Atomic structure

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(2) Calculation of radius of an orbit →

By Putting the value of v from eqⁿ (3) in eqⁿ (2)

$$m\left(\frac{2\pi Kze^2}{nh}\right) r = \frac{nh}{2\pi}$$

$$r = \frac{n^2h^2}{4\pi^2 m Kze^2}$$

$$\boxed{r = 0.529 \times \frac{n^2}{Z} \ \text{Å}}$$

where Z = atomic no.

n = orbit no.

(3) Calculation of K.E., P.E., T.E. →

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}\frac{Kze^2}{r}$$

$$P.E. = \frac{Kq_1q_2}{r} = \frac{K(ze)(-e)}{r}$$

$$P.E. = -\frac{Kze^2}{r}$$

$$T.E. = K.E. + P.E. = -\frac{1}{2}\frac{Kze^2}{r}$$

$$T.E. = -\frac{1}{2} \frac{Kze^2}{n^2h^2} \times 4\pi^2 mKze^2$$

$$\boxed{\begin{array}{l} T.E. = -2.18 \times 10^{-18} \times \dfrac{z^2}{n^2} \ J/atom \\ \\ T.E. = -13.6 \dfrac{z^2}{n^2} \ eV/atom \end{array}}$$

$$\boxed{T.E. = -K.E. = \frac{P.E.}{2}}$$

(4) Calculation of time taken for one revolution of e^- in an orbit $\longrightarrow$

$$T = \frac{2\pi r}{v}$$

$$r \propto \frac{n^2}{Z} \quad , \quad v \propto \frac{Z}{n}$$

$$\Rightarrow T \propto \frac{n^2}{Z} \times \frac{n}{Z}$$

$$\Rightarrow \boxed{T \propto \frac{n^3}{Z^2}}$$

(5) Calculation of no. of revolution per sec. or frequency of revolution $\longrightarrow$

$$f = \frac{1}{T} \Rightarrow \boxed{f \propto \frac{z^2}{n^3}}$$

(6) Ionisation enthalpy $\longrightarrow$ It is the amount of energy required to remove most loosely bound e^- (outermost e^-)

For H– like species ($H, He^+, Li^{2+}, Be^{3+}$ etc.)

$$\left(n=1 \xrightarrow[\text{I.E}]{} n=\infty\right)$$

$$I.E. = E_{n=\infty} - E_{n=1}$$

$$= 0 - \left(-13.6\,\frac{z^2}{1}\right)$$

$$\boxed{I.E. = 13.6\,z^2 \text{ ev/atom}}$$

Note $\rightarrow$ For H– like species $\Rightarrow$

Ground state $\Rightarrow$ $n = 1$

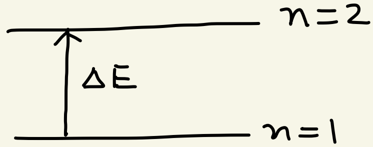
First excited state $\Rightarrow$ $n=2$

Second excited state $\Rightarrow$ $n=3$

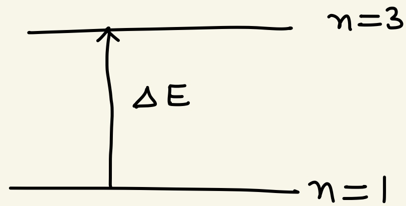
(7) Excitation energy →

For H- like species ⇒

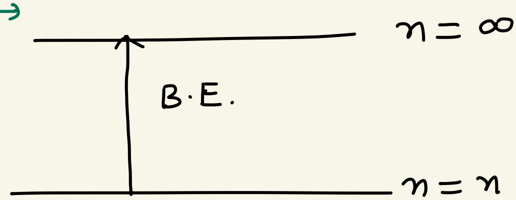
First excitation energy ⇒



Second excitation energy ⇒



(8) Binding energy →



$$B.E. = E_{n=\infty} - E_{n=n}$$

$$= 0 - \left(-13.6 \frac{z^2}{n^2}\right)$$

$$\boxed{B.E. = 13.6 \frac{z^2}{n^2} \text{ ev/atom}}$$

Q. In Bohr's model of the hydrogen atom the ratio between the period of revolution of an electron in the orbit of n = 1 to the period of the revolution of the electron in the orbit n = 2 is -

