

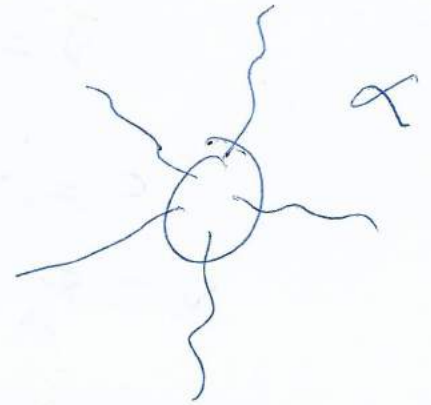
# Atomic structure

## Quantum theory of radiation

 or particle



a photon (a quantum)



- ~~coll~~ plural  $\rightarrow$  quanta (many photons)

$E = h\nu \rightarrow$  frequency of radiation  
           ↓  
 Planck's constant

$$\nu = \frac{c}{\lambda} \Rightarrow E = \frac{hc}{\lambda}$$

↓  
wavelength

$$E = h\nu, 2h\nu, 3h\nu, \dots, nh\nu$$

→ Quantisation of Energy

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = 6.626 \times 10^{-27} \text{ erg}\cdot\text{s}$$

**Example 2.** Calculate the frequency and wave number of radiation with wavelength 480 nm.

**Solution:** Given,

$$\lambda = 480 \text{ nm} = 480 \times 10^{-9} \text{ m} \quad [\because 1 \text{ nm} = 10^{-9} \text{ m}]$$

$$c = 3 \times 10^8 \text{ m/sec}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{480 \times 10^{-9} \text{ m}} = 6.25 \times 10^{14} \text{ s}^{-1}$$

$$= 6.25 \times 10^{14} \text{ Hz}$$

**Example 3.** Calculate the energy associated with photon of light having a wavelength 6000 Å. [ $h = 6.624 \times 10^{-27} \text{ erg-sec.}$ ]

**Solution:** We know that,  $E = h\nu = h \cdot \frac{c}{\lambda}$

$$h = 6.624 \times 10^{-27} \text{ erg-sec; } c = 3 \times 10^{10} \text{ cm/sec;}$$

$$\lambda = 6000 \text{ Å} = 6000 \times 10^{-8} \text{ cm}$$

$$\text{So, } E = \frac{(6.624 \times 10^{-27}) \times (3 \times 10^{10})}{6 \times 10^{-5}} = 3.312 \times 10^{-12} \text{ erg.}$$

**Example 4.** Which has a higher energy, a photon of violet light with wavelength 4000 Å or a photon of red light with wavelength 7000 Å? [ $h = 6.62 \times 10^{-34} \text{ Js}$ ]

**Solution:** We know that,  $E = h\nu = h \cdot \frac{c}{\lambda}$

$$\text{Given, } h = 6.62 \times 10^{-34} \text{ Js, } c = 3 \times 10^8 \text{ ms}^{-1}$$

For a photon of violet light,

$$\lambda = 4000 \text{ Å} = 4000 \times 10^{-10} \text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{4 \times 10^{-7}} = 4.96 \times 10^{-19} \text{ J}$$

For a photon of red light,

$$\lambda = 7000 \text{ Å} = 7000 \times 10^{-10} \text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{7000 \times 10^{-10}} = 2.83 \times 10^{-19} \text{ J}$$

Hence, photon of violet light has higher energy than the photon of red light.

**Example 5.** What is the ratio between the energies of two radiations one with a wavelength of 6000 Å and other with 2000 Å?

**Solution:**  $\lambda_1 = 6000 \text{ Å}$  and  $\lambda_2 = 2000 \text{ Å}$

$$E_1 = h \cdot \frac{c}{\lambda_1} \text{ and } E_2 = h \cdot \frac{c}{\lambda_2}$$

$$\text{Ratio, } \frac{E_1}{E_2} = \frac{h \cdot c}{\lambda_1} \times \frac{\lambda_2}{h \cdot c} = \frac{\lambda_2}{\lambda_1} = \frac{2000}{6000} = \frac{1}{3}$$

$$\text{or } E_2 = 3E_1$$

**Example 6.** Calculate the wavelength, wave number and frequency of photon having an energy equal to three electron volt. ( $h = 6.62 \times 10^{-27} \text{ erg-sec.}$ )

**Solution:** We know that,

$$E = h \cdot \nu$$

$$\nu = \frac{E}{h} \quad (1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg})$$

$$= \frac{3 \times (1.602 \times 10^{-12})}{6.62 \times 10^{-27}}$$

$$= 7.26 \times 10^{14} \text{ s}^{-1}$$

$$= 7.26 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10}}{7.26 \times 10^{14}} = 4.132 \times 10^{-5} \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{4.132 \times 10^{-5}} = 2.42 \times 10^4 \text{ cm}^{-1}$$

**Example 7.** Calculate the energy in kilocalorie per mol of the photons of an electromagnetic radiation of wavelength 7600 Å.

**Solution:**  $\lambda = 7600 \text{ Å} = 7600 \times 10^{-8} \text{ cm}$

$$c = 3 \times 10^{10} \text{ cm s}^{-1}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{7600 \times 10^{-8}} = 3.947 \times 10^{14} \text{ s}^{-1}$$

$$\text{Energy of one photon} = h\nu = 6.62 \times 10^{-27} \times 3.947 \times 10^{14}$$

$$= 2.61 \times 10^{-12} \text{ erg}$$

$$\text{Energy of one mole of photons} = 2.61 \times 10^{-12} \times 6.02 \times 10^{23}$$

$$= 15.71 \times 10^{11} \text{ erg}$$

Energy of one mole of photons in kilocalorie

$$= \frac{15.71 \times 10^{11}}{4.185 \times 10^{10}} [1 \text{ kcal} = 4.185 \times 10^{10} \text{ erg}]$$

$$= 37.538 \text{ kcal per mol}$$

**Example 8.** Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy in  $\text{kJ mol}^{-1}$ ,  $h = 6.6256 \times 10^{-34} \text{ Js}$ .

