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CSIR-NET

Council of Scientific & Industrial Research

PHYSICAL SCIENCE

VOLUME - I

ATOMIC & MOLECULAR

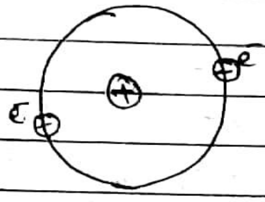
SIERRA INNOVATIONS

ATOMIC & MOLECULOR PHYSICS

Atomic Physics

Atomic Structure :-

$$_{Z}X^{A}$$



Z - atomic no. - no. of protons.
A - mass no. - no. of protons + no. of neutrons
$= (p+n)$

$_6C^{13}$, $_6C^{14}$ — $Z=6$, $p=6$, $n=8$.

$Z=6$, $p=6$, $n=7$

Bohr atomic Model :-

According to Bohr's atomic model following assumptions and poschulates must be consider -

(i) electrons move in the circular orbits around the nucleus under the action of coulomb force.

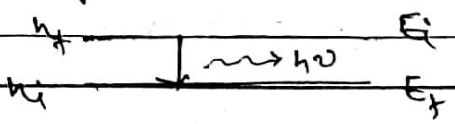
(ii) Electrons can move only in those orbit for which magnitude of angular momentum is integer multiple of $h/2\pi$.

$$|\vec{L}| = n\hbar = \frac{nh}{2\pi} \qquad n = 1, 2, 3 \ldots$$

Electrons don't emitt EM radiation while orbitting in these orbits.

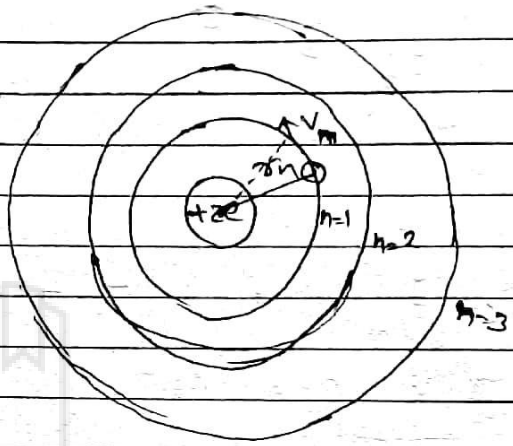
(iii) EM radiation would be emitted only if e^- will jump from one allowed orbit to another allowed orbits. And frequency of radiation is given by -

$$\boxed{\nu = \frac{E_i - E_f}{h}}$$



Bohr atomic model is applicable to only one e^- atom like H, $_1H^2$, $_1H^3$, He^+, Li^{2+} - - - , positronium, muoni atom.

+Ze



Total energy of one e^- atom

$$E = K.E. + P.E.$$

$$= \frac{1}{2}mv_n^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r_n}\right) \quad \text{— (1)}$$

$$\frac{mv_n^2}{r_n} = \frac{Ze^2}{4\pi\epsilon_0 r_n^2}$$

$$mv_n^2 = \frac{Ze^2}{4\pi\epsilon_0 r_n} \quad \text{— (2)}$$

$$E = \frac{1}{2}\frac{Ze^2}{4\pi\epsilon_0 r_n} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

$$\boxed{E = \frac{-Ze^2}{8\pi\epsilon_0 r_n} = \frac{-kZe^2}{2r_n}} \quad \text{— (3)}$$

Bohr's Condition –

$$|\vec{L}| = mv_n r_n = \frac{nh}{2\pi} \quad \text{— (4)}$$

$$v_n = \frac{nh}{2\pi m r_n}$$

$$m\left(\frac{nh}{2\pi m r_n}\right)^2 = \frac{ze^2}{4\pi\epsilon_0 r_n}$$

$$\frac{n^2h^2}{\cancel{4}\pi^2 m r_n} = \frac{ze^2}{\cancel{4\pi}\epsilon_0}$$

$$\boxed{r_n = \frac{n^2h^2\epsilon_0}{\pi m z e^2}} \quad - (5)$$

$$v_n = \frac{n\cancel{h}}{2\pi \cancel{m} \frac{n^2 h^2 \epsilon_0}{\pi \cancel{m} z e^2}}$$

$$\boxed{v_n = \frac{ze^2}{2nh\epsilon_0}} \quad - (6)$$

Speed of e^- in 1^{st} orbit of H-atom -

$$v_n = \frac{(1.6\times10^{-19})^2 \, Z}{2\,(6.62\times10^{-34})\,(8.85\times10^{-12})\,n}$$

