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Paper II

Introduction to Atomic
Spectra

Introduction:-

The analysis in ~~last chapter~~ is a straightforward application of Newton's laws of motion and Coulomb's law of electric force and is in accord with the experimental observation that atoms are stable. However, it is not in accord with electromagnetic theory, which predicts that accelerated electric charges radiate energy in the form of em waves. An electron pursuing a curved path is accelerated and therefore should continuously lose energy, spiraling into the nucleus in a fraction of a second as shown in Fig. 1. But atoms do not collapse. This contradiction further illustrates that the laws of physics that are valid in the macro world do not always hold true in the microworld of the atom.

Classical physics fails to provide a meaningful analysis of atomic structure because it approaches nature in terms of pure particles and pure waves.

In reality particles and waves have many properties in common, though the smallness of Planck's constant makes the wave-particle duality imperceptible in the macro world. The usefulness of classical physics decreases as the scale of the phenomena under study decreases, and we must allow for the particle behavior of waves and the wave behavior of particles to understand the atom. Bohr atomic model, which combines classical and modern notions, accomplishes part of the latter task.

Atomic stability is not the only thing that a successful theory of the atom must account for. The existence of spectral lines is another important aspect of the atom that finds no explanation in classical physics.

When normal materials, solid and liquid, are made white hot, they emit continuous spectrum, gases or vapours show line spectra and band spectra along with continuous spectra. Line spectra occurs for atoms and band spectra occurs for molecules while the continuous spectra can be for atoms as well as molecules. It has been monitoring that line spectra of different atoms is different, thus is the characteristic spectrum. Normally it consists of discrete lines or in some cases complexes of lines. Within the line spectra there exist a sequence of lines and these sequences may be grouped together into series with definite laws. Band spectra consists of shaded bands, and in each band the intensity varies from maximum to minimum from one edge to the other edge. Band spectra is basically a collection of very large number of lines very close to each other. The line spectra and band spectra occur both during emission as well as absorption processes. Hydrogen being the simplest atom produces the simplest spectrum so we will discuss it in details.

Bohr's Atom Model :- Neil Bohr 1913 put forth a model of atomic structure which was in accurate quantitative agreement with the observed spectrum of simplest atom, hydrogen and hydrogen like atoms. His theory is based on the principle of the quantum theory of radiation as enunciated by Planck and Einstein. Following Rutherford he assumed that an atom consists of a positively charged nucleus surrounded by a cluster of electrons. The nucleus carries a positive charge equal to Ze where Z is the atomic number and e is the charge on the electron. In the case of hydrogen, he concluded, following Rutherford, that it consisted of a proton of charge $+e$ in the nucleus and an electron of charge $-e$. Bohr model is based on following assumptions in formulating his theory.



Fig 1:- An atomic electron should, classically, spiral rapidly into the nucleus as it radiates energy due to its acceleration.

1. Bohr's first postulate :- In an atom, an electron rotates around the nucleus in circular orbits under the influence of a coulombian field of force. Since the mass of an electron had been shown to be much smaller than that of a proton he assumed at first that the nucleus is practically at rest. The electrostatic force of attraction between the electron and the nucleus is given by

$$F = \frac{eE}{4\pi\epsilon_0 a^2} = \frac{ze^2}{4\pi\epsilon_0 a^2} \quad \text{--- (1)}$$

where 'a' is the distance between the electron and the nucleus, z is equal to 1 for hydrogen and 2 for helium.

This force of attraction provides the centripetal force $\frac{mv^2}{a}$. (where m is the mass of the electron and v is its velocity in the orbit) that is needed to keep the electron moving in a circular orbit of radius a. The condition for stable orbit therefore is

$$\frac{ze^2}{4\pi\epsilon_0 a^2} = \frac{mv^2}{a} \quad \text{--- (2)}$$

The velocity of the electron in its orbit is therefore given by

$$v^2 = \frac{ze^2}{4\pi\epsilon_0 ma} \quad \text{--- (3)}$$

The kinetic energy of the rotating electron then is

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2} \frac{ze^2}{4\pi\epsilon_0 a} = T \quad \text{--- (4)}$$

The potential energy of the system (consisting of an electron and the nucleus) is zero when the electron is at an infinite distance from the nucleus, the potential energy at a distance a from the nucleus is $\frac{ze}{4\pi\epsilon_0 a}$ per unit positive charge. Hence, the potential energy of the electron (charge, -e) at a

distance 'a' from the nucleus is given by

$$P.E. = -\frac{eze}{4\pi\epsilon_0 a} = -\frac{ze^2}{4\pi\epsilon_0 a} = V = -2T \quad \text{--- (5)}$$

The total energy W, being the sum of the kinetic energy and the potential energy of the electron, is therefore given by

$$W = T + V = T - 2T = -T = -\frac{ze^2}{8\pi\epsilon_0 a} \quad \text{--- (6)}$$

This shows that the total energy of the electron in any closed orbit is negative.