**Solution:**  $\lambda = 242 \text{ nm} = 242 \times 10^{-9} \text{ m}$

$$c = 3 \times 10^8 \text{ ms}^{-1}$$

$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.6256 \times 10^{-34} \times \frac{3 \times 10^8}{242 \times 10^{-9}}$$

$$= 0.082 \times 10^{-17} \text{ J} = 0.082 \times 10^{-20} \text{ kJ}$$

$$\text{Energy per mole for ionisation} = 0.082 \times 10^{-20} \times 6.02 \times 10^{23}$$

$$= 493.6 \text{ kJ mol}^{-1}$$

**Example 9.** How many photons of light having a wavelength 4000 Å are necessary to provide 1.00 J of energy?

**Solution:** Energy of one photon

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

$$= \frac{(6.62 \times 10^{-34}) (3.0 \times 10^8)}{4000 \times 10^{-10}}$$

$$= 4.965 \times 10^{-19} \text{ J}$$

$$\text{Number of photons} = \frac{1.00}{4.965 \times 10^{-19}} = 2.01 \times 10^{18}$$



$$\boxed{1 \text{ eV} = 10^{-7} \text{ J}} \rightarrow \text{Energy}$$

$\downarrow$  CGS                       $\downarrow$  SI

Ex. 2       $E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$

$$\bar{\nu} = \frac{1}{\lambda} \text{ (wave number)}$$

$$c = \nu\lambda$$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{480 \times 10^{-9} \text{ m}} = 6.25 \times 10^{14} \text{ s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{480} \text{ nm}^{-1}$$

Ex. 3       $E = \frac{hc}{\lambda} = \frac{6.624 \times 10^{-27} \times 3 \times 10^{10} \text{ eV}}{6000 \times 10^{-8}} \quad \text{CGS}$

$$= 3.312 \times 10^{-12} \text{ eV}$$

Ex. 4.       $\boxed{1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}}$        $1 \text{ eV} = 10^{-7} \text{ J}$

$\boxed{\text{CGS}}$        $1 \text{ J} = 10^7 \text{ eV}$

$$E = h\nu$$

$$3 \times 1.6 \times 10^{-19} \text{ J} = 6.62 \times 10^{-27} \times \nu$$

$\times 10^7$

$$\nu = 7.26 \times 10^{14} \text{ Hz}$$

$$E = \frac{hc}{\lambda}$$

$$(cm) \quad \lambda = \frac{hc}{E} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{3 \times 1.6 \times 10^{-19} \times 10^7} \text{ cm.}$$

$$= 4.132 \times 10^5 \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} = 2.42 \times 10^4 \text{ cm}^{-1}$$

Ex 7

$$\boxed{1 \text{ cal} = 4.184 \text{ J}}$$

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J-s} \times 3 \times 10^8 \text{ m/s}}{7600 \times 10^{-10}} \text{ J}$$

$$E (\text{Kcal/mol}) = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times N_A}{7600 \times 10^{-10} \times \frac{4.184 \times 10^3}{\text{cal} \cdot \text{Kcal}}}$$

$$= 37.538 \text{ Kcal/mol}$$

Ex 8

$$E = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8 \times N_A}{242 \times 10^{-9} \times 10^3}$$

Ex 9

$$\underset{\substack{\uparrow \\ \text{photons}}}{n} \times h\nu = 1 \text{ J} = n \frac{hc}{\lambda}$$

$$n \times \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} = 1 \Rightarrow n = 2.01 \times 10^{18}$$



**Example 10.** Find the number of quanta of radiations of frequency  $4.67 \times 10^{13} \text{ s}^{-1}$ , that must be absorbed in order to melt 5 g of ice. The energy required to melt 1 g of ice is 333 J.

**Solution:** Energy required to melt 5 g of ice  
 $= 5 \times 333 = 1665 \text{ J}$

Energy associated with one quantum  
 $= h\nu = (6.62 \times 10^{-34}) \times (4.67 \times 10^{13})$   
 $= 30.91 \times 10^{-21} \text{ J}$

Number of quanta required to melt 5 g of ice  
 $= \frac{1665}{30.91 \times 10^{-21}} = 53.8 \times 10^{21} = 5.38 \times 10^{22}$

**Example 11.** Calculate the wavelength of the spectral line, when the electron in the hydrogen atom undergoes a transition from the energy level 4 to energy level 2.

**Solution:** According to Rydberg equation,

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

$R = 109678 \text{ cm}^{-1}$ ;  $x = 2$ ;  $y = 4$

$$\frac{1}{\lambda} = 109678 \left[ \frac{1}{4} - \frac{1}{16} \right]$$

$$= 109678 \times \frac{3}{16}$$

On solving,  $\lambda = 486 \text{ nm}$

**Example 12.** A bulb emits light of wavelength  $\lambda = 4500 \text{ Å}$ . The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?

**Solution:** Energy emitted per second by the bulb

$$= 150 \times \frac{8}{100} \text{ J}$$

$$\text{Energy of 1 photon} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}}$$

$$= 4.42 \times 10^{-19} \text{ joule}$$

Let  $n$  photons be evolved per second.

$$\therefore n \times 4.42 \times 10^{-19} = 150 \times \frac{8}{100}$$

$$n = 27.2 \times 10^{18}$$

**Example 13.** A near ultraviolet photon of 300 nm is absorbed by a gas and then remitted as two photons. One photon is red with wavelength of 760 nm. What would be the wave number of the second photon?