(A) 1 : 2 (B) 2 : 1 (C) 1 : 4 (D) 1 : 8

$\underline{Sol^n \rightarrow}$ $\dfrac{T_{1,H}}{T_{2,H}} = \dfrac{(1)^3}{(2)^3} = 1:8$

$\underline{Q.}$ 1^{st} excitation potential for the H-like (hypothetical) sample is 24 V. Then :

(A) Ionisation energy of the sample is 36 eV
~~(B)~~ Ionisation energy of the sample is 32 eV
~~(C)~~ Binding energy of 3^{rd} excited state is 2 eV
~~(D)~~ 2^{nd} excitation potential of the sample is $\frac{32 \times 8}{9}$ V

$\underline{Sol^n \rightarrow}$ 1^{st} excitation energy = 24 ev/atom

$$E_2 - E_1 = 24$$

$$-13.6\frac{z^2}{4} + 13.6\frac{z^2}{1} = 24$$

$$13.6\,z^2 = \frac{24 \times 4}{3} = 32$$

$$I.E. = 13.6\,z^2 = 32 \text{ ev/atom}$$

$$B.E. = 13.6\frac{z^2}{n^2} = \frac{32}{(4)^2} = 2 \text{ ev/atom}$$

$$2^{nd} \text{ excitation Potential} = E_3 - E_1$$

$$= -13.6\frac{z^2}{9} + 13.6\frac{z^2}{1}$$

$$= 13.6\,z^2 \times \frac{8}{9} = \frac{32 \times 8}{9} \text{ V}$$

Illustration - 11 *Find the wavelength of radiation required to excite the electron in ground level of Li^{++} (Z = 3) to third energy level. Also find the ionisation energy of Li^{2+}.*

Solⁿ →

$$\Delta E = E_3 - E_1$$

$$= -13.6 \times \frac{9}{9} + 13.6 \times \frac{9}{1}$$

$$= 108.8 \text{ eV}$$

$$108.8 \, e\cancel{V} = \frac{hc}{\lambda} = \frac{1240 \, e\cancel{V} - n\cancel{m}}{\lambda \, (n\cancel{m})}$$

$$\lambda = \frac{1240}{108.8} = 11.397$$

$$\simeq 11.4 \text{ nm}$$

$$\simeq 114 \text{ A}^{\circ}$$

$$\text{I.E.} = 13.6 \times Z^2$$

$$= 13.6 \times 9 = 122.4 \text{ eV/atom}$$

Hydrogen spectrum →

* It is an emission line spectrum.
* H-atom contains only one e⁻ which is Present in 1st orbit. on absorbing energy, this e⁻ may come to some higher energy level.

Now when this e^- comes back to ground state from given excited state, it may do so in one step or in different steps.

These different steps will involve different energies. Thus different lines appear in the H-atom spectrum. These different lines correspond to different wavelengths.

wavelength of these lines can be calculated by following formula ⟶

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = R_H \cdot Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

Where $\bar{\nu}$ = wave no.

λ = wavelength

R_H = Rydberg const.

$= 109{,}700 \ cm^{-1}$

$= 1.097 \times 10^7 \ m^{-1}$

$$\boxed{R_H \simeq \frac{1}{911.5 \ A^\circ}}$$

Z = atomic no.

