UNIT-2 : ATOMIC STRUCTURE [JEE – MAIN CRASH COURSE]

Atomic Models

As a prelude to Bohr's theory, we should have an introduction to (i) nature of radiations, (ii) atomic spectra, and (iii) quantum theory.

Radiations

Ordinary light, X-rays, and γ-rays are called electromagnetic radiations, and they have wave characteristics. These radiations are called electromagnetic because when they pass through a point in space, they produce oscillating electric and magnetic fields at that point. In 1873, James Clark Maxwell, a Scottish physicist, showed that a static charge or a charge with uniform velocity sets up electric and magnetic fields which give rise to an energy density in space associated with the electric and magnetic fields, but the energy density remains constant. On the other hand, if we were to change the velocity of the charged particle, the energy density varies and then gives rise to electromagnetic waves.

There are three fundamental characteristics associated with wave motion: (i) wavelength (λ), (ii) frequency (ν), and (iii) velocity (c).

(i) *Wavelength*: Consider a wave profile as shown in Fig. 2.1. The distance between the two successive crests or troughs is known as wavelength (λ). It is measured in cm or Angstrom unit (Å).

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

Sometimes it is also measured in nanometer (1 nm = 10^{-9} m).

(ii) *Frequency*: The number of waves that passes through a given point in one second is called its frequency (number of waves per second). Frequency (ν) is expressed in cycles per second (cps) or Hertz (Hz).

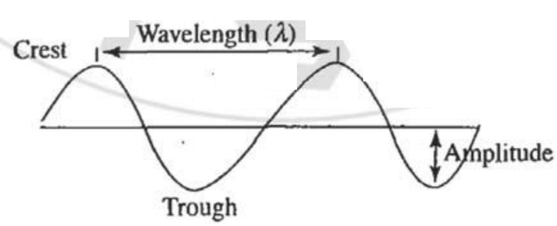

Fig. 2.1

(iii) *Velocity*: The distance traveled by a wave in one second is its velocity.

$$\text{Velocity} = \frac{\text{Wavelength}}{T} = \frac{\text{Distance traveled in a wavelength}}{\text{Time taken to travel one wavelength}}$$

$$= \frac{\lambda}{T} = \lambda \times \nu$$

Atomic spectra

When white light is passed through a prism, it is separated into light of seven colors (VIBGYOR) or radiations of different wavelengths. The pattern obtained by splitting or sorting out of radiations into its component wavelengths is called a spectrum. The spectrum of white light when analyzed by spectrometer (an instrument that indicates the wavelengths/frequencies of individual components of a radiation) is a continuous spectrum, suggesting that white light is made up of all possible wavelengths or frequencies of radiations. If a gas is heated, it emits light. When this emitted light is analyzed in a spectrometer, the spectra obtained consist of a series of well-defined sharp lines, each line corresponding to a definite wavelength or frequency. These line spectra are characteristic of atoms.

Quantum theory

According to quantum theory, a body cannot emit or absorb energy in the form of radiation of continuous energy; energy can be taken up or given out as whole number multiples of a definite amount known as a quantum. Light is imagined to consist of a stream of particles called photons. If E is the energy of a photon, its quantum for a particular radiation of frequency $\nu\ \text{s}^{-1}$ is given by quantum theory as

$$E = h\nu$$

where h is a universal constant known as Planck's constant ($h = 6.626 \times 10^{-27}$ erg-s or 6.626×10^{-34} Js).

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

Bohr's Model

In any atom, electrons can rotate only in a certain selected (or permissible) orbits without radiating energy. Such orbits are known as stable or non-radiating orbits or stationary states. These orbits are circular with well-defined radii. These radii are numbered 1, 2, 3, ... (from the nucleus). Orbits are paths of revolution of electrons. A spherical surface around the nucleus, which contains orbits of equal energy and radius, is called a shell. The shell are denoted as $K, L, M, N, \ldots$.

Each stationary state (or orbit) corresponds to a certain energy level (i.e., as long as the electron is in the particular stationary state, it has a definite amount of energy). The energy associated with an electron is least in the K shell and it increases as we pass to $L, M, N, \ldots$ shells.

An electron can jump from one stationary state to another. For an electron to jump from an inner orbit of energy E_1 to an outer orbit of energy E_2, it should absorb the equivalent of a quantum of energy $= E_2 - E_1 = h\nu$, where ν is the frequency of radiation absorbed. Similarly, when it jumps back from the outer to the inner orbit, it will emit an equal amount of energy in the form of radiation.

