UNIT-2

Modern physics

Atomic structure

Atom is stable # Atom shows line spectra # Atom is electrically neutral

Model of Atom

Thomson model (Element model)

Can be explained thermionic emission, photoelectric effect

But line spectra, intensity of variation of diff. line couldn't explained.

Rutherford model (1911)

Based on observation of α-scattering experiment on Au.

Nucleus contains all +ve charge & almost all of the mass of atom. Have radius 10^{-15} m.

electron's revolves around nucleus on various shells.

Drawbacks:

Stability problem:

e^- oscillates → radiates → spiral path → fall in nucleus → Unstable atom

Spectra:

Rutherford correlated the freq. ~~with~~ of spectral lines with angular freq of e^-. But spiral ~~freq.~~ motion has all freq. which shows atomic spectra continuous.

⇒ Removal of these shortcoming results Bohr model.

Bohr model (Year 1913)

(Modified Rutherford model)

Mixture of classical & non classical ideas.

Two postulates:

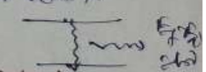
① Stationary orbit concept: only those orbits are possible for which

$$mvr = \frac{nh}{2\pi} \quad \text{—(1)}$$

In Rutherford model, no rectification of energy level.

no radiation in these orbits

② Origin of spectra: Spectra arises due to transition between various energy level and not due to e^- revolution.



Discussion of H-atom & spectra (Here)

Shortcomings:-

Couldn't explain intensity ~~variation~~ of spectral line variation

Unable to explain fine structure

valid only for simple system, not for complex system.

Couldn't explain the effect of E & B field on spectral line ⇒ Bohr Sommerfeld model

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Bohr model

(suggested by Bohr in 1913)

~~Two~~ three Postulates:

(i) e^- revolve in the circular orbit under coulombian attraction between e^- & nucleus nucleus.

(ii) Electron will revolve around a circular path for which the magnitude of ang. momentum is integral multiple of $\frac{h}{2\pi}$ or $\hbar$.

These orbits are called stationary orbits

i.e $|\vec{L}| = m_e v_e r_n = \frac{nh}{2\pi} = n\hbar$

where $n = 1, 2, 3$ - - -

(III) When an e^- makes a transition from one orbit of total energy E_i to another orbit of total energy E_f - then emission or ~~emit~~ absorption takes place in the form of electromag. radiation. The energy emitted or absorbed photon

$h\nu = E_i - E_f$. For emission $(E_i > E_f)$ and the frequency of radiation $\nu = \frac{E_i - E_f}{h}$

Explanation of spectra of Hydrogen like atom:

Let $+Ze \rightarrow$ charge of nucleus
$-e \rightarrow e^-$ charge
$m_e \rightarrow$ electron mass

The centripetal force is provided by coulombian attraction.

$$\frac{mv_n^2}{r_n} = \frac{1}{4\pi\epsilon_0}\frac{(Ze)e}{r_n^2}$$

$$\Rightarrow \frac{m^2v_n^2r_n^2}{r_n} = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n^2}mr_n^2 \quad \text{(multiplying by } mr_n^2 \text{ on both sides)}$$

$$\Rightarrow \left(\frac{nh}{2\pi}\right)^2 \times \frac{1}{r_n} = \frac{Ze^2}{4\pi\epsilon_0} \quad \text{as } mv_nr_n = \frac{nh}{2\pi}$$

$\Rightarrow r_n = \dfrac{n^2h^2\epsilon_0}{\pi m Z e^2}$; $n = 1, 2, 3 \ldots$

$\Rightarrow \boxed{r_n \propto n^2}$

For H-atom, $n = 1$, $Z = 1$

$\Rightarrow r_1 = \dfrac{h^2\epsilon_0}{\pi m e^2} = \dfrac{6.6\times10^{-34} \times 8.85\times10^{-12}}{3.14\times 9.1\times10^{-31} \times (1.6\times10^{-19})^2} = 5.27\times10^{-11}\,m$

$\Rightarrow \boxed{r_1 = 0.53 A^\circ}$ Called Bohr ~~model~~ radius (a_0)

for $n = 2$, $\boxed{r_2 = 4 r_1}$ $\Rightarrow r_2 = 4\times 0.53 A^\circ = 2.12 A^\circ$

