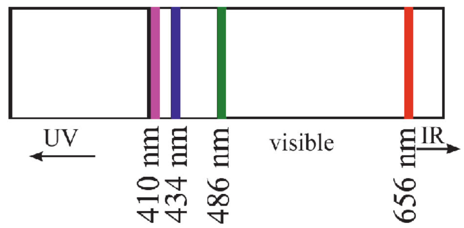
Atomic Spectra:

We know that when a metallic object is heated, it emits radiation of different wavelengths. When this radiation is passed through a prism, we get a continuous spectrum. However, the case is different when we heat hydrogen gas inside a glass tube to high temperatures. The emitted radiation has only a few selected wavelengths and when passed through a prism we get what is called a line spectrum as shown for the visible range in Fig. It shows that hydrogen emits radiations of wavelengths 410, 434, 486 and 656 nm and does not emit any radiation with wavelengths in between these wavelengths. The lines seen in the spectrum are called emission lines.



Hydrogen spectrum

Example :

Determine the energies of the first two excited states of the electron in hydrogen atom. What are the excitation energies of the electrons in these orbits ?

Sol : The energy of the electron in the nth orbit is given by $E_n = -13.6\frac{1}{n^2}eV$

The first two exccited states have n = 2 and 3. Their energies are

$E_2 = -13.6\frac{1}{2^2} = -3.4eV$ and $E_3 = -13.6\frac{1}{3^2} = -1.51eV$

Excitation energy of an electron in nth orbit is the difference between its energy in that orb it and the energy of the electron in its ground state, i.e. -13.6eV. Thus, the excitation energies of the electrons in the first two excited states are 1.2 eV and 12.09 eV respectively.

Example : Calculate the wavelengths of the first three lines in Paschen series of hydrogen atom.

Sol : The wavelengths of lines in Paschen series (n = 3) are given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = 1.097\times10^7\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

For the first three lines in the series, m = 4, 5 and 6. Substituting in the above formula

we get $\frac{1}{\lambda_1} = 1.097\times10^7\left(\frac{1}{3^2} - \frac{1}{4^2}\right)$

$= 1.097\times10^7 \times 7/(9\times16)$

$= 0.0533\times10^7 m^{-1}$

$\lambda_1 = 1.876\times10^{-6} m$

$\frac{1}{\lambda_2} = 1.097\times10^7\left(\frac{1}{3^2} - \frac{1}{5^2}\right)$

$= 1.097\times10^7 \times 16/(9\times25)$

$0.075 \times 10^7 m^{-1}$

$\lambda_2 = 1.282 \times 10^{-6} m$

$$\frac{1}{\lambda_3} = 1.097 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{6^2}\right)$$

$= 1.097 \times 10^7 \times 27 - (9 \times 36)$

$= 1.0914 \times 10^7 m^{-1}$

$\lambda_3 = 1.094 \times 10^{-6} m$

Ex. 4 Wavelength of $H \propto$ line of Balmer series is $6560\,A^0$. Calculate wavelength of 1^{st} line of Lyman & Paschan series

Soln : - For Balmer series -

P = 2 ; n = 3, 4, 5 ....

For $H \propto$ line i.e. 1st Balmer series - P = 2, n = 3

$\lambda \propto = 6560 A^0$

$$\therefore \frac{1}{\lambda \propto} = R\left[\frac{1}{P^2} - \frac{1}{n^2}\right] \qquad \therefore \frac{1}{\lambda \propto} = R\left[\frac{1}{4} - \frac{1}{9}\right] \qquad \therefore \frac{1}{\lambda_\propto} = \frac{5}{36} R$$

$$\therefore \lambda_\propto = \frac{36}{5R} \qquad \text{.......... (I)}$$

For 1st Line of lyman series P = 1, n = 2

$$\therefore \frac{1}{\lambda_L} = R\left[\frac{1}{1} - \frac{1}{4}\right] \qquad \therefore \frac{1}{\lambda_L} = R\left[\frac{3}{4}\right]$$

$$\therefore \lambda_L = \frac{4}{3R} \qquad \text{...........(II)}$$

For 1st Line of Paschen series - P = 3, n = 4

$$\therefore \frac{1}{\lambda_P} = R\left[\frac{1}{9} - \frac{1}{16}\right] = R\left[\frac{7}{144}\right] \qquad \therefore \lambda_P = \frac{144}{7R} \text{ ....(III)}$$