According to Bohr, angular momentum is given by

$$mvr = n\hbar \qquad \left(\text{where } \hbar = \frac{h}{2\pi}\right)$$

$$\therefore \qquad mvr = \frac{nh}{2\pi}$$

where n is a positive integer 1, 2, 3, … and is known as a quantum number. Therefore,

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

Solving for r, we get

$$r = \frac{n^2 h^2}{4\pi^2 KZme^2} \quad (\text{where } r_n = 0.529\, n^2 \text{ Å})$$

$$\text{PE} = \frac{-KZe^2}{r}$$

$$E = \frac{-2\pi^2 K^2 Z^2 me^4}{n^2 h^2}$$

$$= -2.179 \times 10^{-18} \text{ J per atom} = -13.6 \text{ eV per atom}$$

$$E = -1312 \text{ kJ/mol}$$

$$\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]; \quad R = \frac{2\pi^2 k^2 me^4}{h^3 C} = 109737 \text{ cm}^{-1}$$

Hydrogen Spectrum

The hydrogen atom contains only one electron in the first orbit (K shell). This is the normal orbit or ground state and represents the stationary state of the unexcited atom. Energy may be absorbed by this electron, which is then raised from its normal orbit to a higher energy level. In this new level, the electron possesses more energy and is less stable than before. It will, therefore, fall toward the nucleus until it reaches either the normal orbit or some intermediate level. In this process, energy is released as a photon of frequency, $E = h\nu$.

Spectral lines are produced by radiation of photons, and the position of the lines on the spectrum is determined by the frequency of photons emitted. Transition to innermost level ($n = 1$) from higher levels ($n = 1, 3, 4$, etc.) gives the first, second, third, etc., line of the Lyman series (Fig. 2.2).

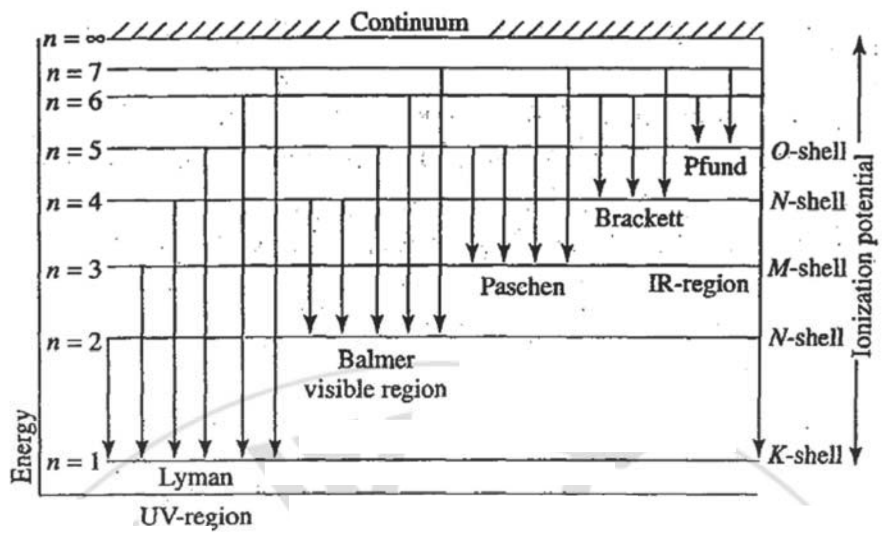

Fig. 2.2

Hydrogen atom contains only one electron, but its spectrum consists of several lines. Why? A sample of hydrogen contains a very large number of atoms. When energy is supplied, the electrons present in different atoms may be excited to different energy level. These electrons when they fall back to various lower levels emit radiations of different frequencies. Each electronic transition produces a spectral line. Energy is absorbed by an atom when an electron moves from the inner energy level to the outer energy level. The amount of energy necessary to remove an electron from its lowest level ($n = 1$) to infinite distance resulting in the formation of a free ion is called the ionization potential. The ionization energy of hydrogen is 2.18×10^{-18} J or 13.595 eV (1 eV = 1.602×10^{-19} J).

If an electron acquires more than enough energy to permit its removal from the atom, the extra energy is carried off by the free electron as kinetic energy. Because of the very small magnitude of the quanta of translational (i.e., kinetic) energy, this energy is essentially continuously variable. The spectrum beyond the series limit thus appears continuous. From the position of continuum, we may calculate the ionization potential.

Dual Nature of Matter

de Broglie wavelength

An electron of energy E and linear momentum p could be defined by a matter wave whose wavelength and frequency are given by

$$\lambda = \frac{h}{p}; \quad \nu = \frac{E}{h}$$

where h is Planck's constant. The wavelength of a moving particle calculated above is called its de Broglie wavelength.

Heisenberg's uncertainty principle

It is not possible to measure, simultaneously, the position and the momentum of a particle with unlimited precision. If Δx is the uncertainty in position and Δp is uncertainty in momentum, then

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

The Quantum Model

Shell	K	L		M			N			
Sublevels	1s	2s	2p	3s	3p	3d	4s	3p	4d	4f
Maximum number of electrons	2	2	6	2	6	10	2	6	10	14

The principle quantum number, *n*, can have values 1, 2, 3, … and is indicative of the major energy levels of the electron in an atom in a gross way. This is similar to the quantum levels in Bohr's theory. The azimuthal quantum number, *l*, has values from 0 to $(n-1)$, for each value of *n*. It is a measure of the angular momentum of the electron. which is $(h/2\pi)\sqrt{l(l+1)}$ in magnitude. Values of $l = 0, 1, 2, 3, \ldots$ and are designated by the letters *s*, *p*, *d*, *f*, …. The magnetic quantum number *m* is indicative of the component of the angular momentum vector in any one chosen direction, usually the *z*-axis. The values of *m* are from $-l$ to $+l$ including zero for any value of *l*. An electron can spin either in clockwise direction or in anticlockwise direction. Spin quantum number, *s*, can have two values + ½ and –½, which are also represented by arrow pointing in opposite directions, i.e., ↿ and ↾, for any particular value of magnetic quantum number.

