \end{array}$ |
| ${}_3\text{Li}$ | $1s^2 2s^1$ | $\begin{array}{ c c } \hline \uparrow\downarrow & \uparrow \\ \hline 1s & 2s \end{array}$ |
| ${}_4\text{Be}$ | $1s^2 2s^2$ | $\begin{array}{ c c } \hline \uparrow\downarrow & \uparrow\downarrow \\ \hline 1s & 2s \end{array}$ |
| ${}_9\text{F}$ | $1s^2 2s^2 2p^5$ | $\begin{array}{ c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow\uparrow \\ \hline 1s & 2s & 2p \end{array}$ |

Condensed orbital notation of electronic configuration : The orbital notation of electronic configuration of an element with high atomic number comprises a long train of symbols of orbitals with an increasing order of energy. It can be condensed by dividing it into two parts. Electronic configuration of the preceding inert gas is a part of the electronic configuration of any element. In the condensed orbital notation it is implied by writing symbol of that inert gas in a square bracket. It is core part of the electronic configuration of that element. The outer configuration is specific to a particular element and written immediately after the bracket. For example, the orbital notation of potassium 'K ($Z = 19$) is, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ '. Its core part is the electronic configuration of the preceding inert gas argon 'Ar : $1s^2 2s^2 2p^6 3s^2 3p^6$ ', while ' $4s^1$ ' is an outer part. Therefore the condensed orbital notation of electronic configuration of potassium is 'K : [Ar] $4s^1$.' Table 4.12 displays detailed and condensed orbital notations of electronic configuration of various elements with atomic numbers from 1 to 30.



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Electronic configurations of Cu and Cr

Chromium : Atomic number of chromium is 24. Expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$; In that case 3d is not half-filled. Hence, it has less stability.

Interelectronic repulsion makes one 4s electron enter into one of empty 3d orbitals, thereby both 4s and 3d orbitals become half-filled so that chromium atom acquires extra stability. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$.

Copper : Atomic number of copper is 29. The expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$. Here 3d orbital is neither half-filled nor fully filled. Due to interelectronic repulsions forces one 4s electron to enter into 3d which makes it completely filled with 4s being half-filled. Hence copper atom acquires extra stability. Now electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$.

Isoelectronic species : Atoms and ions having the **same number of electrons** are **isoelectronic**. The electronic configuration of the isoelectronic species is the same. Consider K^+ formed by removal of one electron from K atom.

Which has 19 electrons ($Z = 19$). Therefore K^+ has 18 electrons

| | | | | |
|-----------|----------------|---------------|--------------|---------|
| Number of | K ($Z = 19$) | \rightarrow | K^+ | $+ e^-$ |
| electrons | 19 | | 18 | |

Species such as Ar, Ca^{2+} containing 18 electrons are isoelectronic with K^+ .


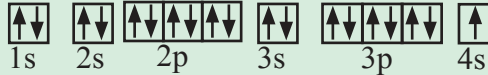
Electronic configuration of all these species with 18 electrons is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Table 4.12 Electronic configuration of the first thirty elements