**Solution:**

Energy absorbed = Sum of energy of two quanta

$$\frac{hc}{300 \times 10^{-9}} = \frac{hc}{760 \times 10^{-9}} + \frac{hc}{\lambda \times 10^{-9}}$$

On solving, we get,

$$\bar{\nu} \text{ (wave number)} = \frac{1}{\lambda} = 2.02 \times 10^{-3} \text{ m}^{-1}$$

**Example 14.** Calculate the wavelength of the radiation which would cause the photodissociation of chlorine molecule if the Cl—Cl bond energy is  $243 \text{ kJ mol}^{-1}$ .

**Solution:** Energy required to break one Cl—Cl bond  
 $= \frac{\text{Bond energy per mole}}{\text{Avogadro's number}}$

$$= \frac{243}{6.023 \times 10^{23}} \text{ kJ} = \frac{243 \times 10^3}{6.023 \times 10^{23}} \text{ J}$$

Let the wavelength of the photon to cause rupture of one Cl—Cl bond be  $\lambda$ .

$$\text{We know that, } \lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{243 \times 10^3}$$

$$= 4.90 \times 10^{-7} \text{ m} = 490 \text{ nm}$$

**Example 15.** How many moles of photon would contain sufficient energy to raise the temperature of 225 g of water  $21^\circ\text{C}$  to  $96^\circ\text{C}$ ? Specific heat of water is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$  and frequency of light radiation used is  $2.45 \times 10^9 \text{ s}^{-1}$ .

**Solution:** Energy associated with one mole of photons  
 $= N_0 \times h \times \nu$   
 $= 6.02 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.45 \times 10^9$   
 $= 97.727 \times 10^{-2} \text{ J mol}^{-1}$

Energy required to raise the temperature of 225 g of water by  $75^\circ\text{C} = m \times s \times t = 225 \times 4.18 \times 75 = 70537.5 \text{ J}$

Hence, number of moles of photons required

$$= \frac{mst}{N_0 h \nu} = \frac{70537.5}{97.727 \times 10^{-2}} = 7.22 \times 10^4 \text{ mol}$$

**Example 16.** During photosynthesis, chlorophyll absorbs light of wavelength 440 nm and emits light of wavelength 670 nm. What is the energy available for photosynthesis from the absorption-emission of a mole of photons?

$$\text{Solution: } \Delta E = \left[ \frac{Nhc}{\lambda} \right]_{\text{absorbed}} - \left[ \frac{Nhc}{\lambda} \right]_{\text{evolved}}$$

$$= Nhc \left[ \frac{1}{\lambda_{\text{absorbed}}} - \frac{1}{\lambda_{\text{evolved}}} \right]$$

$$= 6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times$$

$$3 \times 10^8 \left[ \frac{1}{440 \times 10^{-9}} - \frac{1}{670 \times 10^{-9}} \right]$$

$$= 0.1197 [2.272 \times 10^6 - 1.492 \times 10^6]$$

$$= 0.0933 \times 10^6 \text{ J/mol} = 93.3 \text{ kJ/mol}$$

**Example 17.** Photochromic sunglasses, which darken when exposed to light, contain a small amount of colourless  $\text{AgCl(s)}$  embedded in the glass. When irradiated with light, metallic silver atoms are produced and the glass darkens.



Escape of chlorine atoms is prevented by the rigid structure of the glass and the reaction therefore, reverses as soon as the light is removed. If  $310 \text{ kJ/mol}$  of energy is required to make the reaction proceed, what wavelength of light is necessary?

Ex 10  $E = h\nu$

$$n \times 6.62 \times 10^{-34} \times 4.67 \times 10^{13} = 0.5 \times 333$$

$$n = 5.38 \times 10^{22}$$

Ex 12  $150 \text{ J/s} \times \frac{8}{100} = n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}} \text{ J}$

$$n = 27.2 \times 10^{18}$$

Ex 13  $\frac{hc}{300} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$

$$\frac{1}{300} = \frac{1}{760} + \frac{1}{\lambda_2}$$

$$\frac{1}{\lambda_2} = \frac{1}{300} - \frac{1}{760}$$

$$= \left( \frac{1}{300 \times 10^{-9}} - \frac{1}{760 \times 10^{-9}} \right) \text{ m}^{-1}$$

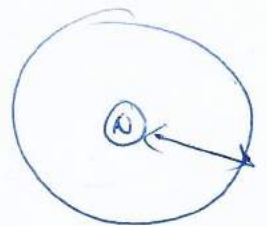
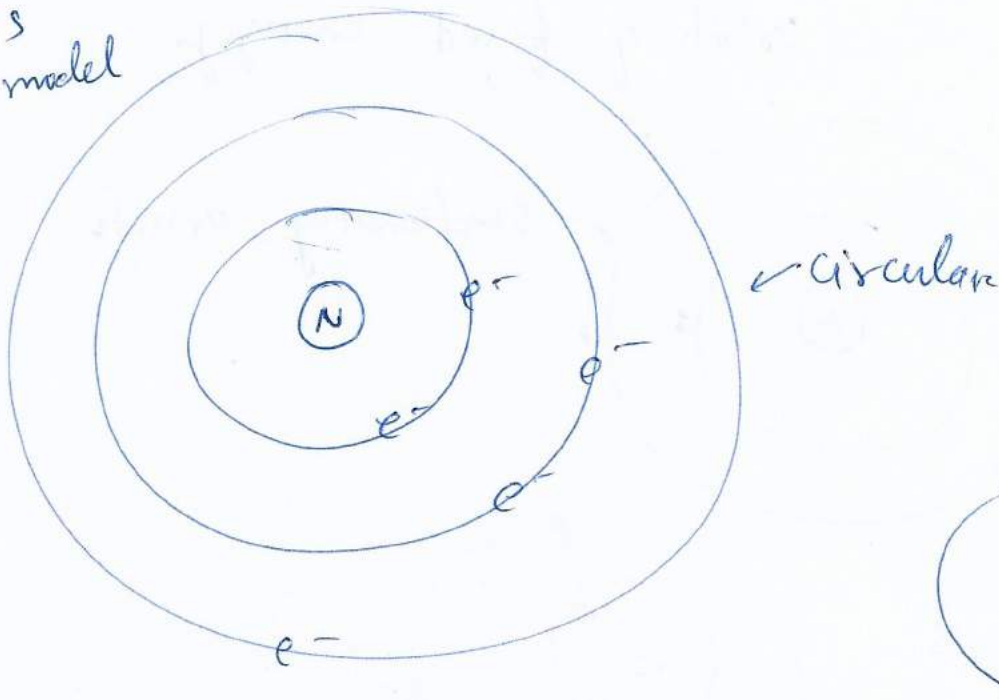
$$= 2.02 \times 10^3 \text{ m}^{-1}$$