n_1 = lower energy level

n_2 = higher energy level

Proof →

$$\Delta E = E_{n_2} - E_{n_1}$$

$$= -13.6\frac{Z^2}{n_2^2} + 13.6\frac{Z^2}{n_1^2}$$

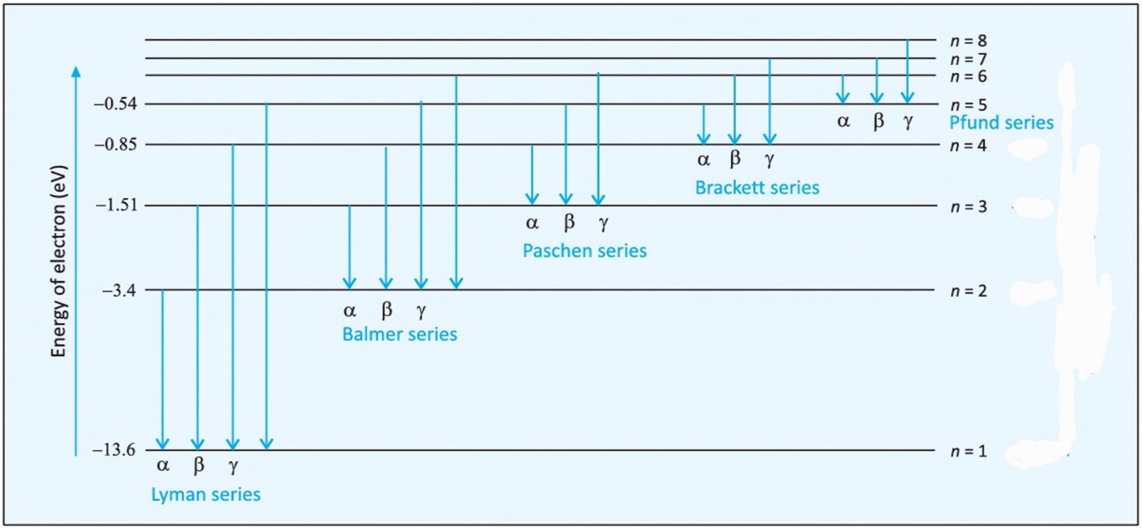
$$\frac{hc}{\lambda} = 13.6\, Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ eV}$$

$$\frac{12400 \text{ eV} - A^\circ}{\lambda\,(A^\circ)} = 13.6\, Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{eV}$$

$$\frac{1}{\lambda} = \frac{13.6}{12400}\, Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

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

Name of Series	n_1	n_2	Region of spectrum In H-atom
1. Lyman	1	2,3,4,- -	U.V.
2. Balmer	2	3,4,5, - -	visible
3. Paschen	3	4,5,6, - -	Infrared
4. Brackett	4	5,6,7, - - -	— " —
5. Pfund	5	6,7,8, - -	— " —
6. Humphry	6	7,8,9, - - -	— " —



Spectral Lines and Energy Levels of Hydrogen atom

Note → (1) Last line of balmer series ($\infty \rightarrow 2$) of H-atom belongs to UV region.

(2) α-line (Ist line) of a series $\Rightarrow$

$$n_2 = n_1 + 1$$

(3) β- line (2nd line) of a series $\Rightarrow$

$$n_2 = n_1 + 2$$

(4) γ- line (3rd line) of a series $\Rightarrow$

$$n_2 = n_1 + 3$$

(5) marginal line (limiting line) $\Rightarrow$ $n_2 = \infty$

(6) Max. λ $\Rightarrow$ Min. ΔE $\Rightarrow$ $n_2 = n_1 + 1$

(7) min. $\lambda \Rightarrow$ Max. $\Delta E \Rightarrow n_2 = \infty$

Q. Calculate the max. wavelength of balmer series for H-atom spectrum?

Sol$^n \rightarrow$

$$\frac{1}{\lambda_{max.}} = R_H \cdot Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$\frac{1}{\lambda_{max.}} = \frac{1}{911.5\ A^\circ} \times 1 \left(\frac{1}{4} - \frac{1}{9} \right)$$

$$\lambda_{max.} = 911.5 \times \frac{36}{5} = 6562.8\ A^\circ$$

Q. In a hydrogen spectrum, for a spectral line wavelength is x cm. If Li^{2+} ion is taken for the same transition then determine wavelength for that spectral line.

Sol$^n \rightarrow$

$$\frac{1}{\lambda} = \frac{1}{x} = R_H \cdot 1 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (1)}$$

$$\frac{1}{\lambda'} = R_H \times 9 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (2)}$$

(1) ÷ (2) $\Rightarrow \lambda' = \frac{x}{9}$ cm.

