Chapter 12

Atoms

Atoms are electrically neutral but contain charged constituents : the electron (-e) and the nucleus (+Ze). How are they arranged ?

Discovery of Electron (Thomson, 1897) :

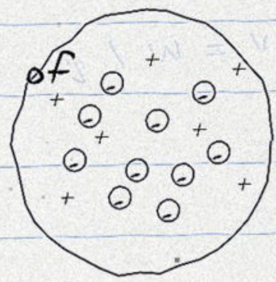
J. J. Thomson studied cathode rays in a discharge tube and measured e / m of the electron. Concluded : atoms contain electrons.

$e / m = 1.76 \times 10^{11}$ C / kg

Millikan (1909) : $e = 1.6 \times 10^{-19}$ C

Thomson then proposed :
Atom = uniform ~~solid~~ sphere of positive charge with electrons embedded inside like seeds in a watermelon.

plum - pudding



Thomson's

Atom is overall neutral ; size 10^{-10} m.

But this model failed in 1911 . . .

(Rutherford's alpha - scattering)

Rutherford's Alpha - Scattering

Geiger & Marsden (1911), under Rutherford, bombarded a thin gold foil with alpha particles.

Setup

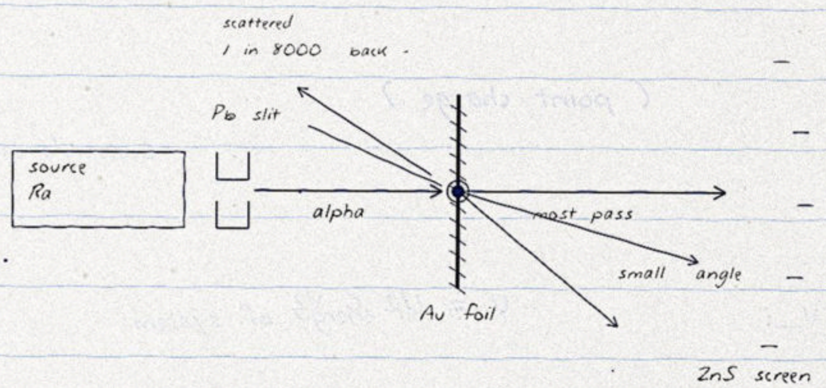


Fig. Geiger - Marsden alpha - scattering apparatus.

Observations

(i) Most alpha pass through with no deflection.

(ii) Few are deflected by small angles.

(iii) 1 in 8000 deflected by > 90 degrees.

(iv) Very rarely, bounces straight back.

Rutherford's Nuclear Model

Conclusions from the experiment

(1) Most space in an atom is empty, because most alpha particles go straight through.

(2) The positive charge and almost all the mass are concentrated in a tiny core -> the nucleus.

(3) Electrons revolve around it in orbits, held by Coulomb attraction.

Sizes

Atom radius 10^{-10} m

Nucleus radius 10^{-15} m (1 fm)

Ratio 10 5 -> atom is mostly empty !

Why most alpha are undeflected

Because they pass far from any nucleus and feel negligible Coulomb force.

Backscattering needs head - on collision with the heavy positive nucleus.

Rutherford : ' as if a 15 - inch shell bounced

Distance of Closest Approach

For a head - on collision, the alpha particle stops momentarily at distance r_0 from the nucleus. At that instant :

K.E. of alpha = P.E. at r_0

$$\boxed{E = (1/4\pi\varepsilon_0) \cdot 2Ze^2} / r_0$$

<- energy balance

$$\boxed{r_0 = (1/4\pi\varepsilon_0) \cdot 2Ze^2} / E$$

<- distance of closest approach

Numerical estimate

Take E = 5.5 MeV , Z = 79 (gold) :

$$r_0 = (9 \times 10^9) \cdot 2 \cdot 79 \cdot (1.6 \times 10^{-19})^2 / (5.5 \times 1.6 \times 10^{-13})$$

$$4.1 \times 10^{-14} \text{ m}$$

So nucleus size < 4×10^{-14} m .

Impact parameter b

b = perpendicular distance of initial path from nucleus. Small b -> large deflection.

Trajectory of alpha near Nucleus

Each alpha follows a hyperbolic path with the nucleus at one focus.