The above analysis is not in accordance with the electromagnetic theory which predicts that an accelerated charge would radiate energy in the form of electromagnetic waves. As an electromagnetic wave moving in a circular orbit would be continuously accelerated it must continuously lose energy, thereby spiralling inward as it decreases until it is swallowed up by the nucleus. The conventional physics therefore completely fails to account for the existence of stable atoms with electrons remaining at a distance from the nucleus.

2. Bohr's second postulate :- To avoid this spiralling down of the electron into the nucleus, Bohr predicted the quantum hypothesis that the electron can move in only certain discrete non-radiating orbits, called stationary orbits, for which the angular momentum of the moving electron is an integral multiple of $\frac{h}{2\pi}$ where h is the Planck's constant.

$$J = I\omega = n \frac{h}{2\pi} \quad \text{--- (7)}$$

where I is the moment of inertia of the electron about the nucleus, ω is its angular velocity and n is 1, 2, 3, ... and is known as the principal quantum number. The angular momentum is thus said to be quantised. As $I = ma^2$, the above relation can also be written as

$$ma^2\omega = n \frac{h}{2\pi} \quad \text{--- (8)}$$

The kinetic energy of the electron is given by

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m(a\omega)^2 = \frac{1}{2}ma^2\omega^2 \quad \dots (9)$$

From Eq. (3), $v^2 = a^2\omega^2 = \frac{ze^2}{4\pi\epsilon_0 ma}$

$v = a\omega$

or $a^3\omega^2 = \frac{ze^2}{4\pi\epsilon_0 m} \quad \dots (10)$

From Eq. (8): $a^2\omega = \frac{nh}{2\pi m} \quad \dots (11)$

Dividing Eq. (10) by Eq. (11) we get $a\omega = \frac{ze^2}{2\epsilon_0 nh} \quad \dots (12)$

Substituting the value of $a\omega$ in Eq. (9) we get

$$T = \frac{1}{2}m \left[\frac{ze^2}{2\epsilon_0 nh} \right]^2 = \frac{mz^2e^4}{8\epsilon_0^2 h^2 n^2} = -W \quad \dots (13)$$

$$a\omega = \frac{ze^2}{m} \frac{2\pi h}{h^2} = \frac{2\pi ze^2}{nh}$$

$$T = \frac{1}{2}m \left[\frac{2\pi ze^2}{nh} \right]^2 = \frac{2\pi^2 m z^2 e^4}{nh^2} = -W$$

$$R = \frac{2\pi^2 m e^4}{h^3}$$

Total energy $W = -\frac{mz^2e^4}{8\epsilon_0^2 h^2 n^2} \quad \dots (14)$

or $W = -\frac{Rchz^2}{n^2}$

where $R = \frac{me^4}{8\epsilon_0^2 c^2 h^3}$ is the Rydberg constant and is equal to $1.09678 \times 10^7 / m$

[In C.G.S. units $W = -\frac{2\pi^2 me^4 z^2}{n^2 h^2}$]

The total energy of the electron is thus quantised in that it can take only discrete values determined by the integral values of the quantum number n .

The energy content W has the algebraically smallest value in the first (innermost) orbit. If we call it W_1 , then, for the second and third orbits respectively, we have

$$W_2 = \frac{1}{4}W_1 \quad \text{and} \quad W_3 = \frac{1}{9}W_1$$

These amounts are greater than W_1 , since $W_1 < 0$. Hence, the electron can be lifted from an inner to an outer orbit only by imparting energy to the atom. It can fall from an outer to an inner orbit by losing energy. The innermost orbit is therefore most stable and represents the normal (or ground) state of the revolving electron. All the other states, in which the electron describes a more external orbit, are called excited states.

The above postulate is also stated in a different manner according to the wave concept of electron: the electron can circle a nucleus indefinitely without radiating energy provided the length of its orbit is an integral multiple of de-Broglie wavelength i.e.