# Bohr's Atomic Model

Postulates  
of Bohr's model

→



→ The  $e^-$  can revolve only in those orbits in which its angular momentum is an integral multiple of  $h/2\pi$

momentum =  $mv$



angular momentum  
=  $mvr$

$r \rightarrow$   
radius  
of  
circular  
orbit

$$mvr = n \frac{h}{2\pi}$$

$m \rightarrow$  mass of  $e^-$   
 $v \rightarrow$  velocity of  $e^-$

$n = 1, 2, 3, \dots$   
↳ orbit no.

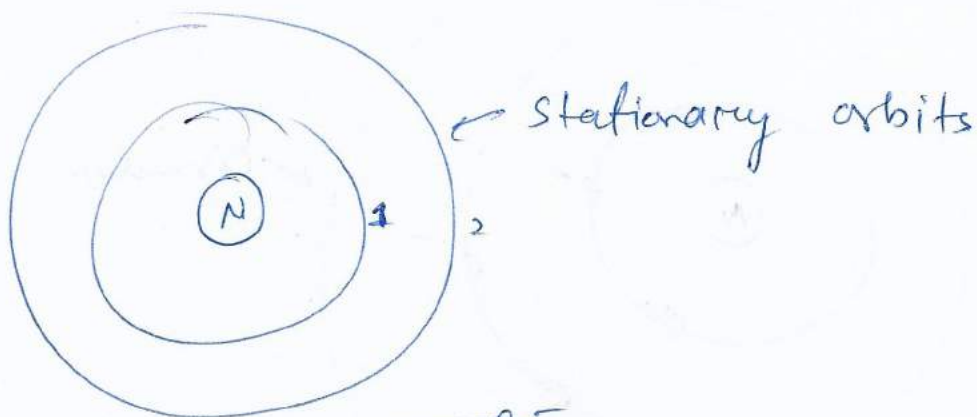
integral values

$$mvr = \frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \dots, n \frac{h}{2\pi}$$

→ Quantisation of angular momentum  
or angular momentum is quantised

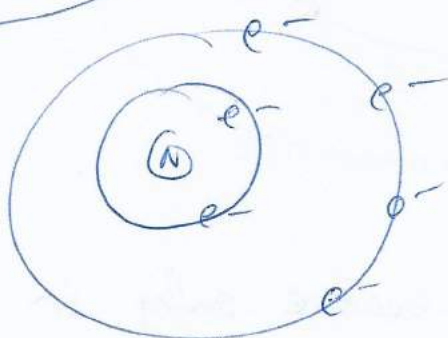
→ Stationary orbits

orbits of fixed energy



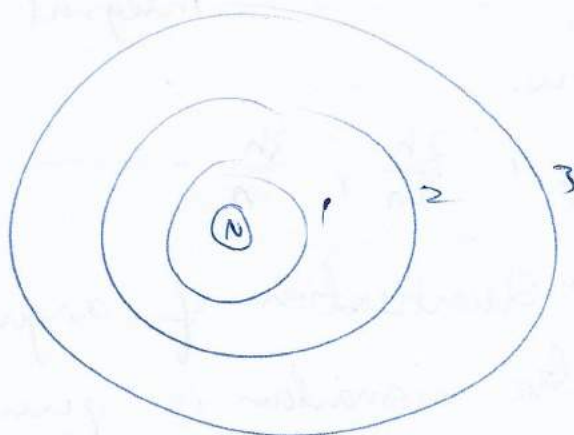
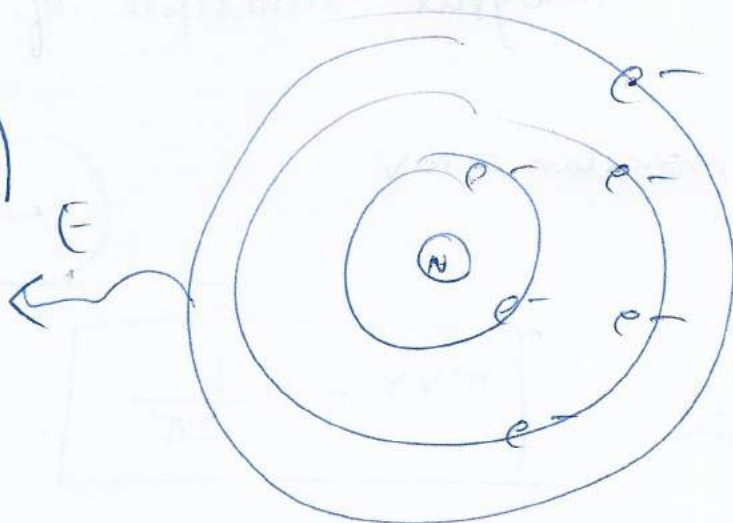
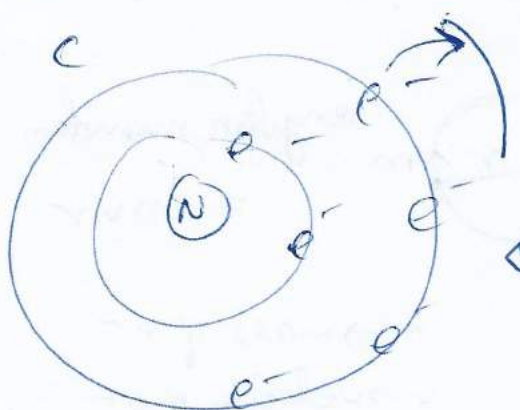
C-6