Now as $v_n = \dfrac{nh}{\cancel{2\pi m r_n}} = \dfrac{nh}{}$ $\quad m v_n r_n = \dfrac{nh}{2\pi}$

$\Rightarrow v_n = \dfrac{nh}{2\pi m r_n} = \dfrac{nh}{2\pi m \left(\dfrac{n^2h^2\epsilon_0}{\pi m Z e^2}\right)}$

$\Rightarrow v_n = \dfrac{Ze^2}{2nh\epsilon_0}$, where $n = 1, 2, 3 \ldots$

And the total energy $E_n = K.E + P.E = \frac{1}{2} m \left[\dfrac{Ze^2}{2nh\epsilon_0}\right]^2 + \dfrac{-Ze^2}{4\pi\epsilon_0 \left(\dfrac{n^2h^2\epsilon_0}{\pi m Z e^2}\right)}$

$= -\dfrac{me^4}{8\epsilon_0^2 h^3 c}\left[\dfrac{Z^2hc}{n^2}\right]$; after multiplying by hc in numerator & denominator.

$\Rightarrow E_n = -R_\infty Z^2 hc\left(\dfrac{1}{n^2}\right)$, where $\boxed{R_\infty = \dfrac{me^4}{8\epsilon_0^2 h^3 c}}$ This is Called Rydberg constant

$R_\infty = 1.0974\times10^7/m$

For Hydrogen $E_n = -\dfrac{R_\infty hc}{n^2}$

$\Rightarrow \boxed{E_n = -\dfrac{13.6}{n^2}\,eV}$ $\quad \boxed{E \propto Z^2,\ \propto \frac{1}{n^2}}$ $\boxed{r \propto n^2,\ \propto \frac{1}{Z}}$ $\boxed{v \propto \frac{1}{n}}$

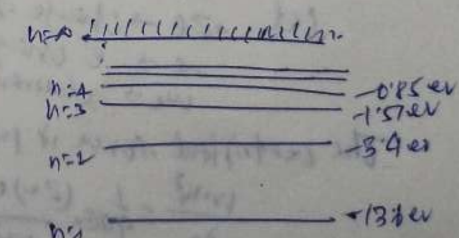
for $n = 1$ $\quad E_1 = -13.6\,eV$

$n = 2$ $\quad E_2 = -3.4\,eV$

$n = 3$ $\quad E_3 = -1.51\,eV$

$\vdots$

$n = \infty$ $\quad E_\infty = 0\,eV$



Minimum energy required to remove the e^- completely from the orbit is called binding energy or ionization energy.

Binding energy of Hydrogen $= 13.6\,eV$

Ionization energy of H $= 13.6\,eV$

Similarly ionization energy of $Li = 5.39\,eV$

Sometimes energy is expressed in terms of Term value (T)

$$T = \frac{E}{hc} = \bar{\nu} = \text{wave no. with unit } m^{-1} \text{ or } cm^{-1}$$

Thus, the wave no. of nth state = $-\frac{13.6}{n^2 hc} z^2 \; m^{-1}$.

and $\boxed{\nu = c\bar{\nu}}$

where $\bar{\nu}$ = wave no.
c = velo. of light
ν = freq. of light.

Hydrogen atom

The observed data for hydrogen atom:

simplest atom having one proton & one e^-.
Shows a group of spectral lines called Lyman, Balmer, Paschen, Brackett & Pfund lines.

(1) Lyman series (UV) region:

$\cancel{\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)}$; $n = 2, 3, 4 - - -$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{c} = \frac{1}{c}\left(\frac{E_i - E_f}{h}\right) = \frac{1}{hc}(E_i - E_f)$$

$$= \frac{1}{hc}\left\{\frac{-13.6z^2}{n_i^2} - \left(\frac{-13.6z^2}{n_f^2}\right)\right\}$$

$$= \frac{1}{hc}-(13.6z^2)\left\{\frac{1}{n_i^2} - \frac{1}{n_f^2}\right\}$$

$$= \frac{-13.6z^2}{hc}(-)\left\{\frac{1}{n_f^2} - \frac{1}{n_i^2}\right\} = \frac{13.6z^2}{hc}\left\{\frac{1}{n_f^2} - \frac{1}{n_i^2}\right\}$$

for Lyman series ~~$n_f = 1, n_i =$~~ all the transition will stop at $n=1$.