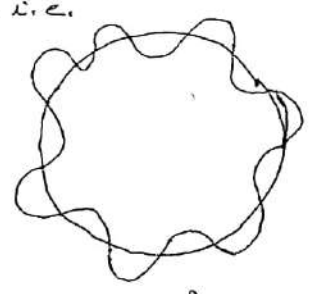
$$2\pi a = n\lambda \quad \dots (15)$$

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

$\therefore 2\pi amv = nh$

or $2\pi am a\omega = nh$

or $ma^2\omega = \frac{nh}{2\pi}$



$2\pi a = n\lambda$

3. Bohr's third postulate :- In order to explain how an atom emits or absorbs radiation, Bohr, following Planck's quantum theory, made another postulate which may be stated in the following manner.

If an electron is rotating in a stationary orbit around the nucleus, for which the energy is W_i , then it can shift to another stationary orbit of lower energy W_f and in doing so it will radiate energy of frequency ν given by

$$h\nu = W_i - W_f = T_i - T_f \quad \dots \dots (16)$$

Substituting the value of W from Eq (13) and giving in the values n_i and n_f corresponding to the initial and final energy states W_i and W_f respectively we get

$$h\nu = \frac{me^4 z^2}{8\epsilon_0^2 h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots \dots (17)$$

[In C.G.S. units,
$$h\nu = \frac{2\pi^2 me^4 z^2}{h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$
]

Above equation can be written in terms of the wave number $\bar{\nu}$ i.e. the number of waves per meter,

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

$$\bar{\nu} = \frac{me^4 z^2}{8\epsilon_0^2 hc^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots \dots (18)$$

$$\bar{\nu} = R z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots \dots (19)$$

where $R = \frac{me^4}{8\epsilon_0^2 hc^3}$ is the Rydberg constant and is equal to $1.09678 \times 10^7 / m$

For hydrogen atom, $z=1$, therefore

$$\bar{\nu} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

This is identical with the Balmer's experimental formula for the hydrogen series.

Radius, Frequency and Energy of the permitted orbits :- Let M and E be the mass and charge of the nucleus; m, e and

v the mass, charge and linear velocity respectively of the electron which is assumed to revolve in a circular orbit of radius a . In general, the nuclear charge $E = Ze$, where Z is the atomic number of the element; for hydrogen $Z=1$ and $E=e$. The nuclear mass M is so large compared to the electronic mass m that, for the present, the nucleus is assumed to remain at rest.

The electrostatic force of attraction between the nucleus and the electron = $\frac{Ee}{a^2}$. The centrifugal force of repulsion between the two resulting from the circular motion of the electron = $\frac{mv^2}{a}$. The system will be stable, if

$$\frac{Ee}{a^2} = \frac{mv^2}{a}$$

$$\therefore v^2 = \frac{Ee}{am} \quad \dots \dots (1)$$

The quantum condition for the orbit, $\oint p = n \frac{h}{2\pi}$

$$\text{or } m a v = n \frac{h}{2\pi}$$

$$\text{and } v = \frac{nh}{2\pi m a} \quad \dots \dots (2)$$

Dividing Eq(1) by Eq(2), we get

(3)

$$v = \frac{Ee}{an} \cdot \frac{2\pi na}{nh} = \frac{2\pi Ee}{nh} \quad \dots (3)$$

From Eq(3),

$$a = \frac{nh}{2\pi mv}$$

Substituting the value of v from Eq(3), we get

$$a = \frac{nh}{2\pi mv} = \frac{nh}{2\pi m} \cdot \frac{nh}{2\pi Ee} = \frac{n^2 h^2}{4\pi^2 Ee m} \quad \dots (4)$$

Thus, the radius 'a' of the permitted orbit is directly proportional to n^2 , since all the other quantities are constant. This means that the radii of successive permitted orbits are proportional to the square of the integers 1, 2, 3, ----. These integers are called the quantum numbers of the respective orbits.