2, 4



Ground state

Excited state



$$E_1 < E_2 < E_3 \dots$$

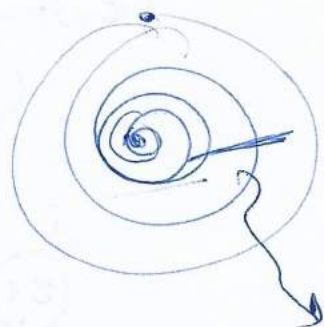
$$E_2 - E_1 > E_3 - E_2$$

$$> E_4 - E_3 \dots$$



→ The energy is absorbed or emitted only when  $e^-$  moves from one stationary orbit into another stationary orbit

→ The  $e^-$  in stationary orbits do not radiate energy



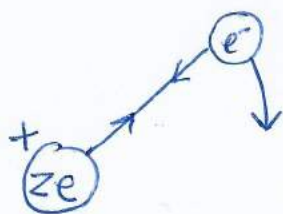
H-atom or H like atoms

Radii of orbits

H atom

$z \rightarrow$  atomic NO.  
= No. of protons

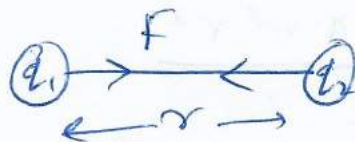
$z$



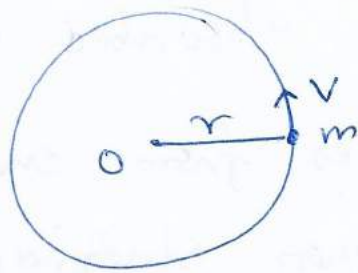
Each proton has

a charge =  $+1.602 \times 10^{-19} \text{ C}$   
=  $e$

Electrostatic force =  $\frac{k q_1 q_2}{r^2}$



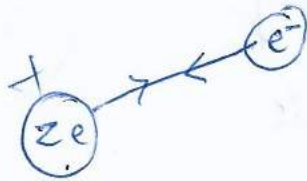
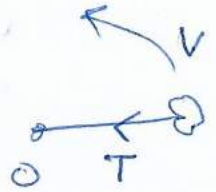
$k = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$



Circular motion

$$\text{Centripetal force} = \frac{mv^2}{r}$$

( $F_c$ )



$$F_c = \frac{kq_1q_2}{r^2} = \frac{mv^2}{r}$$

$$q_1 = ze, \quad q_2 = -e$$

$$F_c = \frac{-kze^2}{r^2}$$

force is attractive

$$\frac{kze^2}{r^2} = \frac{mv^2}{r}$$

$$\Rightarrow r = \frac{kze^2}{mv^2}$$

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

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

$$\Rightarrow r = \left(\frac{n^2}{Z}\right) \frac{h^2}{4\pi^2 m k e^2}$$



$$r = \frac{n^2}{Z} \left[ \frac{(6.626 \times 10^{-34})^2}{4 \times (3.14)^2 \times (9.1 \times 10^{-31}) \times (9 \times 10^9) \times (1.602 \times 10^{-19})^2} \right]$$

$$r_n = \frac{n^2}{Z} \times 0.529 \text{ \AA} \rightarrow \text{for H \& H like atoms}$$

H-atom ( $z=1$ )

$$r_1 = 0.529 \text{ \AA}$$

$$r_2 = 4 \times 0.529 \text{ \AA}$$

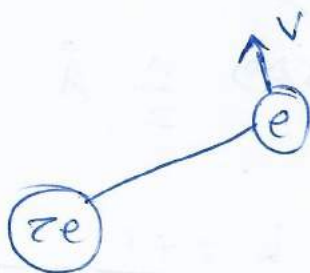
He<sup>+</sup>

$$r_2 = \frac{z^2}{Z} \times 0.529$$

$$= 2 \times 0.529$$

~~3~~

Energy of an e<sup>-</sup>



Energy = Kinetic energy + Potential energy  
(E) (KE) (PE)

$$KE = \frac{1}{2} mv^2, \quad \frac{(mv^2)}{r} = \frac{kze^2}{r^2}$$

$$\Rightarrow mv^2 = \frac{kze^2}{r}$$

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

$$P.E. = \frac{q_1 q_2}{r} = \frac{kq_1 q_2}{r}$$

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

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

$e^-$  is bound to the nucleus

$$E = K + P = \frac{1}{2} \frac{kze^2}{r} - \frac{kze^2}{r}$$

$\underbrace{\hspace{1cm}}_K \qquad \underbrace{\hspace{1cm}}_{PE}$

$$= -\frac{1}{2} \frac{kze^2}{r}$$

$$\boxed{K.E. = -\frac{1}{2} P.E. = -E}$$

$$E = -\frac{1}{2} \frac{kze^2}{r}$$

$$r_n = 0.529 \frac{n^2}{Z} \text{ \AA}$$

$$E_n = -\frac{1}{2} \frac{kze^2}{0.529 \frac{n^2}{Z} \times 10^{-10}} \quad J$$

$$= -\frac{Z^2}{n^2} \left( \frac{-9 \times 10^9 \times (1.6 \times 10^{-19})^2}{0.529 \times 10^{-10}} \right)$$