$$\boxed{v_n = 2.2\times10^6 \, m/s}$$

Bohr radius $a_0 = \frac{h^2\epsilon_0}{\pi m e^2}$

$$\boxed{a_0 = 0.53 A^0}$$

$$\boxed{r_n = \frac{n^2 a_0}{Z}} \quad - (7)$$

$$E_n = \frac{-kze^2 Z}{2 \cdot n^2 a_0}$$

$$\boxed{E_n = \frac{-mz^2e^4}{8\epsilon_0^2 n^2 h^2}} \quad - (8)$$

$$\boxed{E_n = -13.6\frac{Z^2}{n^2}\, eV} \quad - (9)$$

Energy of ground state of hydrogen atom

$E_1 = -13.6\ eV$

B.E. $\boxed{E_B = +13.6\ eV}$

B.E., energy required to remove the e^- completely.

Ionization Energy $= +13.6\ eV$

For ionization energy

Ionization potential energy of hydrogen atom $= +13.6\ V$

Excited the e^- from $n=1$ to $n=2$

$E_1 = -13.6\ eV$

$E_2 = \frac{-13.6\ z^2}{n^2} = \frac{-13.6}{4} = -3.4\ eV$

$\Delta E = (-3.4) - (-13.6)$

$\boxed{\Delta E = 10.2\ eV}$

Wavelength of photon -

$$\lambda = \frac{12400}{E(eV)} = \frac{12400}{10.2}\ A^\circ$$

$$\boxed{\lambda = 1215.7\ A^\circ}$$

Energy sometimes expressed in term values.

$$T = \frac{E}{hc} = \bar{\nu}\ \text{(wave no.)}$$

$$\boxed{\bar{\nu}_n = \frac{-13.6\ z^2}{n^2 hc}\ m^{-1}}$$

$$E_n = \frac{-mz^2e^4}{8\epsilon_0^2 n^2 h^2}$$

$$E_n = \frac{-me^4}{8\epsilon_0^2 h^3 c}\left(\frac{hcz^2}{n^2}\right)$$

$$\boxed{E_n = -R_\infty\left(\frac{hcz^2}{n^2}\right)} \qquad R_\infty = \frac{me^4}{8\epsilon_0^2 h^3 c}$$

Rydberg Const. $\boxed{\begin{aligned} R_\infty &= 1.097\times10^7 \, m^{-1} \\ &= 1.097\times10^5 \, cm^{-1}\end{aligned}}$

$\boxed{R_\infty \propto m_e}$

R_∞ — Nucleus is infinitly heavy as compare to e^-.

Finite Nuclear mass correction in the expression of energy-

$$\mu = \frac{M_{nucleus} M_{electron}}{M_{nucleus} + M_{electron}}$$

$$\boxed{\frac{m_p}{m_e} = 1836}$$

$$\mu_H = \frac{m_p m_e}{m_p + m_e} = \frac{1836}{1837} m_e$$

$\boxed{\mu_H < M_e}$

$\boxed{R_H < R_\infty}$

$$E_n = \frac{-13.6}{n^2}\left(\frac{1836}{1837}\right) eV \quad (\text{For H-atom})$$

Positronium Atom :- Positronium atom is bound state of an e^- and a positron (+e)

$$\mu_{Positronium} = \frac{m_e}{2}$$

$$E_n = \frac{-13.6}{2}\frac{Z^2}{n^2} \qquad Z = 1$$

$$\boxed{E_n = -6.8\frac{Z^2}{n^2}\ eV}$$

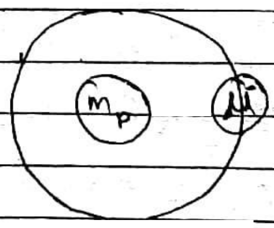
$$\boxed{r_{Posi} = 2r_H}$$

$$\boxed{\bar{\nu} \propto E \propto R_p}$$

Muonic Atom :-

$$m_{\mu^-} = 207 m_e$$

Muonic atonic atom is hydrogen like atom in which e^- is replace by Muon.