The radius of the first smallest orbit in the hydrogen atom comes out to be equal to 0.53×10^{-8} cm, and is known as the Bohr radius. The diameter of the first orbit is, of the order of 10^{-8} cm., which agrees with the values of the diameters of atoms computed by various other methods.

orbital frequency :- If f be the orbital frequency

$$f = \frac{\omega}{2\pi} = \frac{v}{2\pi a} = \frac{2\pi Ee}{nh} \cdot \frac{1}{2\pi a} = \frac{Ee}{nha}$$

$$= \frac{Ee}{nh} \cdot \frac{4\pi^2 Ee m}{n^2 h^2} = \frac{4\pi^2 E^2 e^2 m}{n^3 h^3} \quad \dots (5)$$

According to the classical theory, this orbital frequency is equal to the frequency of the spectral line emitted by the atom.

Orbital energy :- The total energy W of the electronic system is equal to the sum of the kinetic energy and potential energies.

The kinetic energy = $\frac{1}{2}mv^2 = \frac{Ee}{2a}$ and the potential energy = $-\frac{Ee}{a}$. The total energy is thus given by

$$W = \frac{Ee}{2a} - \frac{Ee}{a} = -\frac{Ee}{2a}$$

Substituting the value of a from Eq(4) we get

$$W = W_n = -\frac{Ee}{2} \cdot \frac{4\pi^2 Ee m}{n^2 h^2} = -\frac{2\pi^2 m E^2 e^2}{n^2 h^2} \quad \dots (6)$$

W_n being the energy of the electron when it is in the n^{th} orbit, or the energy corresponding to the n^{th} orbit.

In Eq(6), all the quantities except n are constants, the orbital energy is inversely proportional to the square of the quantum number of the orbit. Evidently for any one particular orbit the energy is constant, which means that as long as the electron remains in that orbit it cannot lose energy by radiation, in contradiction to the classical electromagnetic theory.

The interpretation of the negative sign associated with the expression for the orbital energy is important. As 'n' increases, the absolute numerical value of the energy decreases, but on account of the negative sign, the actual energy will increase. This means that the outer orbits have greater energy than the inner ones. In the case of the hydrogen atom, taking the relation

$$W_n = -\frac{2\pi^2 m E^2 e^2}{n^2 h^2}$$

Since $E = ze$,

$$W_n = -2m \left(\frac{\pi e^2}{h} \right)^2 \cdot \frac{1}{n^2} = -\left(\frac{2\pi^2 e^4 m}{ch^3} \right) \frac{z^2 ch}{n^2} = -R \frac{z^2 ch}{n^2} \quad \text{using } E = ze$$

and $R = \frac{2\pi^2 e^4 m}{ch^3}$, Rydberg constant.

Energy of the first orbit
(In C.G.S.)

$$W_1 = -\frac{2 \times 9 \times 10^{-20} \times \pi^2 (4.77 \times 10^{-10})^4}{(6.55 \times 10^{-27}) \times (1)^2} = -2.155 \times 10^{-11} \text{ erg.}$$

P.T.O.

Energy of the second orbit $w_2 = -\frac{2.155 \times 10^{-11}}{2^2} = -0.535 \times 10^{-11} \text{ erg}$.

Energy of the third orbit $w_3 = -\frac{2.155 \times 10^{-11}}{3^2} = -0.238 \times 10^{-11} \text{ erg}$ and so on.

Since the first orbit has the least energy it is the most stable and is the one which the electron occupies in the normal unexcited atom.

It is seen that both radius and energy of electron in the atom are quantized. The zero of energy occurs when $n = \infty$, that is, electron is away from the atom. The lowest energy state ($n=1$) is called ground state and states $n > 1$ are termed as excited states.

Critical Ionisation and Excitation potentials :-

Critical potential :- The least energy, in electron volts, which is necessary to excite a free neutral atom from its ground state to a higher energy state, is called a critical potential of the atom.

Ionisation potential :- A ~~critical potential~~ critical potential is called an ionisation potential, when the absorption of energy by the excited atom just removes an electron from it. i.e. the electron is raised from the level $n=1$ to $n=\infty$.

Excitation potential :- A critical potential is called an excitation potential, when the absorption of energy by the unexcited atom just raises it to a higher energy state (but does not ionise it). On the basis of Bohr's theory, the various energy states in a hydrogenic atom are given by

$$E_n = -\frac{2\pi^2 k^2 Z^2 m e^4}{n^2 h^2} \left\{ \begin{array}{l} -13.6 \text{ eV} \text{ for hydrogen } Z=1 \\ = -Rhc \frac{Z^2}{n^2} \end{array} \right.$$

Thus the energy of the electron in a hydrogen atom for the first, second, third etc., orbits are $-13.6 \text{ eV} (n=1)$, $-3.4 \text{ eV} (n=2)$, $-1.51 \text{ eV} (n=3)$ and $0 \text{ eV} (n=\infty)$.