| Atomic Number | Element | K ($n = 1$) | L ($n = 2$) | M ($n = 3$) | N ($n = 4$) | Condensed notation of electronic configuration |
|---------------|-------------|------------------|---------------------------------|--|------------------|--|
| 1 | Hydrogen | 1s ¹ | | | | 1s ¹ |
| 2 | Helium | 1s ² | | | | 1s ² |
| 3 | Lithium | 1s ² | 2s ¹ | | | [He] 2s ¹ |
| 4 | Beryllium | 1s ² | 2s ² | | | [He]2s ² |
| 5 | Boron | 1s ² | 2s ² 2p ¹ | | | [He] 2s ² 2p ¹ |
| 6 | Carbon | 1s ² | 2s ² 2p ² | | | [He] 2s ² 2p ² |
| 7 | Nitrogen | 1s ² | 2s ² 2p ³ | | | [He] 2s ² 2p ³ |
| 8 | Oxygen | 1s ² | 2s ² 2p ⁴ | | | [He] 2s ² 2p ⁴ |
| 9 | Fluorine | 1s ² | 2s ² 2p ⁵ | | | [He] 2s ² 2p ⁵ |
| 10 | Neon | 1s ² | 2s ² 2p ⁶ | | | [He] 2s ² 2p ⁶ |
| 11 | Sodium | 1s ² | 2s ² 2p ⁶ | 3s ¹ | | [Ne]3s ¹ |
| 12 | Magnesium | 1s ² | 2s ² 2p ⁶ | 3s ² | | [Ne]3s ² |
| 13 | Aluminium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ¹ | | [Ne]3s ² 3p ¹ |
| 14 | Silicon | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ² | | [Ne]3s ² 3p ² |
| 15 | Phosphorous | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ³ | | [Ne]3s ² 3p ³ |
| 16 | Sulfur | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁴ | | [Ne]3s ² 3p ⁴ |
| 17 | Chlorine | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁵ | | [Ne]3s ² 3p ⁵ |
| 18 | Argon | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ | | [Ne]3s ² 3p ⁶ |
| 19 | Potassium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ | 4s ¹ | [Ar] 4s ¹ |
| 20 | Calcium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ | 4s ² | [Ar] 4s ² |
| 21 | Scandium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ¹ | 4s ² | [Ar] 4s ² 3d ¹ |
| 22 | Titanium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ² | 4s ² | [Ar]4s ² 3d ² |
| 23 | Vanadium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ³ | 4s ² | [Ar] 4s ² 3d ³ |
| 24 | Chromium | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ⁵ | 4s ¹ | [Ar] 4s ² 3d ⁵ |
| 25 | Manganese | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ⁵ | 4s ² | [Ar] 4s ² 3d ⁵ |
| 26 | Iron | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ⁶ | 4s ² | [Ar]4s ² 3d ⁶ |
| 27 | Cobalt | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ⁷ | 4s ² | [Ar] 4s ² 3d ⁷ |
| 28 | Nickel | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ⁸ | 4s ² | [Ar] 4s ² 3d ⁸ |
| 29 | Copper | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ¹⁰ | 4s ¹ | [Ar] 4s ¹ 3d ¹⁰ |
| 30 | Zinc | 1s ² | 2s ² 2p ⁶ | 3s ² 3p ⁶ 3d ¹⁰ | 4s ² | [Ar] 4s ² 3d ¹⁰ |

Problem 4.11 : Write electronic configuration of $_{18}\text{Ar}$ and $_{19}\text{K}$ using orbital notation and orbital diagram method.

Solution : From the atomic numbers it is understood that 18 electron are to be filled in Ar atom and 19 electrons are to be filled in K atom. These are to be filled in the orbitals according to the aufbau principle. The electronic configuration of these atoms can be represented as.

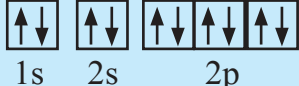
| | Orbital notation | Orbital diagram |
|------------------|---------------------------------|--|
| $_{18}\text{Ar}$ | $1s^2 2s^2 2p^6 3s^2 3p^6$ |  |
| $_{19}\text{K}$ | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ |  |

Problem 4.12

Find out one dinegative anion and one unipositive cation which are isoelectronic with Ne atom. Write their electronic configuration using orbital notations and orbital diagram method.

Solution:

Ne has $Z = 10$. Therefore Ne and its isoelectronic species contain 10 electrons each. The dinegative anionic species isoelectronic with Ne is obtained by adding two electrons to the atom with $Z = 8$. This is O^{2-} . The unipositive cationic species isoelectronic with Ne is obtained by removing one electron from an atom of $Z = 11$. It is Na^+ . These species and their electronic configuration are shown below :

| | Number of electron | Orbital Notation | Orbital diagram |
|---|--------------------|------------------|---|
| Ne | 10 | $1s^2 2s^2 2p^6$ |  |
| $\text{O} + 2e^- \rightarrow \text{O}^{2-}$ | 10 | | |
| $\text{Na} - e^- \rightarrow \text{Na}^+$ | 10 | | |