$$\mu_{\mu^-} = \frac{207}{208} m_e$$

$$\mu_{\mu}\, m_{\mu^-} = \frac{m_p m_{\mu}}{m_p + m_{\mu}}$$

$$= \frac{1836 \times 207}{1836 + 207} m_e$$

$$\mu_{\mu}\, m_{\mu^-} = 186 m_e$$

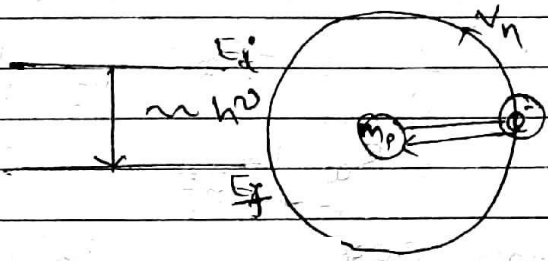
B.E. of Muonic atom $E_B = \frac{13.6 \times 186}{1^2}$ eV

$$E_B = 2529.6\ eV$$

series lim $\infty \rightarrow 1$

Frequency Of Revolution in H-like Atom :-

Time - period of revolution



$$T = \frac{2\pi r_n}{v_n}$$

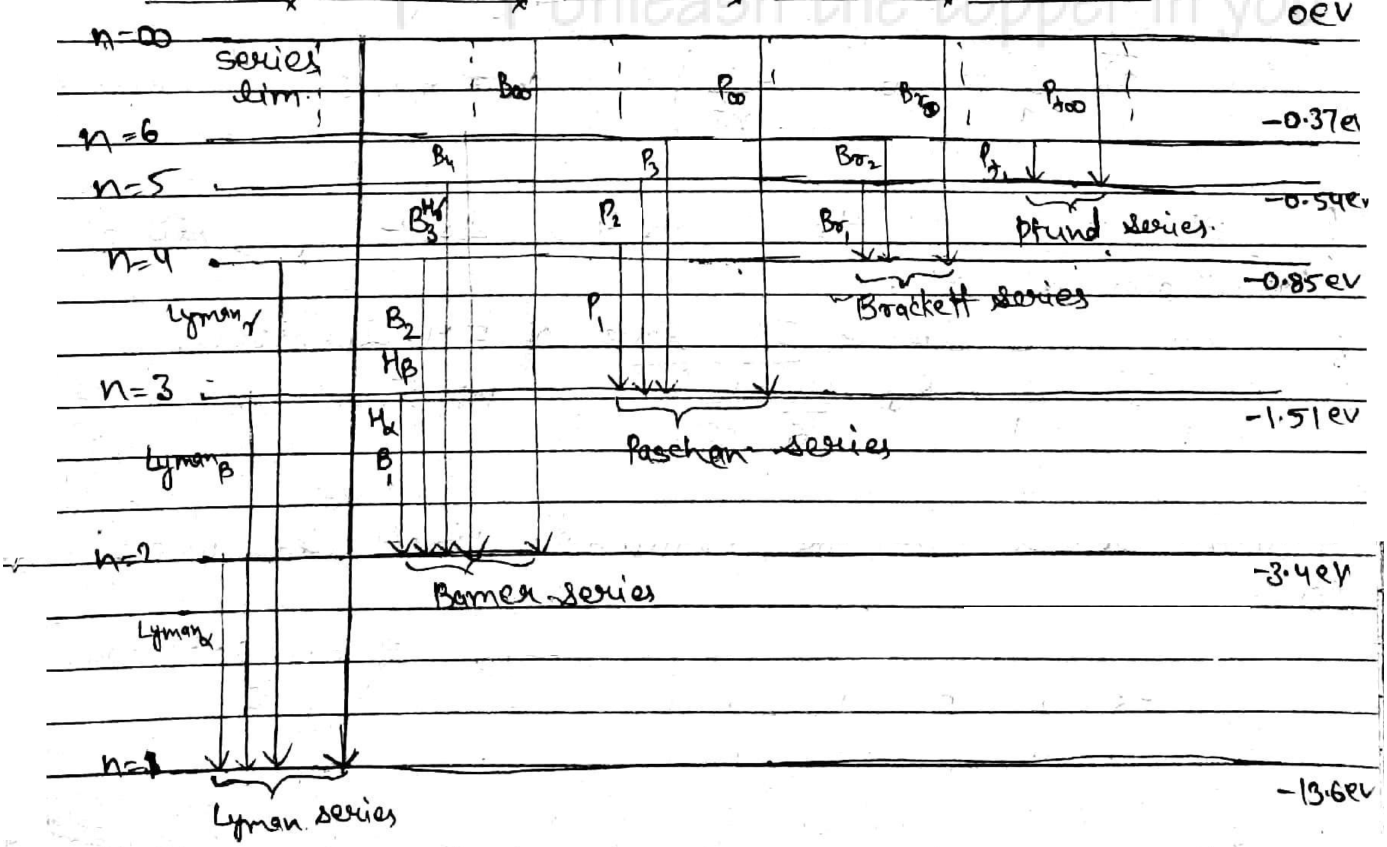
$$T = \frac{(2\pi r)^2 m}{nh}$$

$$T = \frac{4\pi^2 m}{nh}$$

$$T_n = \frac{4\epsilon_0^2 n^3 h^3}{m z^2 e^4}$$

$$\boxed{f_n = \frac{m z^2 e^4}{4\epsilon_0^2 n^3 h^3}}$$

Various Series Observed in H- Spectrum :-



Lyman –

All the transitions ~~starts~~ from 1 and ~~equal~~ terminate at one is lyman series.

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = R_{\infty} Z \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)}$$

$$\frac{1}{\lambda} = \bar{\nu} = R_{\infty} \left(1 - \frac{1}{n_i^2} \right) \qquad n_i = 2, 3, 4 \ldots$$

Lyman series falls in UV region of EM spectrum.

Bamar Series: All the transition starts from n=2 and terminate at n=2.

This series lies in visible range of EM spectrum.

Paschen Series – All the transition starts from n=3 & terminate at n=3.

This series lies in Near IR range of EM spectrum.

$$\bar{\nu} = \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{9} - \frac{1}{n_i^2} \right) \qquad n_i = 4, 5, 6 \ldots$$

Brackett Series – All the transitions starts from n=4 & terminates at n=4

This series lies in IR range of EM spectrum.

$$\bar{\nu} = \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{16} - \frac{1}{n_i^2} \right) \qquad n_i = 5, 6, 7 \ldots$$