Hence the energy required to raise the hydrogen atom from the ground state to the first excited state is equal to $(13.6 - 3.4) = 10.2 \text{ eV}$, that required to raise it to the second excited state is $(13.6 - 1.51) = 12.09 \text{ eV}$ and the energy required to ionise it is $(13.6 - 0) = 13.6 \text{ eV}$.

In other words, discrete amounts of energy are required to excite the hydrogen atom to different energy states, which are thus quantised. The first and second excitation potentials are 10.2 and 12.09 volts respectively and the ionisation potential is 13.6 volts.

Hydrogen Spectra :- If hydrogen gas is filled in an evacuated glass tube and high potential difference is applied between the electrodes of the glass tube, hydrogen can emit electromagnetic radiation. If these radiations are analysed with a spectroscope, a series of discrete lines is observed. In case of hydrogen when it is excited by providing sufficient energy. It goes to higher energy state, but cannot stay there for ever. So, it makes a transition from higher energy state (let E_2) to lower energy state (let E_1). The difference of these energies appears in the form of a photon of frequency ν .

$$E_2 - E_1 = h\nu = -\frac{2\pi^2 e^4 m Z^2}{n_2^2 h^2} + \frac{2\pi^2 e^4 m Z^2}{n_1^2 h^2} = \frac{2\pi^2 e^4 m Z^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\nu = \frac{2\pi^2 e^4 m Z^2}{h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Frequency in wave number i.e. $\bar{\nu} = \frac{\nu}{c}$ then,

$$\bar{\nu} = \frac{2\pi^2 e^4 m Z^2}{c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = R Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $R = \frac{2\pi^2 m e^4}{c h^3}$ is the Rydberg's constant.

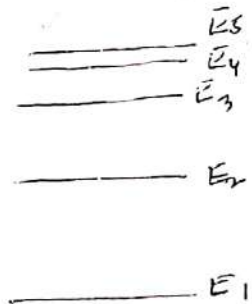
For hydrogen, $Z=1$ and then $\bar{\nu} = \frac{2\pi^2 m e^4}{c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

Energy level diagram :- For orbit $n=1$, for $z=1$ $E_n = -Rhc \frac{z^2}{n^2}$ (195/4)

$$\left. \begin{array}{l} \text{for orbit } n=2 \\ E_1 = -Rhc \frac{1}{1} = -K \\ E_2 = -(Rhc) \frac{1}{4} = -\frac{K}{4} \end{array} \right\} E_2 - E_1 = \frac{3}{4} K$$

$$E_3 = -\frac{K}{9} \quad E_3 - E_2 = \frac{5}{36} K$$

$$E_4 = -\frac{K}{16} \quad E_4 - E_3 = \frac{7}{144} K$$



$$\Rightarrow E_4 > E_3 > E_2 > E_1$$

and separation between energy levels goes on decreasing with increase in 'n'.

Bohr's frequency conditions :- Whenever an e^- jumps from a higher orbit to a lower orbit, it radiates energy and frequency of emitted radiation is given by

$$E_{n_2} - E_{n_1} = h\nu = \frac{hc}{\lambda}$$

$$\text{or} \quad \frac{hc}{\lambda} = -Rhc \frac{z^2}{n_2^2} + Rhc \frac{z^2}{n_1^2}$$

$$\text{or} \quad \frac{1}{\lambda} = Rz^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For H_2 atom, $z=1$

$$\boxed{\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

P.T.O.

Spectral Series of H-atom :- ^{giving different values to n_1 and n_2 the different series observed in hydrogen spectrum.} In H₂ atom a series of spectral lines are obtained which are

- (1) Lyman Series :- falls in U-V region, $n_2 = 2, 3, 4, \dots$, $n_1 = 1$
- (2) Balmer Series :- fall in visible region, $n_1 = 2$, $n_2 = 3, 4, 5, \dots$
- (3) Paschen Series :- fall in IR region, $n_1 = 3$, $n_2 = 4, 5, 6, \dots$
- (4) Brackett Series :- fall in IR region, $n_1 = 4$, $n_2 = 5, 6, 7, \dots$
- (5) Pfund Series :- fall in IR region, $n_1 = 5$, $n_2 = 6, 7, 8, \dots$