Also, Lyman series is observed when transition starts from $n=1$ or ends at $n=1$.

$n=1$ starts $\xrightarrow{\text{this leads to}}$ Absorption Spectra.

$n=1$ ends $\xrightarrow{\text{This leads to}}$ Emission Spectra.

For emission $n=1 = n_f$

and $n = 2, 3, 4 \cdots n_i$

$$\frac{1}{\lambda} = \frac{13.6 z^2}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{\lambda} = R_\infty z^2 \left(\frac{1}{1^2} - \frac{1}{n_i^2}\right)$$

Where R_∞ is the Rydberg constant when nucleus is infinitely heavy in comparision to e^-.

$$R_\infty = \frac{me^4}{8\epsilon_0^2 c h^3} = 1.097 \times 10^7 \, m^{-1}$$

or $1.097 \times 10^5 \, cm^{-1}$.

Series limit of Lyman : $n_f = 1$, $n_i = \infty$.

~~This line of Lyman series will have highest frequency.~~

Ex:1 Find the wavelength corresponding to α-line in Lyman series.

α line in Lyman series is when

$$n_f = 1, \; n_i = 2$$

$$\frac{1}{\lambda_\alpha} = R_\infty (1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = R_\infty\left(1 - \frac{1}{4}\right) = \frac{3}{4} R_\infty$$

$$= 1.097 \times 10^7 \times \frac{3}{4} \, m^{-1}$$

$$\boxed{\frac{1}{\lambda_\alpha} = 0.82275 \times 10^7 \, m^{-1} = \bar{\nu}}$$

$$\Rightarrow \lambda_\alpha = \frac{1}{0.82275 \times 10^7} = \frac{10^{-7}}{0.82275} = 1.215436 \times 10^{-7} m$$

$$= 1215.4 \times 10^{-10} m$$

$$\boxed{\lambda_\alpha = 1215 Å}$$ and

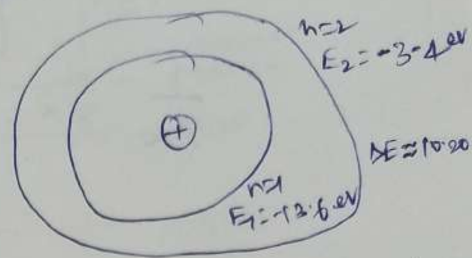
For λ_β, $n_i = 3$, $n_f = 1$, $\Rightarrow \lambda_\beta = 1025 Å$

and series limit is when $n_i = \infty$, $n_f = 1$, $\lambda_\infty =$

Ex:2 Find the energy difference for α-line which have $\lambda_\alpha = 1215\,A^\circ$

Soln:

$$\lambda(A^\circ) = \frac{12400}{(\Delta E)\,ev}$$



given, $\lambda_\alpha = 1215\,A^\circ$

$$\Rightarrow \Delta E(ev) = \frac{12400}{\lambda_\alpha} = \frac{12400}{1215} = 10.205\,ev.$$

$$\boxed{\Delta E = 10.205\,ev = E_2 - E_1 = 10.20\,ev}$$

$\frac{1}{4} - \frac{1}{9} = \frac{9-4}{36} = \frac{5}{36}$

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② Balmer series: $n_f = 2,\ n_i = 3, 4, 5 \ldots \infty$

for α-line in Balmer series, $n_f = 2$, $n_i = 3$

$$\Rightarrow \frac{1}{\lambda_\alpha} = 1.097\times10^{7}\,m^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 1.097\times10^{7} \times \frac{5}{36} = 0.1523\times10^{7}\,m^{-1}$$

$$\Rightarrow \lambda_\alpha = 6.5659\times10^{-7}\,m$$

$$= 6565\times10^{-10}\,m$$

$$\boxed{\lambda_\alpha \simeq 6565\,A^\circ}$$ Visible region.