Divide (II) by (I)

$$\frac{\lambda_L}{\lambda \propto} = \frac{(4/3 \times R)}{\left(\frac{36}{5 \times R}\right)} \qquad \therefore \lambda_L = \frac{5}{27} \times 6560 \qquad \left[\therefore \lambda_L = 1214 A^0\right]$$

Divide (III) by (I)

$$\frac{\lambda_p}{\lambda \propto} = \frac{\left(\frac{144}{7}\right)R}{\left(\frac{36}{5}\right)R} \qquad \therefore \lambda_P = \frac{20}{7} \times 6560 \qquad \therefore \lambda_P = 18742 A^0$$

Ex. 5 Calculate wavelength and requency of 1^{st} line of lyman series of hydrogen atom Given Rydberg constant R = $1.097 \times 10^7 / m$

Soln For Lyman series P = 1 & n = 2, 3, 4, ...

For 1st Lyman series P = 1, & n = 2

$$\therefore \frac{1}{\lambda_L} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] \qquad \therefore \frac{1}{\lambda_L} = R\left[\frac{1}{1} - \frac{1}{4}\right]$$

$$\therefore \frac{1}{\lambda_L} = R\left[\frac{3}{4}\right] \qquad \therefore \frac{1}{\lambda_l} = \frac{1.097\times10^{7}\times3}{4}$$

$$\left[\lambda_L = \frac{4}{3\times1.097\times10^{7}}\right] \qquad \therefore\ \lambda_l = 1215\times10^{-10}m$$

Frequency $(\upsilon) = C/\lambda$

$$(\upsilon) = \frac{3\times10^{8}}{1215\times10^{-10}} \qquad \therefore \upsilon = 24.69\times10^{14}$$

Ex. 6 State the tranzition correponding to shortest and longest wavelength line in i) Lyman series ii) Balmer sereis iii) Paschen series

Sol^n : $\frac{1}{\lambda} = R\left[\frac{1}{P^2} - \frac{1}{n^2}\right]$

Shortest wavelength line (series limit)

For shortest wavelength line an e^- makes transition from ∞ to particular orbit.

$\Rightarrow$ i.e. For shortest wavelength of line of Lyman series P = 1, n = ∞

$$\frac{1}{(\lambda_L)_S} = R\left[\frac{1}{1^2} - \frac{1}{\infty}\right] \qquad \therefore \frac{1}{(\lambda_L)_S} = R \qquad (\lambda_L)_S = \frac{1}{R}$$

$\Rightarrow$ For shortest wavelength line of balmer series

P = 2 and n = ∞

$$\therefore \frac{1}{(\lambda_B)_S} = R\left[\frac{1}{4} - \frac{1}{\infty}\right] \qquad \therefore (\lambda_B)_S = \frac{4}{R}$$

$\Rightarrow$ For shortest wavelength line of paschen series

P = 3 & n = ∞

$$\therefore \frac{1}{(\lambda_P)_S} = R\left[\frac{1}{9} - \frac{1}{\infty}\right] \qquad \therefore (\lambda_P)_S = \frac{9}{R}$$

The difference in wavelengths of successive lines in each series (fixed value of p) can be calculated from Eq. and shown to decrease with increase in n. Thus, the successive lines in a given series come closer and closer and ultimately reach the values of $\lambda = \frac{p^2}{R}$ in the limit $n \to \infty$, for different values of p. Atoms of other elements also emit line spectra. The wavelengths of the lines emitted by each element are unique, so much so that we can identify the element from the wavelengths of the spectral lines that it emits. Rutherford's model could not explain the atomic spectra.