Exercises

1. Choose correct option.

- The energy difference between the shells goes on when moved away from the nucleus.
 - Increasing
 - decreasing
 - equalizing
 - static
- The value of Plank's constant is -
 - $6.626 \times 10^{-34}\text{Js}$
 - $6.023 \times 10^{-24}\text{Js}$
 - $1.667 \times 10^{-28}\text{Js}$
 - $6.626 \times 10^{-28}\text{Js}$
- p-orbitals are..... in shape.
 - spherical
 - dumb bell
 - double dumbell
 - diagonal
- "No two electrons in the same atoms can have identical set of four quantum numbers". This statement is known as -
 - Pauli's exclusion principle
 - Hund's rule

c. Aufbau rule

d. Heisenberg uncertainty principle

E. Principal Quantum number describes-

- shape of orbital
- size of the orbital
- spin of electron
- orientation of in the orbital electron cloud

2. Make the pairs:

- | | |
|-----------------------|------------------------------------|
| 'A' | 'B' |
| a. Neutrons | i. six electrons |
| b. p-orbital | ii. $-1.6 \times 10^{-19}\text{C}$ |
| c. charge on electron | iii. Ultraviolet region |
| d. Lyman series | iv. Chadwick |

3. Complete the following information about the isotopes in the chart given below :

| Substance | Mass Number | Number of | | |
|-------------|-------------|-----------|----------|-----------|
| | | Protons | Neutrons | Electrons |
| Carbon-14 | | | | |
| Lead-208 | | | | |
| Chlorine-35 | | | | |
| Uranium-238 | | | | |
| Oxygen-18 | | | | |
| Radium-223 | | | | |

(Hint: Refer to Periodic Table if required)

4. Match the following :

| Element | No. of Neutron |
|--------------------------|----------------|
| a. $^{40}_{18}\text{Ar}$ | i. 7 |
| b. $^{14}_6\text{C}$ | ii. 21 |
| c. $^{40}_{19}\text{K}$ | iii. 8 |
| d. $^{14}_7\text{N}$ | iv. 22 |

5. Answer in one sentence :

- If an element 'X' has mass number 11 and it has 6 neutrons, then write its representation.
- Name the element that shows simplest emission spectrum.
- State Heisenberg uncertainty principle.
- Give the names of quantum numbers.
- Identify from the following the isoelectronic species:
Ne, O^{2-} , Na^+ OR Ar, Cl^{2-} , K^{\oplus}

6. Answer the following questions.

- Differentiate between Isotopes and Isobars.
- Define the terms:
 - Isotones
 - Isoelectronic species
 - Electronic configuration
- State and explain Pauli's exclusion principle.
- State Hund's rule of maximum multiplicity with suitable example.
- Write the drawbacks of Rutherford's model of an atom.
- Write postulates of Bohr's Theory of hydrogen atom.
- Mention demerits of Bohr's Atomic model.
- State the order of filling atomic orbitals following Aufbau principle.

- Explain the anomalous behavior of copper and chromium.
- Write orbital notations for electrons in orbitals with the following quantum numbrs.
 - $n = 2, l = 1$
 - $n = 4, l = 2$
 - $n = 3, l = 2$
- Write electronic configurations of Fe, Fe^{2+} , Fe^{3+}
- Write condensed orbital notation of electronic configuration of the following elements:
 - Lithium ($Z=3$)
 - Carbon ($Z=6$)
 - Oxygen ($Z=8$)
 - Silicon ($Z=14$)
 - Chlorine ($Z=17$)
 - Calcium ($Z=20$)
- Draw shapes of 2s and 2p orbitals.
- Explain in brief, the significance of azimuthal quantum number.
- If $n=3$, what are the quantum number l and m ?
- The electronic configuration of oxygen is written as $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ and not as $1s^2 2s^2 2p_x^2, 2p_y^2 2p_z^0$, Explain.
- Write note on 'Principal Quantum number.
- Using concept of quantum numbers, calculate the maximum numbers of electrons present in the 'M' shell. Give their distribution in shells, subshells and orbitals.
- Indicate the number of unpaired electrons in :
 - Si ($Z=14$)
 - Cr ($Z=24$)
- An atom of an element contains 29 electrons and 35 neutrons. Deduce-
 - the number of protons
 - the electronic configuration of that element



Activity :

Collect information about discoveries of sub atomic particles and present in class by using power point presentation.