Q. Calculate the ratio of wave no., wavelength, frequency for β-line of balmer series and marginal line of brackett series of He^+ ion spectrum ?

Sol^n →

$$(\bar{\upsilon})_{\beta,\ Balmer} = R_H \times (2)^2 \left(\frac{1}{4} - \frac{1}{16}\right)$$

$$(\bar{\upsilon})_{Marginal,\ Brackett} = R_H \times (2)^2 \left(\frac{1}{16} - 0\right)$$

$$\frac{(\bar{\upsilon})_{\beta,\ balmer}}{(\bar{\upsilon})_{mar.,\ Brackett}} = 3 : 1$$

$$\frac{(\lambda)_{\beta,\ balmer}}{(\lambda)_{mar.,\ Brackett}} = 1 : 3$$

$$\frac{(\upsilon)_{\beta,\ balmer}}{(\upsilon)_{mar.,\ Brackett}} = 3 : 1$$

Illustration - 12 *Find the energy released (in ergs) when 2.0 gm atom of Hydrogen atoms undergo transition giving spectral line of lowest energy in visible region of its atomic spectra.* $(1\,J = 10^{7}\,erg)$

$n_1 = 2$, $n_2 = 3$, $z = 1$

$$\frac{1}{\lambda} = \frac{1}{911.5\,(A^\circ)} \times 1\left(\frac{1}{4} - \frac{1}{9}\right)$$

$$\lambda = 6562.8\ A^\circ$$

$$\Delta E = \frac{hc}{\lambda} = \frac{12400}{6562.8} = 1.9\ eV/atom$$

1 atom $\longrightarrow$ 1.9 eV

2 mol atom $\longrightarrow$ $1.9 \times 2 \times 6 \times 10^{23}$ eV

$= 22.8 \times 10^{23}$ eV

$= 22.8 \times 10^{23} \times 1.6 \times 10^{-19} \times 10^{7}$ erg

$= 3.648 \times 10^{12}$ erg

Q. If e⁻ is present in 5th bohr orbit then determine the max. no. of spectral lines obtained from different transitions.

Solⁿ → $5 \to 1,\ 4 \to 1,\ 3 \to 1,\ 2 \to 1 \Rightarrow 4$

$5 \rightarrow 2,\ 4 \rightarrow 2,\ 3 \rightarrow 2 \quad \Rightarrow 3$

$5 \rightarrow 3,\ 4 \rightarrow 3 \quad \Rightarrow 2$

$5 \rightarrow 4 \quad \Rightarrow 1$

$$\boxed{\frac{n(n-1)}{2}} \qquad \underline{\underline{10}}$$

Q. If e^- can undergo transition between 7^{th} and 2^{nd} bohr orbits. Then find max. no. of spectral lines in H-atom spectrum?

<u>Sol^n</u> $\rightarrow$

$7 \rightarrow 2,\ 6 \rightarrow 2,\ 5 \rightarrow 2,\ 4 \rightarrow 2,\ 3 \rightarrow 2 \quad \Rightarrow 5$

$7 \rightarrow 3,\ 6 \rightarrow 3,\ 5 \rightarrow 3,\ 4 \rightarrow 3 \quad \Rightarrow 4$

$7 \rightarrow 4,\ 6 \rightarrow 4,\ 5 \rightarrow 4 \quad \Rightarrow 3$

$7 \rightarrow 5,\ 6 \rightarrow 5 \quad \Rightarrow 2$

$7 \rightarrow 6 \quad \Rightarrow 1$

$\underline{15}$

$$\boxed{\frac{(n_2-n_1)(n_2-n_1+1)}{2}}$$

Limitations of bohr's atomic model →

(1) This model explains the behaviour of only single e^- system. Ex. H, He^+, Li^{2+}, Be^{3+} etc.

(2) No justification was given for principle of quantisation of angular momentum.

(3) This model could not explain stark effect and zeeman effect.

Stark effect → splitting of spectral lines under the influence of electric field.

Zeeman effect → splitting of spectral lines under the influence of magnetic field.