$$\boxed{E_n = -\frac{Z^2}{n^2} \times 2.18 \times 10^{-18} \text{ J/atom}}$$

for H & H like atoms



$$E_n = \frac{-Z^2}{n^2} \times 13.6 \text{ eV/atom}$$

for H atom ( $Z=1$ )

$$E_n = -13.6/n^2 \text{ eV/atom}$$

$$E_1 = -13.6 \text{ eV} \quad \leftarrow e^- \text{ is bound to the nucleus}$$

$$E_2 = -13.6/4 \text{ eV}$$

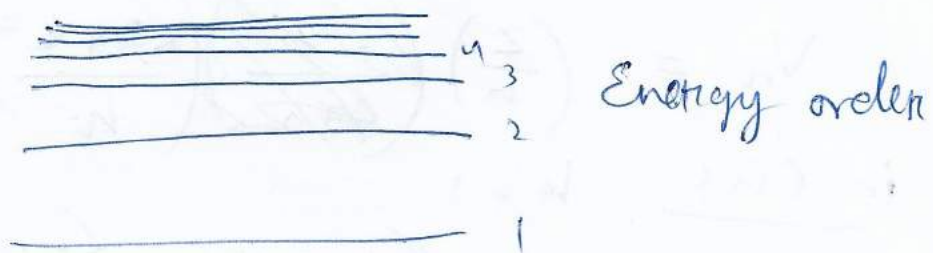
$$E_3 = -13.6/9 \text{ eV}$$

$$E_2 - E_1 = 13.6 \left(1 - \frac{1}{4}\right) = \frac{3}{4} \times 13.6 \text{ eV}$$

$$E_3 - E_2 = 13.6 \left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36} \times 13.6 \text{ eV} \quad \leftarrow$$

$$E_4 - E_3 = 13.6 \left(\frac{1}{9} - \frac{1}{16}\right) = \frac{7}{144} \times 13.6 \text{ eV} \quad \leftarrow$$

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \dots$$



$n = \infty$

(N)

$$E_{\infty} = \frac{-13.6 \times Z^2}{(\infty)^2} \rightarrow 0$$

→ as  $n \uparrow$   $E_n \downarrow$

$$\boxed{E_n = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}}$$

also  $n = 1, 2, 3, \dots$

⇒ Energy is quantised

Velocity of  $e^-$

$$\frac{mv^2}{r} = \frac{kze^2}{r^2} \quad \text{--- (i)}$$

$$\underline{mvr} = \frac{nh}{2\pi} \quad \text{--- (ii)}$$

$$k = 9 \times 10^9 \text{ Nm}^2/\text{C}^2 \rightarrow \text{SI}$$

$$\underline{\text{(i)}} \quad \frac{mv^2}{r} = \frac{kze^2}{r^2}$$

$$\boxed{\begin{array}{l} \text{In CGS} \\ k = 1 \end{array}}$$

$$v(mvr) = kze^2$$

$$v\left(\frac{nh}{2\pi}\right) = kze^2$$

$$V_n = \left(\frac{Z}{n}\right) \left(\frac{kze^2}{2\pi h}\right) \left(\frac{k2\pi e^2}{h}\right)$$

in CGS  $k = 1$

$$V_n = \frac{Z}{n} \times \left( \frac{1 \times 2 \times 3.14 \times (1.6 \times 10^{-19})^2}{6.62 \times 10^{-27} \text{ ergs}} \right)$$

$$\boxed{V_n = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/s}}$$



## Orbital frequency ( $\nu_0$ )

No. of revolutions per second by an  $e^-$  in an orbit is called orbital frequency.

$$v \rightarrow v \text{ m/s}$$

$$1 \text{ rev} = 2\pi r$$

$$2\pi r \rightarrow 1 \text{ rev}$$

$$\text{In 1s } v \text{ m} \rightarrow \frac{v}{2\pi r} \text{ rev/s}$$

$$= \frac{\left(\frac{Z}{n}\right) \left(\frac{2\pi e^2}{h}\right) \leftarrow v}{2\pi r}$$

$$= \frac{ze^2}{nh r_n}$$

$$r_n = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$\nu_0 = \frac{ze^2}{nh \times 0.529 \times \frac{n^2}{Z} \times 10^{-10}} \text{ s}^{-1}$$

$$= \frac{z^2}{n^3} \left( \frac{e^2}{h \times 0.529 \times 10^{-10}} \right)$$

$$\boxed{\nu_0 = \frac{z^2}{n^3} \times 6.66 \times 10^{15} \text{ s}^{-1}} \rightarrow \text{H \& H-like atoms}$$

Time period

$$T = \frac{1}{\nu_0} \quad \text{or} \quad \nu_0 = \frac{1}{T}$$

$$T = \frac{n^3}{Z^2} \times 1.5 \times 10^{-16} \text{ s}$$

time taken for one revolution.

$$\begin{aligned} r_n &= 0.529 \times \frac{n^2}{Z} \text{ \AA} \\ E_n &= -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom} \end{aligned} \quad \left. \vphantom{\begin{aligned} r_n &= 0.529 \times \frac{n^2}{Z} \text{ \AA} \\ E_n &= -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom} \end{aligned}} \right\} \text{Remember}$$