$$(\Delta E)_{\alpha\,line} = \frac{12400}{\lambda_\alpha(A^\circ)} = \frac{12400}{6565} = 1.888\,ev.$$

$$\Rightarrow \boxed{(\Delta E)_{\alpha\,line} = 1.888\,ev.}$$

Similarly λ_β = for $n_f = 2, n_i = 4$, $\lambda_\beta = 486A^\circ$, $\lambda_\gamma = 4340\,A^\circ$

and for series limit λ_∞, $n_f = 2$, $n_i = \infty$ $\lambda_\infty = 3644\,A^\circ$

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(3) Paschen series: $\frac{1}{\lambda_\alpha} = \bar{\nu} = R_\infty\left(\frac{1}{3^2} - \frac{1}{4^2}\right) \Rightarrow \lambda_\alpha = 18746 A^\circ$

$n_f = 3,\ n_i = 4, 5, 6 \cdots \infty$

$$\boxed{(\Delta E)_\alpha = \frac{12400}{18746} = 0.6614\ eV}$$

$$\frac{1}{\lambda_\infty} = \bar{\nu} = R_\infty\left(\frac{1}{3^2} - \frac{1}{\infty}\right) = 8201 A^\circ$$

$$\boxed{(\Delta E)_\infty = \frac{12400}{8201 A^\circ} = 1.51\ eV}$$

(4) Brackett series: $n_f = 4,\ n_i = 5, 6, 7, 8 \cdots \infty$

$\downarrow \downarrow \downarrow \downarrow$

$\alpha\ \beta\ \gamma\ \delta$

$$\frac{1}{\lambda_\alpha} = R_\infty\left(\frac{1}{4^2} - \frac{1}{5^2}\right) \Rightarrow \lambda_\alpha = 40501 A^\circ,\ \boxed{\Delta E_\alpha = \frac{12400}{40501} = 0.3061\ eV}$$

$$\frac{1}{\lambda_\infty} = R_\infty\left(\frac{1}{4^2} - \frac{1}{\infty}\right) \Rightarrow \lambda_\infty = 14580,\ \boxed{\Delta E_\infty = 0.8504\ eV}$$

(5) Pfund series $n_f = 5,\ n_i = 6, 7, 8, 9, 10 \cdots \infty$

$\alpha\ \beta\ \gamma\ \delta$ $\quad \frac{1}{\lambda} = \bar{\nu} = R_\infty\left(\frac{1}{5^2} - \frac{1}{n_i^2}\right)$

$\lambda_\alpha = 74558 A^\circ$, $(\Delta E)_\alpha = 0.16631\ eV$

$\lambda_\infty = 22782$, $(\Delta E)_\infty = 0.5442\ eV$

series	Wave no.	Region	α-line or 1st line	Series limit (A°)
(1) Lyman	$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n_i^2}\right)$ $n_i = 2, 3, 4$	UV	$1215 A^\circ$	$911 A^\circ$
(2) Balmer	$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right)$ $n_i = 3, 4, 5 \cdots$	Visible	$6563 A^\circ$	$3644 A^\circ$
(3) Paschen	$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_i^2}\right)$ $n_i = 4, 5, 6 \cdots$	IR	$18746 A^\circ$	$8201 A^\circ$
(4) Brackett	$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n_i^2}\right)$ $n_i = 5, 6, 7 \cdots$	IR	$40501 A^\circ$	14580
(5) Pfund	$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n_i^2}\right)$ $n_i = 6, 7, 8 \cdots$	far IR	$74558 A^\circ$	22782