(1) Explanation of Lyman Series :- Spectral lines of Lyman series are obtained when an e^- jumps from any higher orbit to the first orbit in H₂ atom and the wavelength of spectral lines of Lyman series are given by

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= R \left(1 - \frac{1}{n_2^2} \right), n_2 = 2, 3, 4, \dots \infty$$

The first line (longest wavelength) of Lyman series is for

$$n_2 = 2 \text{ and } n_1 = 1$$

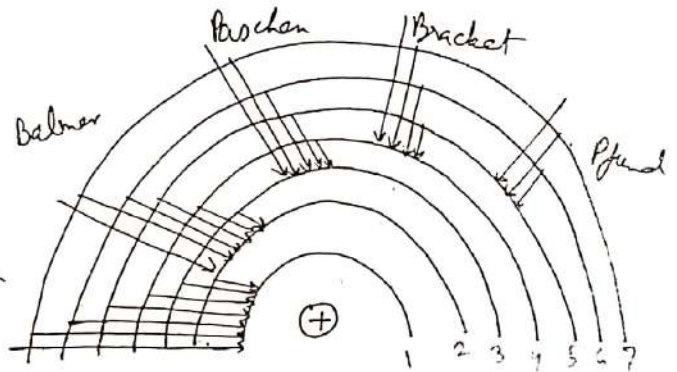
$$\frac{1}{\lambda} = R \left(1 - \frac{1}{4} \right) = \frac{3}{4} R$$

$$\text{or } \boxed{\lambda_{1L} = \frac{4}{3R}}$$

The last line or series limit or shortest wavelength is obtained by $n_2 = \infty$

$$\frac{1}{\lambda} = R \left(1 - \frac{1}{\infty} \right)$$

$$\text{or } \boxed{\lambda_{\infty L} = \frac{1}{R}} = 912 \text{ \AA}$$



(2) Explanation of Balmer Series :- It is obtained when an e^- jumps from any higher orbit to 2nd orbit in the H₂ atom $\Rightarrow n_1 = 2$, $n_2 = 3, 4, 5, \dots$

The wavelength ' λ ' of spectral line of Balmer series are given by

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left(\frac{1}{4} - \frac{1}{n_2^2} \right) = \frac{5}{36} R$$

$$\boxed{\lambda_{1B} = \frac{36}{5R}}$$

for first line (longest wavelength) of Balmer Series is given by

The series limit or shortest wavelength is obtained by $n_2 = \infty$

$$\frac{1}{\lambda_{\infty B}} = R \left(\frac{1}{4} - \frac{1}{\infty} \right) = \frac{R}{4}$$

$$\boxed{\lambda_{\infty B} = \frac{4}{R}} = 3646 \text{ \AA}$$

The first, second, third, ----- etc lines of Balmer series are called as H_{α} , H_{β} , H_{γ} , H_{δ} , ----- etc. and the corresponding wavelengths are 6562 \AA, 4861 \AA, 4340 \AA and 4101 \AA respectively.

(3) Explanation for Paschen Series :- It is obtained when an e^- jumps from any higher orbit to 3rd orbit i.e. $n_1 = 3$, $n_2 = 4, 5, 6, \dots$

$$\therefore \frac{1}{\lambda_{1P}} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda_{1P}} = R \left(\frac{1}{9} - \frac{1}{16} \right)$$

The first line (longest λ) is

$$\frac{1}{\lambda_{1P}} = R \left(\frac{16-9}{144} \right)$$

$$= \frac{7R}{144}$$

$$\boxed{\lambda_{1P} = \frac{144}{7R}}$$

The series limit or shortest λ is obtained by $n_2 = \infty$.

$$\frac{1}{\lambda_{\infty P}} = R \left(\frac{1}{9} - \frac{1}{\infty} \right) = \frac{R}{9}$$

$$\text{or } \boxed{\lambda_{\infty P} = \frac{9}{R}} = 8208 \text{ \AA}$$

(4) Explanation for Brackett Series :- It is obtained when an e^- jumps from any higher orbit to the 4th orbit i.e. $n_1 = 4$, $n_2 = 5, 6, \dots$

$$\therefore \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

First line (longest λ) is $\frac{1}{\lambda} = R \left(\frac{1}{16} - \frac{1}{25} \right) = R \left(\frac{25-16}{16 \times 25} \right) = \frac{9R}{25 \times 16}$

$$\text{or } \lambda_{10r} = \frac{400}{9R} = \boxed{\frac{44.44}{R} = \lambda_{10r}}$$