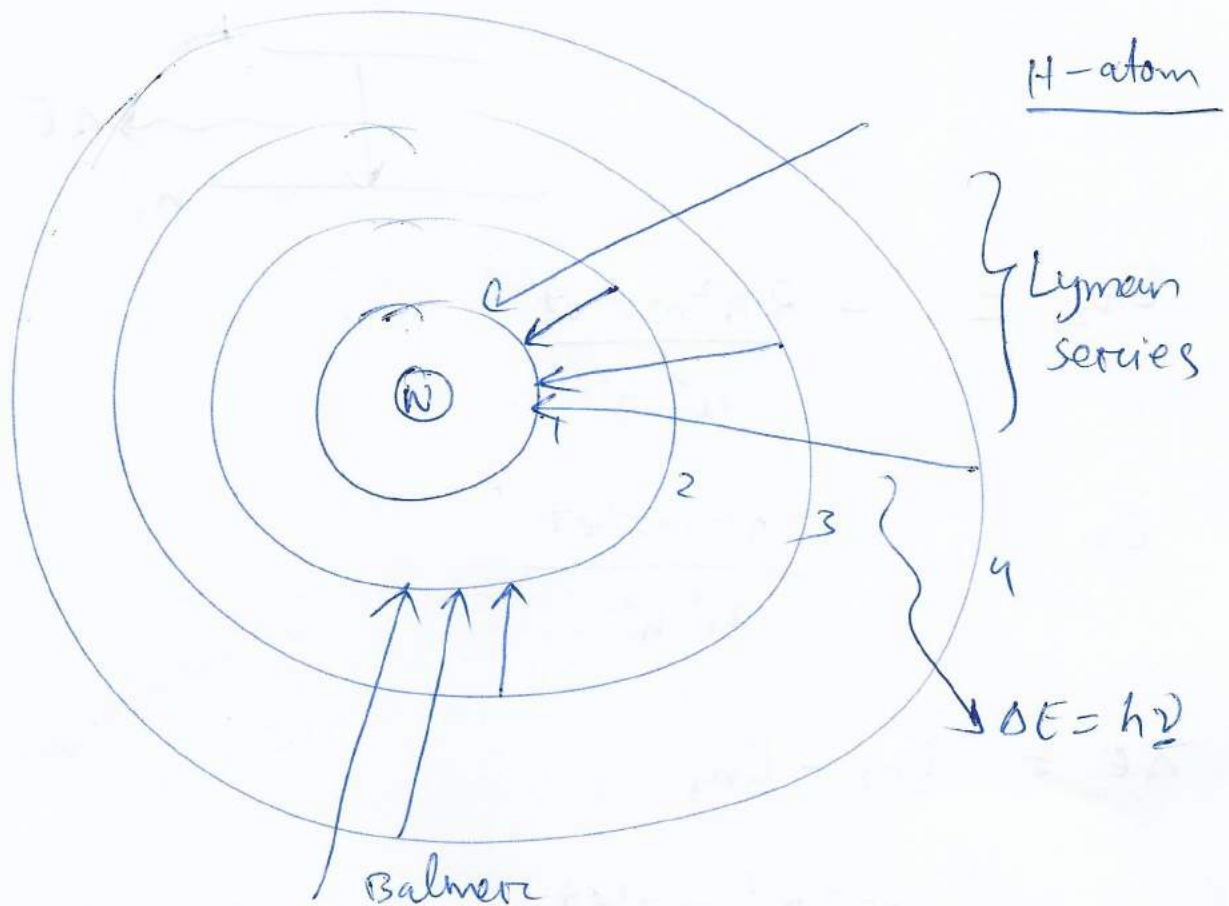
$$v_n = \frac{Z}{n} \times \underbrace{2.188 \times 10^8 \text{ cm/s}}_{v_1} = \frac{Z}{n} \times v_1$$

$$\nu_0 = \frac{Z^2}{n^3} \times \underbrace{6.66 \times 10^{15} \text{ s}^{-1}}_{\nu_{01}} = \frac{Z^2}{n^3} \nu_{01}$$

$$T = \frac{n^3}{Z^2} \times \underbrace{1.5 \times 10^{-16} \text{ s}}_{T_1} = \frac{n^3}{Z^2} T_1$$



# Interpretation of Hydrogen spectrum



## Series

Starting from  $n_2$  to  $n_1$

Lyman  $n = 2, 3, 4, \dots \infty$  1

Balmer  $n = 3, 4, 5, \dots \infty$  2

Paschen  $n = 4, 5, 6, \dots \infty$  3

Brackett  $n = 5, 6, 7, \dots \infty$  4

Pfund  $n = 6, 7, 8, \dots \infty$  5

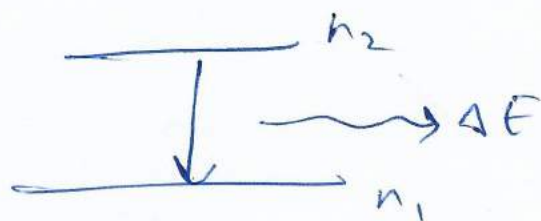
Silent

$\Delta E$

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

→ line spectrum of H

# Rydberg equation



$$E_{n_2} = - \frac{2\pi^2 m z^2 e^4}{n_2^2 h^2}$$

$$E_{n_1} = - \frac{2\pi^2 m z^2 e^4}{n_1^2 h^2}$$

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

$$= - \frac{2\pi^2 m z^2 e^4}{n_2^2 h^2} - \left( - \frac{2\pi^2 m z^2 e^4}{n_1^2 h^2} \right)$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 m z^2 e^4}{h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} = z^2 \left( \frac{2\pi^2 m e^4}{h^3 c} \right) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \bar{\nu} = \underbrace{z^2 \left( \frac{2\pi^2 m e^4}{h^3 c} \right)}_{\text{Rydberg constant}} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 109743 \text{ cm}^{-1}$$

$$\boxed{\bar{\nu} = R z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)} \rightarrow \text{H \& H like atoms}$$

## First line of a series

Lyman

first line

$$2 \rightarrow 1$$

$$2^{\text{nd}} \text{ line} = 3 \rightarrow 1$$

$\vdots$

$$\text{last line} = \infty \rightarrow 1$$

(series limit)