Pfund Series :– All the transitions starts from n=5 & terminates at n=5

This series lies in Far IR range of EM spectrum.

$$\bar{\nu} = \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{25} - \frac{1}{n_i^2} \right) \qquad n_i = 6, 7 \ldots$$

The shortest wavelength ~~of~~ → Lymen series's series limit

Which series can ionized energy - lymen series's series limit.

In the absorbtion spectrum of H-atom which series should be observed.
1. ✓ Lyman 2. Bamar 3 Paschan 4. All three.

because H-atom would excited from its g.s n=1.

emission - All three.

In labs we find H-emission spectrum

De-Broglie interpretation of Bohr's theory :-

According to De-Broglie hypothesis can move only in those orbits for which

$$\boxed{2\pi r_n = n\lambda}$$

De-broglie condn for stationary orbit ($|L| = n\hbar$)

(moving) orbiting e^- behave as a wave.

Wavelength of wave associated with e^-

$$\lambda = h/p$$

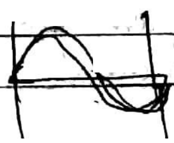
$$2\pi r_n = \frac{nh}{p}$$

$$2\pi r_n = \frac{nh}{mv_n}$$

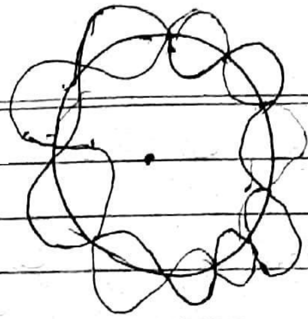
$$\boxed{mv_n r_n = \frac{nh}{2\pi}}$$ (Bohr's Condition)

~~mtor~~

If two waves ~~sperimpose~~ superimpose each other and phase 180°.



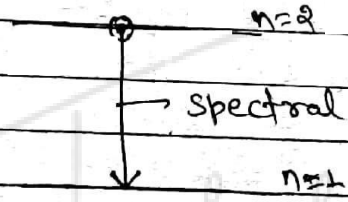
Bohr theory is semi classical theory



Sommerfield's Extension to Bohr's Model :-

Bohr's theory fails to explain fine structure in H-like atoms.

Fine structure is the splitting of a single spectral line into several close but distinct spectral line.



Sommerfield in attempt to explain the fine structure in hydrogen like atom extended the Bohr's model by assuming that e^-s not only revolve in circular orbits but also in elliptical orbits.

$$\boxed{\frac{b}{a} = \frac{k}{n}}$$

This is Sommerfield Quantum condition for elliptical orbits.