The series limit or shortest λ is obtained by $n_2 = \infty$

$$\frac{1}{\lambda_{\infty Br}} = R \left(\frac{1}{16} - \frac{1}{\infty} \right)$$

$$\text{or } \boxed{\lambda_{\infty Br} = \frac{16}{R}} = 14580 \text{ \AA}$$

5) Explanation for Pfund Series :- It is obtained when e^- jumps from any higher orbit to the 5th orbit i.e.

$$n_1 = 5, n_2 = 6, 7, \dots$$

$$\therefore \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

First line (longest λ) is

$$\frac{1}{\lambda} = R \left(\frac{1}{25} - \frac{1}{36} \right)$$

$$= R \left(\frac{36 - 25}{25 \times 36} \right)$$

$$\boxed{\lambda_{1st} = \frac{25 \times 36}{11R}}$$

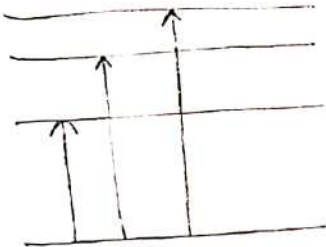
The series limit or shortest wavelength ' λ ' is obtained by $n_2 = \infty$

$$\lambda_{\infty th} = R \left(\frac{1}{25} - \frac{1}{\infty} \right)$$

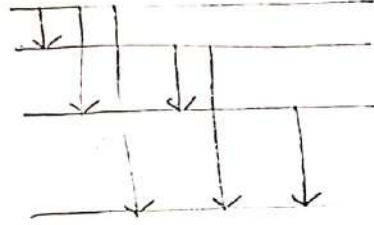
$$\boxed{\lambda_{\infty th} = \frac{25}{R}} = 22800 \text{ \AA}$$

Absorption and Emission Spectrum :- When any atom is in ground state absorbs energy an e^- may go to a higher state and this transition is called as absorption transition. The spectral lines arising out of this transition is called as absorption spectral line.

An atom in excited state remains only for 10^{-8} sec and tries to come back to its ground state by emitting radiations when e^- jump from a higher state to a lower state, this transition is called as emission transition and the spectral line as emission spectral line.



Absorption transition



Emission radiation
Emission transition

The number of emission transitions is always more than the number of absorption transition except for the case when transition is between $n_1=1$ to $n_2=2$ level.

Drawbacks of Bohr's Atom Model :- Bohr's model was successful in explaining many experimental observations of spectra, yet it could not explain

following observations:

- (1) They can explain observations of hydrogen and hydrogen like atoms, but it cannot explain the spectra of Helium (neutral) atom with two electron only.
- (2) They proposed the concept of only circular orbits but electron orbits are elliptical also. The theory could not explain the existence of these orbits.
- (3) The theory was silent in explaining the fine structure of spectral lines. For example, H_{α} contains 5 lines.
- (4) It could not explain the intensity distribution of different spectral lines.
- (5) The theory treated electron as a particle only as it could not explain wave nature of electron.
- (6) The theory was also silent in explaining the distribution of electrons in different orbits and the time spent by an electron in any orbit.
- (7) The theory could not explain why electron follows classical assumptions of electromagnetic principle (Coulomb's law) but does not follow other property of radiation by accelerated charged particles.

*

Ground, excited and ionized state of atom :-

Ground State :- The atom is said to be in ground state when there is normal distribution of e^- in various orbits of the atom.

In magnitude it is the energy of the e^- in a particular orbit. For example H_2 atom the ground state energy

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

for ground state $Z=1, n=1$

$$\therefore E_1 = Rhc$$

$$E_1 = 13.6 \text{ eV}$$

Excited State :- The atom is said to be in excited state when it absorbs energy in the ground state, such that one of the e^- jumps to a higher orbit. The amount of energy absorbed is called as 'excitation energy'. There may be many excited states of an atom and this state lasts only for 10^{-8} sec and e^- comes back to its earlier orbit by emitting energy.

For first excited state e^- goes from 1st to 2nd orbit and 1st excitation energy for H-atom is

$$\begin{aligned} \Delta E &= E_2 - E_1 = -Rhc \frac{1}{2^2} + Rhc \frac{1}{1} \\ &= -\frac{13.6}{4} + 13.6 \\ &= 10.2 \text{ eV} \end{aligned}$$

Ionized State :- The atom is said to be in ionized state when it becomes an ion, the amount of energy absorbed to move out an e^- from the orbit to ∞ is called as ionization energy.