Longest wavelength line

For longest wavelength e^- jumps from next orbit to respective orbit

$\Rightarrow$ i.e. For longest wavelength line of Lyman series

P = 1 & n = 2

$$\therefore \frac{1}{(\lambda_L)_L} = R\left[\frac{1}{1} - \frac{1}{4}\right] \qquad (\lambda_L)_L = \frac{4}{3R}$$

$\Rightarrow$ For longest wavelength line of Balmer series

P = 2 & n = 3

$$\therefore \frac{1}{(\lambda_B)_L} = R\left[\frac{1}{4} - \frac{1}{9}\right] \qquad (\lambda_B)_L = \frac{36}{5R}$$

$\Rightarrow$ For longest wavelength line of paschen series
P = 3, and n = 4

$$\therefore \frac{1}{(\lambda_P)_L} = R\left[\frac{1}{9} - \frac{1}{16}\right] \qquad \therefore (\lambda_P)_L = \frac{144}{7R}$$

Series Limit : (Shortest wavelength line)

The smallest wavelength emitted in a series is called **series limit.** The series limit for particular series is found by taking $n = \infty$ in Bohr's relation.

e.g. Series limit for Balmar Series is

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R}{4}$$

or $\lambda = \dfrac{4}{R}$ is series limit for Balmar series. In general $\lambda = \dfrac{P^2}{R}$

Home Work

Ex 6 (A) Find the ratio of longest to shortest wavelength in Paschen series.

(Ans : 2.286 : 1)

Ex. 7 Show that - Energy of electron in 1st orbit is given by - $E_1 = -Rhc$

Sol^n We know,

Energy of e^- in nth orbit is gien by $E_n = \dfrac{-me^4}{8\varepsilon_0{}^2 n^2 h^2}$

For 1st orbit, n = 1

$$E_1 = \frac{-me^4}{8\varepsilon_0{}^2 h^2} \qquad \therefore E_1 = \frac{-me^4\ h.c}{8\varepsilon_0{}^2 h^2 hc} \qquad \text{But, } \frac{me^4}{8\varepsilon_0{}^2 h^3 c} = R$$

$\therefore\ E_1 = -R\ .\ hc$ Hence proved $\boxed{E_n = \dfrac{-Rhc}{n^2}}$

Ex. 8 Find the value of Rydberg's constant if the energy of electron in second orbit in hydrogen atom is - 3.4 eV

Sol^n We know

$$E = \frac{-me^4}{8\varepsilon_0{}^2 n^2 h^2} \text{ ....(I)}$$

For second orbit n = 2

$$E_2 = \frac{-me^4}{8\varepsilon_0^2\left(2^2\right)h^2} \qquad 4E_2 = \frac{-me^4}{8\varepsilon_0^2 h^2}$$

also Rydberg's constant, $R = \left(\frac{me^4}{8\varepsilon_0^2 h^3 c}\right)$ $\qquad R = \left(\frac{me^4}{8\varepsilon_0^2 h^2}\right) hc$

From (I) $\quad R = \frac{-4E}{hc}$

$$= \frac{-\left[4\times\left(-3.4\times1.6\times10^{-19}\right)\right]}{6.63\times10^{-34}\times3\times10^{8}} \qquad = \frac{21.76\times10^{-19}\times10^{26}}{19.89} \qquad \therefore R = 1.094\times107/m$$

Ex. 9 Show that Centripetal acceleration of an electron in Bohr's orbit is inversly proporational to 4th power of principal quantum number

Soln Centripetal Acel^n = $\frac{\upsilon^2}{r}$

According to 1st postalates of Bohr's theory

$$\frac{m\upsilon^2}{r} = \frac{1}{4\pi\varepsilon_0}\ \frac{e^2}{r^2} \qquad \frac{\upsilon^2}{r} = \frac{e^2}{4\pi\varepsilon_0 m r^2}$$

But, $r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2}$ $\qquad \therefore \frac{\upsilon^2}{r} = \frac{e^2}{4\pi\varepsilon_0 m\times\frac{\varepsilon_0^2 n^4 h^4}{\pi^2 m^2 e^4}}$ $\qquad \therefore \frac{\upsilon^2}{r} = \frac{\pi m e^6}{4\varepsilon_0^3 n^4 h^4}$

But, π, m, e, h, ε_0 are constants $\quad \therefore \frac{v^2}{r} = \frac{k}{n^4}$ $\qquad \therefore \left[\frac{\upsilon^2}{r} = \frac{1}{n^4}\right]$

Thus, centripetal acceln is inversly peoportional to 4th power of principal quantum no.