Node and nodal plane

Node is defined as a region where the probability of finding an electron is zero. Nodes can be of two types: (i) radial node or spherical node and (ii) angular node or planar node.

(i) *Radial node or spherical node*: They correspond to *n* values, i.e., as the distance between nucleus and outermost shell increases, the number of radial nodes increases. For example, 1*s*, 2*p*, 3*d*, and 4*f* orbitals are closest to nucleus (since 1*p*, 1*d*, 2*d*, 1*f*, 2*f*, 3*f* do not exist), so there is no radial node. However, for higher values of *n*, radial nodes can be defined.

(ii) *Angular node or planar node:* They correspond to *l* value. It depends on the shape of orbitals. For example, *s* orbitals are spherically symmetrical in all three planes; so in the *s*-orbital, no angular node exists. *p*-orbitals are not spherically symmetrical but the electron density is concentrated in one plane, either in *x*, *y*, or *z*. So they have one angular node. Similarly, electron density in *d*-orbital is concentrated in two planes, i.e., *xy*, *yz*, *zx*, etc. So the *d*-orbitals have two angular nodes.

Total number of radial nodes = $(n-l-1)$
Total number of angular nodes = l
Total number of nodes = $(n-l-1)+l=n-1$

SOME IMPORTANT EXAMPLES

Example 1 In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen?

(a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$ (c) $2 \rightarrow 5$ (d) $3 \rightarrow 2$

Solution (a)
The electron has minimum energy in the first orbit and its energy increases as n increases. Here n represents the number of orbit, i.e., 1st, 2nd, 3rd, ... The third line from the red end corresponds to yellow region, i.e., 5. In order to obtain less energy, electron tends to come to 1st or 2nd orbit. So jump may be involved either $5 \rightarrow 1$ or $5 \rightarrow 2$. Thus, option (a) is correct here.

Example 2 The number of d-electrons retained in Fe^{2+} (atomic number of Fe = 26) ion is

(a) 4 (b) 5 (c) 6 (d) 3

Solution (c)

$${}_{26}Fe = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2,$$

$$Fe^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$$

The number of d-electrons retained in $Fe^{2+} = 6$.
Therefore, (c) is the correct option.

Example 3 The difference between the wave number of 1st line of Balmer series and the last line of Paschen series for Li^{2+} ion is:

(a) $\frac{R}{36}$ (b) $\frac{5R}{36}$ (c) $4R$ (d) $\frac{R}{4}$

Solution (d)
For 1st line of Balmer series,

$$\overline{V_1} = R_H(3)^2\left[\frac{1}{(2)^2}-\frac{1}{(3)^2}\right] = 9R\left(\frac{5}{36}\right) = \frac{5}{4}R$$

For last line of Paschen series,

$$\overline{V_2} = R_H(3)^2\left[\frac{1}{(3)^2}-\frac{1}{(\infty)^2}\right] = R$$

so, $\quad \overline{v}_1 - \overline{v}_2 = \frac{5}{4}R - R = \frac{R}{4}$

Example 4 Be^{3+} and a proton are accelerated by the same potential. Their de Broglie wavelengths have the ratio (assume mass of proton = mass of neutron):

(a) 1 : 2 (b) 1 : 4 (c) 1 : 1 (d) 1 : $3\sqrt{3}$

Solution (d)

$$\lambda_p = \frac{h}{\sqrt{2eVm_p}}$$

$$\lambda_{Be^{3+}} = \frac{h}{\sqrt{3\times 3eVm_{Be^{3+}}}} = \frac{h}{\sqrt{2\times 3eV\times 9m_p}}$$

Hence,

$$\frac{\lambda_{Be^{3+}}}{\lambda_p} = \sqrt{\frac{2eVm_p}{2\times 3eV\times 9m_p}} = \frac{1}{3\sqrt{3}}$$

Example 5 What is the frequency of revolution of electron present in the 2nd Bohr's orbit of H atom?

(a) $1.016\times 10^{16}\,s^{-1}$ (b) $4.065\times 10^{16}\,s^{-1}$

(c) $1.626\times 10^{15}\,s^{-1}$ (d) $8.13\times 10^{16}\,s^{-1}$

Solution (d)

$$\text{Frequency of revolution} = \frac{\text{Velocity in second orbit } (V_2)}{2\pi r_2}$$

$$= \frac{1.082\times 10^6\ \text{m/s}}{2\times\pi\times(2.12\times 10^{-10})\text{m}} = 8.13\times 10^{16}\,s^{-1}$$