Where b - semi minor axis
a - Semi major axis
$n = n_r + k$ ~~k~~ - total quantum no. of the state (principle quantum no)
~~n~~ -
k - Aziumithle quantum no.
n_r - radial quantum no.

$n_r = 0, 1, 2, 3 \ldots$
$k = 1, 2, 3$

If $n_r = 0$ circular orbit

$\left.\begin{matrix} n_r = 1, k = 1 \\ n_r = 0, k = 2 \end{matrix}\right\} n = 2$

$n = 1, n_r = 0, k = 1$

$$\boxed{a = \frac{a_0 n^2}{Z}} \qquad \boxed{b = \frac{a_0 n k}{Z}}$$

Energy of hydrogen like atom is given by:

$$\boxed{E = \frac{13.6 Z^2}{n^2}}$$ — total quantum no.

energy still depend of total quantum no. despite of diff. path followed by e^- its energy remain same. This theory ~~also is same a~~ is failed to explain

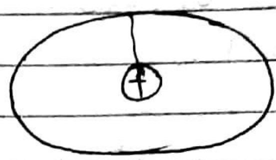
Sommerfield Relativistic Correction of energy –

electron in H-atom waves at very high ~~frequen~~ speed v_0

$v_0 = 2.2 \times 10^6$ m/sec.

If this relativistic correction is combine with elliptical orbit theory. Then the avg. velocity of e^-s in the elliptical orbit depends on its ellipticity.

i) Elliptical orbit
ii) Relativistic speed.



Energy expression for H-like atom –

In Bohr's model $E_n = \frac{-13.6Z^2}{n^2} = \frac{-R_\infty Z^2 hc}{n^2}$

Sommer field relativistically corrected energy –

$$\boxed{E_{nk} = \frac{-R_\infty Z^2 hc}{n^2} - \underbrace{\frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right)}_{\text{correction term (always small)}}}$$

α = Fine structure const. $= \frac{v_1}{c}$

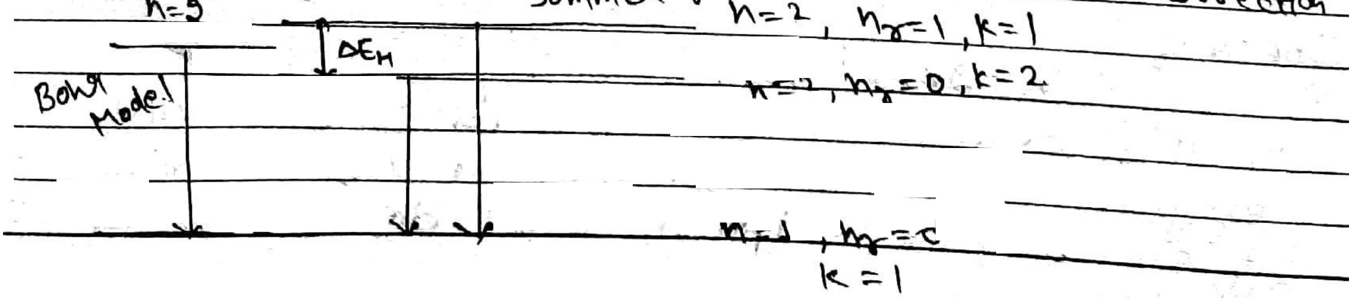
$\alpha = \frac{\text{speed of H-atom's } 1^{st} \text{ orbit}}{c}$

$\alpha = \frac{1}{137} = \frac{e^2}{2\epsilon_0 ch}$

Fine structure energy $\Delta E_H = 10^{-3}$ eV
$\Delta E_{He^+} = ?$

No fine structure observe in $n=1$.

Sommer field's after relativistic correction



$$\boxed{\Delta E_{\text{Fine structure}} \propto Z^4}$$

$$\frac{\Delta E_{He^+}}{\Delta E_H} = \frac{Z_{He^+}^4}{Z_H^4}$$

$$\Delta E_{He^+} = 16 \times 10^{-3}\ eV$$

Assignment - 1

1. $n = 3$, $T = 10^{-8}$ sec.