The ionisation energy for H-atom,

$$\begin{aligned} &= E_{\infty} - E_1 \\ &= -Rhc \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) \\ &= 0 + Rhc \\ &= 13.6 \text{ eV} \end{aligned}$$

Binding Energy of atom :- B.E. of the atom is the amount of energy required to break the atom or it is the energy with which e^- in a particular orbit is bound with nucleus in the atom.

The B.E. of e^- in first orbit $E_1 = Rhc \frac{1}{n^2} = Rhc = 13.6 \text{ eV}$

Similarly B.E. of e^- in second orbit $E_2 = Rhc = \frac{13.6}{4} \text{ eV} = 3.4 \text{ eV}$

Energy level diagram :- We have seen above that energy states of the atom can be represented by orbits of increasing radii and the transitions between these states, giving rise to spectral lines. An energy level diagram shown in figure.

In such a figure, each Bohr orbit or stationary state is denoted by a horizontal line drawn to an energy scale. The quantity $\frac{W}{hc} = -\frac{R}{n^2}$ which is proportional to the energy W , is usually drawn instead of plotting the energy directly. The frequency of the radiation in wave number $\bar{\nu}$ emitted as a result of a transition, is then directly given by the difference between two energy levels, for

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{W_i - W_f}{hc}$$

As the energy w of the quantised states have negative values and approach zero as n approaches infinity, the zero energy level corresponding to $n = \infty$ is drawn at the top and other energy levels are drawn below it. The arrows connecting different levels represent the transition between the corresponding energy states. The energy level diagram for ionised helium can also be drawn in the same way.

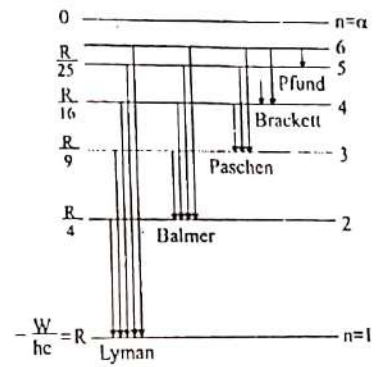


Fig :- Energy level diagram of hydrogen

The spectral series of hydrogen are plotted in terms of wavelength in figure, the Brackett series evidently overlaps the Paschen and Pfund series.

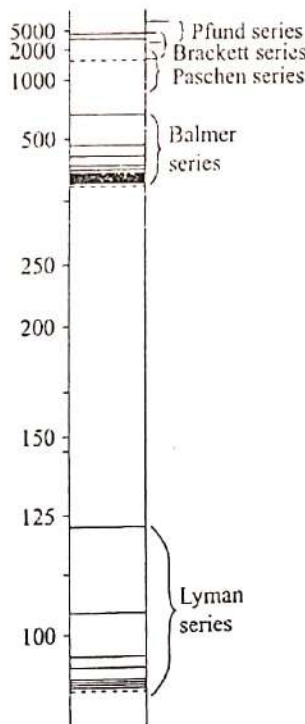


Fig :- The spectral series of hydrogen. The wavelengths in each series are related by simple formula.

Q:- Calculate the ratio of longest wavelength of Lyman to the Brackett series of the H_2 atom.

Ans:- In the Lyman series:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Now for longest wavelength, $n_1=1$, $n_2=2$

$$\lambda_{1L} = R \left(1 - \frac{1}{4} \right)$$

$$\lambda_{1L} = \frac{4}{3R}$$

In Brackett series:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right); n_1=4, n_2=5, 6, \dots$$

for longest λ

$$\lambda_{10} = \frac{400}{9R}$$

$$\text{Now } \frac{\lambda_{1L}}{\lambda_{10}} = \frac{4}{3R} \cdot \frac{9R}{400} = \frac{3}{100} \quad \text{Ans}$$

Q:- Find the wavelength of H_γ line in the Balmer series of the H_2 atom.

Ans:- For Balmer series, $n_1=2$, $n_2=3, 4, 5, \dots$

For H_γ line $n_2=5$

$$\therefore \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= R \left(\frac{1}{4} - \frac{1}{25} \right)$$

$$= R \left(\frac{25-4}{100} \right)$$

$$\lambda_{3B} = \frac{100}{21R}$$