(4) This model is against the heisenberg's uncertainity principle.

(5) It was suggested by De-broglie that a small moving particle like e^- has particle as well as wave nature. but Bohr assumed e^- as a particle only.

(6) It could not explain the ability of atoms to form molecules by chemical bonds.

(7) when spectrum of H-atom is studied by powerful spectroscope of high resolving power,

then it is found that each single line is made up of group of fine lines. The presence of these fine lines in the spectrum of H-atom is called fine spectrum of H-atom.

This model could not explain fine spectrum of H-atom.

Dual behaviour of matter →

De broglie suggested that each small moving particle (e^-, p^+, n, light, α etc.) has the properties of a wave also.

wavelength of small moving particles can be calculated by →

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

where h = Planck const.

m = mass of particle

v = velocity of particle

p = momentum of particle

This expression is valid for photon also.

In case of photon, v = speed of light (c)

Proof $\rightarrow$

$$\text{Light} \swarrow \text{Particle nature (characterised by momentum)} \quad \searrow \text{wave nature (characterised by wavelength)}$$

$$E = mc^2 \quad \text{——— (1)}$$

$$E = h\nu = \frac{hc}{\lambda} \quad \text{——— (2)}$$

$$mc^{\cancel{2}} = \frac{h\cancel{c}}{\lambda}$$

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

For other small moving Particles, $\lambda = \frac{h}{mv}$

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}\frac{(mv)^2}{m}$$

$$\Rightarrow \quad p^2 = 2m\,K.E.$$

$$p = \sqrt{2m\,K.E.}$$

$$\lambda = \frac{h}{\sqrt{2m\,K.E.}}$$

If a charged Particle (q) is accelerated from rest by a Potential difference of V_0 – volts then $K.E. = q \times V$

$$\lambda = \frac{h}{\sqrt{2mqV_0}}$$

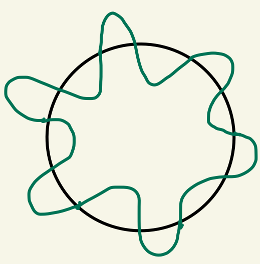
$$\boxed{\lambda = \frac{h}{mV} = \frac{h}{p} = \frac{h}{\sqrt{2m\,K.E.}} = \frac{h}{\sqrt{2mqV_0}}}$$

$$\lambda_{e^-} = \frac{12.27}{\sqrt{V_0}}\ \mathring{A}$$

$$\lambda_{p^+} = \frac{0.286}{\sqrt{V_0}}\ \mathring{A}$$

$$\lambda_{\alpha} = \frac{0.101}{\sqrt{V_0}}\ \mathring{A}$$

Derivation of Bohr's Postulate of angular momentum →



*
$$\boxed{2\pi r = n\lambda}$$

$$2\pi r = n \times \frac{h}{mv}$$

$$\boxed{mvr = \frac{nh}{2\pi}}$$

where n = no. of waves in an orbit
or
orbit no.
or
Principal Q. no.

Q. Find the no. of waves made by a bohr e^- in one complete revolution in its third orbit ?

Ans. = 3

Q. Calculate the de-broglie wavelength of an e^- that has been accelerated from rest through a potential difference of 1 kv ?

Sol^n→

$$\lambda_{e^-} = \frac{12.27}{\sqrt{1000}} \text{ A}^\circ$$

61. A body of mass x kg is moving with a velocity of $100 ms^{-1}$. Its de-Broglie wavelength is $6.62 \times 10^{-35} m$. Hence, x is: $(h = 6.62 \times 10^{-34} Js)$

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

$$6.62 \times 10^{-35} = \frac{6.62 \times 10^{-34}}{x \times 100}$$

$$x = 0.1 \text{ kg}$$

Homework

DTS-1 to 11
Q.8-16,21-23,25,27,29,30,32,34,35,37,39-44,46,53,57,61, 64,65,70,76-78,89,90,94,95,98,102,112,114-116,118,124, 131-134,139

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Q.3-5,10,11,15-17,19,21-24,26-28,30,31,33,35