Ex 10. Show that frequency of revolution of electron in Bohr's orbit is

$\frac{me^4}{4\varepsilon_0^2 h^3 n^3}$ **OR**

Show that period of revolution of electron in Bohr's orbit is proportional to cube of the principle quantum no.

OR

Show that angular speed of elctron in Bohr's orbit is inversly proportional to cube of principle quantum no.

Soln $\boxed{\text{By 2}^{\text{nd}}\text{ postalates of Bohr's theory}}$

$$m\upsilon r = \frac{nh}{2\pi} \qquad \text{but } \upsilon = r\omega \qquad \therefore mr\omega r = \frac{nh}{2\pi}$$

But, $\omega = 2\pi f$ $\qquad \therefore m2\pi fr^2 = \frac{nh}{2\pi}$ $\qquad \therefore f = \frac{nh}{4\pi^2 m r^2}$

but $\quad r = \frac{\varepsilon_o n^2 h^2}{\pi m e^2}$ $\qquad \therefore f = \frac{nh}{4\pi^2 m\times\frac{\varepsilon_0^2 n^4 h^4}{\pi^2 m^2 e^4}}$ $\qquad \therefore \left[f = \frac{me^4}{4\varepsilon_0^2 n^3 h^3}\right]$

Hence proved

Now, period of revolution of electron is given by period (T) = $\frac{1}{f}$

$$\therefore T = \frac{\frac{1}{me^4}}{4\varepsilon_0{}^2 n^3 h^3} \qquad \therefore T = \frac{4\varepsilon_0{}^2 n^3 h^3}{me^4}$$

Here ε_0 $h, m, \&\ e$ are constants $\quad \therefore T = Kn^3 \qquad \therefore \left[T \propto n^3\right]$

Hence period of revolution of electron is directly proportional to cube of principle quantum no

We know that $\omega = 2\pi f$

$$\therefore \quad \omega = 2\pi \frac{me^4}{4\varepsilon_0{}^2 n^3 h^3}$$

Here $\pi, \varepsilon_0, h, m, \&\ e$ are constants

$$\therefore \quad \omega = \frac{K}{n^3} \qquad \text{ie. } \therefore \left[\omega \propto \frac{1}{n^3}\right]$$

Hence angular speed of electron in Bohr's orbit is inversly proportional to cube of principle quantum no.

Ex 11. Derive an expression for linear momentum of electron in Bohr's orbit

OR

Derive an expression for linear momentum of electron in Bohr's orbit

OR

Show that linear momentum of electron in Bohr's orbit is inverstly proportional to principal quantum no.

Soln :- Consider, an electron of mass 'm' & charge 'e' revolving around the nucleus with velocity v in sircular orbit o radius 'r'

We know that Linear momentum (p) = mv

But, according to 2nd portulates of Bohr's theory

$$\text{mvr} = \frac{\text{nh}}{2\pi} \qquad \therefore \quad vm = \frac{nh}{2\pi r}$$

$$But, \quad r = \frac{\varepsilon_0 h^2 n^2}{\pi me^2} \qquad \therefore \quad mv = \frac{nh}{2\pi \times \frac{\varepsilon_0 n^2 h^2}{\pi me^2}}$$

But, $\quad mv = p$ (Linear momentum)

$$\therefore \quad p = \frac{me^2}{2\varepsilon_0 nh}$$

$$P = mv \quad mv = \frac{me^2}{2 \in_0 nh}$$

$$v = \frac{e^2}{2 \in_0 nh}$$

Here, m, e, ε_0, h are constant

$$\therefore \quad P = K/n \qquad \therefore \quad P \propto \frac{1}{n}$$

Hence, linear momentum is inversly proportional to principle quantum no.

Hence proved