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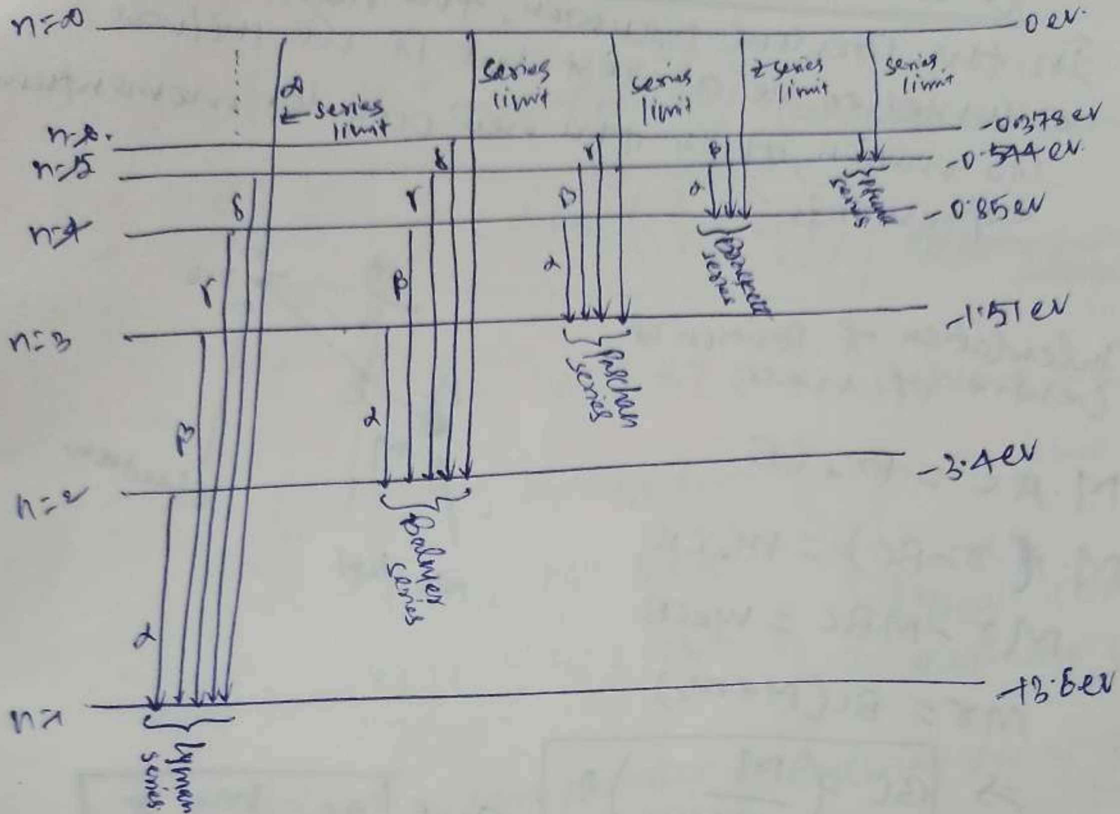

<u>short comings:</u>

① Unable to explain intensity variation of spectral lines.

② Unable to explain the fine structure ~~of~~.

③ Valid only for simple system, not for complex system.

④ Can not explain the effect of electric & magnetic field on spectral lines.

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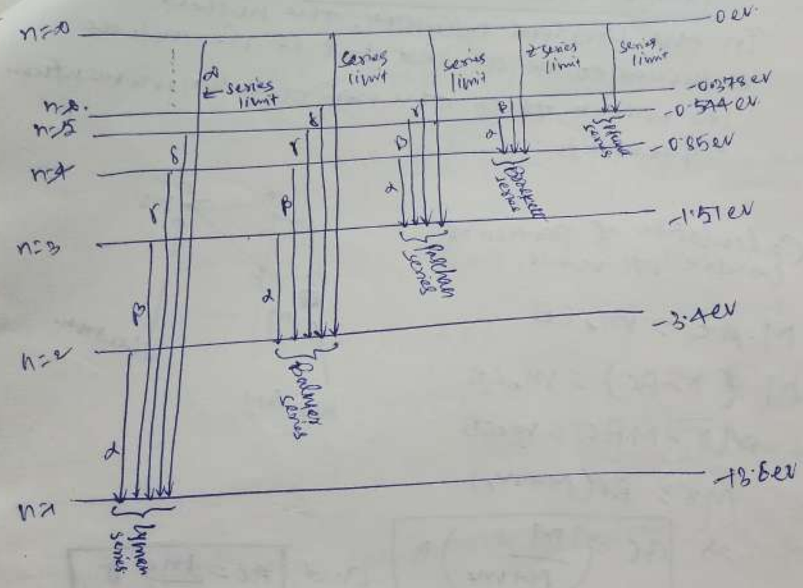

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