$n = 3$

$f = \frac{1}{T}$ (frequency of revolution)

$n = 2$

$$T = \frac{2\pi r_n}{v_n} = \frac{2\pi n^2 h^2 \epsilon_0}{\pi m z e^2} \cdot \frac{2nh\epsilon_0}{ze^2}$$

$$= \frac{4 n^3 h^3 \epsilon_0^2}{m z^2 e^4}$$

$10^{7-24} - 2$

$$f = \frac{m z^2 e^4}{4 n^3 h^3 \epsilon_0^2} = \frac{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{4 \times (3)^3\ (6.02 \times 10^{-34})^3\ (8.85 \times 10^{-12})^2}$$

$$= \frac{\cancel{9.1} \times \cancel{1.6} \times \cancel{1.6} \times 1.6 \times 1.6 \times 10 \times}{\cancel{4} \times 27 \times \cancel{6} \times \cancel{6} \times \cancel{6} \times \cancel{9} \times 9} = \frac{.128}{3 \times 3 \times 3 \times 9 \times 27}$$

$$= 2.4 \times 10^{14}\ /\text{sec. or Hz}$$

no. of revolution in 1 sec — 2.4×10^{14}

10^{-8} sec no. of revolution — $2.4 \times 10^{14} \times 10^{-8}$

2.4×10^{6}

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

$$= 1.097\times10^{7}\left(\frac{1}{4} - \frac{1}{(9)^2}\right)$$

$$= 1.097\times10^{7}\left(\frac{81-4}{81\times4}\right)$$

$$= 1.097\times10^{7} \times \frac{77}{81\times4}$$

$$\lambda = \frac{81\times4}{77\times1.097} \times10^{-7} = 384\text{nm}$$

3. $$E = 13.6\,\frac{Z^2}{n^2} \quad (\text{B.E.})$$

$$= \frac{\cancel{13.6}^{\,3.4}\times\cancel{4}}{\cancel{64}\ \cancel{16}\ 4} = 0.85\ \text{ev}$$

4. $$E = pc$$

$$p = \frac{\Delta E}{c}$$

n=10

n=1

$$= \frac{1}{c}\left(\frac{-13.6}{1} + \frac{13.6}{100}\right)$$

$$= \frac{1}{c}\left(-13.6 + .136\right)$$

$$= \frac{-13.464}{c}$$

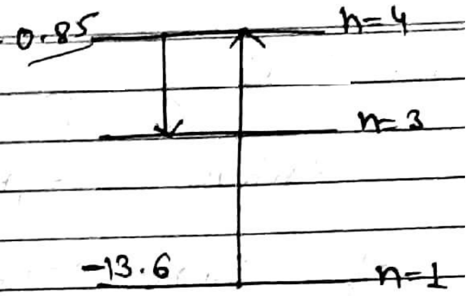
$$= \frac{-\cancel{13.464}^{\,4.15}\times1.6\times10^{-19}}{\cancel{3}\times10^{8}\times\cancel{1.6\times10^{-19}}}$$

$$= 6.640\times10^{-27}\ \text{kg m s}^{-1}$$

5. $\Delta E = -\frac{\cancel{13.6}}{3.4}\left(\frac{1}{9}-\frac{1}{16}\right)$

$= -\cancel{13.6}\left(\frac{7}{\cancel{9\times16}_{4}}\right)$

$=$



$\Delta E_{1\to4} = -13.6 + 0.85$

$= -12.75\,eV$ (For get 1st paschen series)

~~For absorption~~

8. $r \propto \frac{1}{m} \propto \frac{1}{\mu}$ $\quad \mu = 186 m_e$

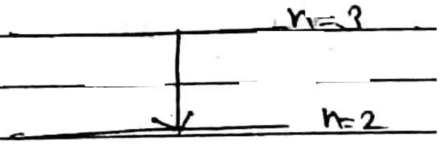
$r_1 = \frac{a_0}{186} = \frac{0.539\times10^{-10}}{186} = \frac{.53}{186}$ Pm $= 0.285$ Pm

9. $E/7$ ~~-13~~ -18.6

$E \propto \mu$

$E = 13.6\times186$

10. $\frac{1}{\lambda} = \frac{186\times \mu e^4}{8\epsilon_0 c h^3}\left(\frac{1}{4}-\frac{1}{9}\right)$



$= \overset{31}{\cancel{186}}\times1.097\times10^7\left(\frac{5}{\underset{6}{\cancel{36}}}\right)$

$= 28.339\times10^7$

$\lambda = 0.03528\times10^{-7}$

$= 35.28$ Å