Balmer series

first line  $3 \rightarrow 2$

}

For H atom

Series limit of Lyman series

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

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

$$\begin{array}{c} n_2 \quad \infty \\ \downarrow \\ n_1 \quad 1 \end{array}$$

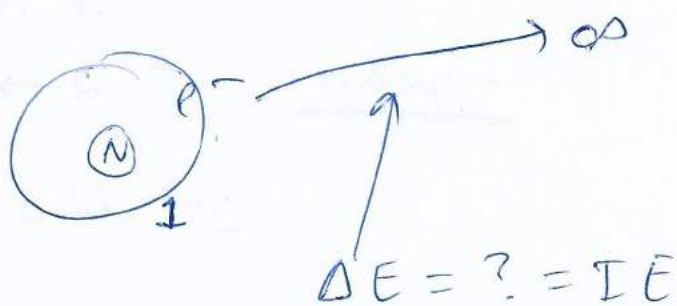
$$\underline{\underline{\bar{\nu} = R}}$$



# Ionization energy

for H atom ( $z=1$ )

$$E_n = -13.6 \frac{z^2}{n^2} \text{ eV}$$



$$E_{\infty} = 0$$

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

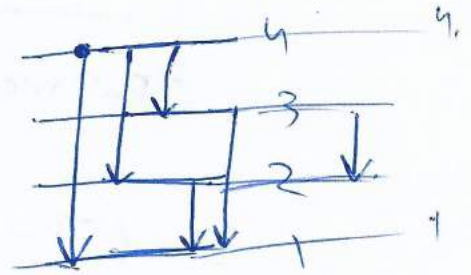
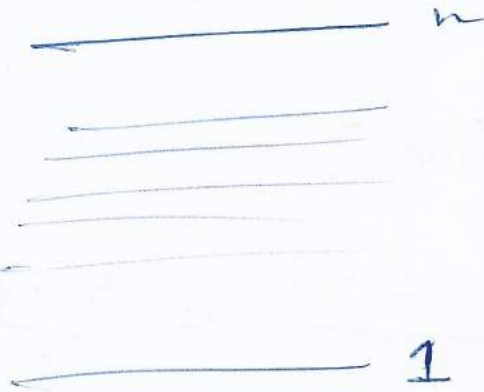
$$\begin{aligned} \Delta E &= E_{\infty} - E_1 = 0 - (-13.6) \\ &= \underline{13.6 \text{ eV}} \text{ (for 1st orbit)} \end{aligned}$$

He<sup>+</sup> (1st orbit)

$$E_1 = -13.6 \times \frac{2^2}{1^2} \text{ eV}$$

$$I.E. = 13.6 \times 4 \text{ eV}$$

I.E. → The energy required to  
take an  $e^-$  from an orbit to  $\infty$   
(when atom is isolated & gas is in  
gaseous phase)



$$3 + 2 + 1$$

$$\downarrow$$

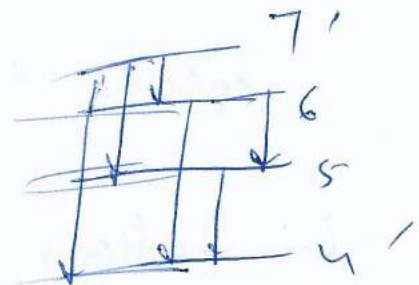
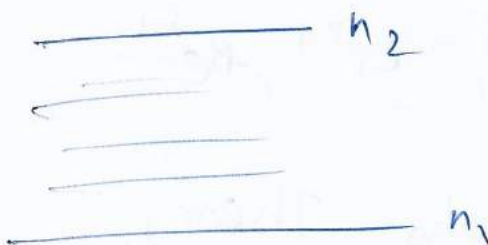
$$4 - 1$$

$$(n-1) + \dots + 3 + 2 + 1$$

$$1 + 2 + 3 + \dots + n = \frac{n(n+1)}{2}$$

$$\frac{(n-1)(n-1+1)}{2} = \frac{n(n-1)}{2}$$

total No. of lines produced  
when  $e^-$  comes from  $n \rightarrow 1$



$$3 + 2 + 1$$

$$\uparrow$$

$$(7 - 4)$$

$$(n_2 - n_1)$$

$$(n_2 - n_1) + \dots + 3 + 2 + 1$$

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

total No.  
of lines

$n_2 \rightarrow n_1$

$$\underline{7 \rightarrow 2}$$

How many line ?

$$\frac{(7-2)(7-2+1)}{2} = \frac{5 \times 6}{2} \\ = 15 \text{ lines}$$

$$6 \rightarrow 1$$

$$\frac{6 \times 5}{2} = \underline{\underline{15}}$$

### Significance of Bohr Theory

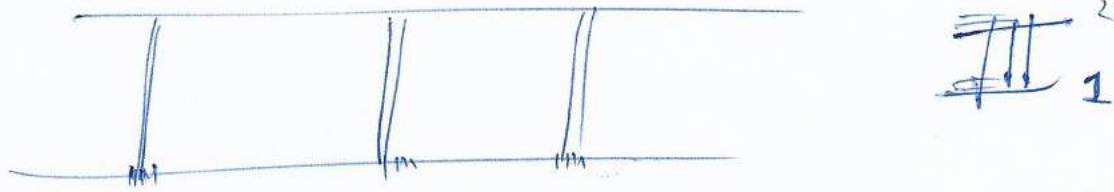
- Can explain H-spectrum
- R (Rydberg constant) matches with experimental value
- can explain spectrum of H like species e.g.  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$

### Limitations of Bohr Theory

- does not explain spectra of multielectron atoms.
- does not explain the fine spectrum of hydrogen.



## high resolution spectroscopy



→ Does not explain Zeeman effect  
& Stark effect

~~mag~~ magnetic field  
(Zeeman effect)

↘ Electric field

→ No justification why  $mvr = n \frac{h}{2\pi}$

$$\left( \frac{h}{2\pi} = \hbar \text{ (h bar)} \right)$$

$$mvr = n\hbar$$