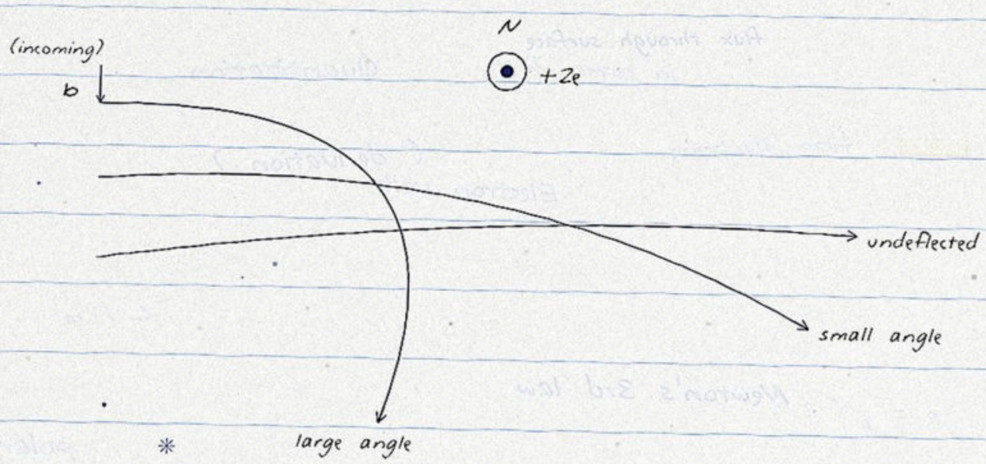


Fig. trajectories for varying impact parameter b.

Small b -> alpha gets very close -> large deflection angle.

Large b -> almost no deflection.

The number scattered at angle theta gave Z.

Limitations of Rutherford Model

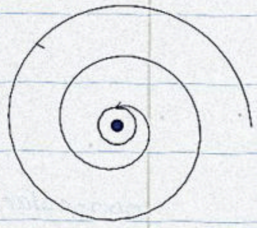
Problem 1 - Stability

An electron in a circular orbit has acceleration (centripetal). Classical EM says any accelerated charge radiates EM waves, losing energy.

Therefore the electron should :

- lose energy continuously,
- spiral into the nucleus in 10^{-8} s ?

But atoms are stable for ~~hours~~ years.



predicted
spiral fall

Problem 2 - Spectrum

Spiralling electron should emit a continuous spectrum of all frequencies.

But hydrogen actually emits a discrete line spectrum (sharp wavelengths only).

Classical physics could not explain this.
Needed a new idea $\rightarrow$ Bohr, 1913.

Bohr's Postulates (1913)

Postulate 1 - Stationary orbits

Electron revolves in certain 'allowed' circular orbits without radiating energy. These are stationary states.

Postulate 2 - Quantised angular momentum

Angular momentum is an integer multiple of $h / 2\pi$.

$$\boxed{L = m v r = n h / 2 \pi , \quad n = 1, 2, 3} \ldots$$

<- quantisation rule

$h = 6.63 \times 10^{-34}$ J s (Planck constant)

n = principal quantum number.

Postulate 3 - Frequency condition

Atom radiates / absorbs only when electron jumps between two stationary states.

$$h \nu = E_i - E_f \quad \text{(emission)}$$

$$\nu = (E_i - E_f) / h$$

$E_i > E_f \rightarrow$ emission ; $E_i < E_f \rightarrow$ absorption.

Bohr Orbit - Radius

Hydrogen - like atom : nucleus charge +Ze , electron of mass m in circular orbit of radius r , speed v .

Centripetal = Coulomb

$m v^2 / r = (1 / 4 \pi \varepsilon_0) . Z e^2 / r^2$

=> $m v^2 = Z e^2$ / (4 pi eps_0 r) ... (1)

Quantisation

$m v r = n h / 2 \pi$ ... (2)

=> $v = n h / (2 \pi m r)$

Sub in (1) and solve for r :

$\boxed{\text{r\_n = n 2 h 2 eps\_0 / (pi m Z e 2)}}$

<- radius of nth orbit

For hydrogen (Z = 1) , n = 1 :

$\boxed{\text{a\_0 = 0.529 Angstrom}}$ <- Bohr radius

So $r_n = 0.529\, n^2 / Z$ Angstrom

Radius increases as n 2.

Bohr Orbit - Velocity

From m v r = n h / 2 pi and the radius expression , the speed in the nth orbit :

$\boxed{v\_n = Z e \quad 2 / (2 eps\_0 n h)}$ <- speed in nth orbit

v decreases as 1 / n .

Innermost orbit -> highest speed.

Fine - structure constant alpha

For H (Z = 1) , n = 1 :

$v_1 / c = e^2 / (2 \varepsilon_0 h c)$

$\boxed{alpha = 1 / 137 \quad (approx)}$ <- fine - structure const.

v_1 c / 137 -> electron is non - relativistic ; Bohr's model is consistent.

Time period T

$T = 2 \pi r_n / v_n$

prop n^3 / Z^2

Frequency f = 1 / T prop Z 2 / n 3 .

Energy of the nth Orbit

Total energy $E = K.E. + P.E.$

$K.E. = (1/2)\, m v^2 = Z e^2 / (8 \pi \, \mathrm{eps}_0 \, r)$

$P.E. = - Z e^2 / (4 \pi \, \mathrm{eps}_0 \, r)$

$E = K + U = - Z e^2 / (8 \pi \, \mathrm{eps}_0 \, r)$

Substitute $r = r\_n$:

$\boxed{E\_n = - m \; e \;\; 4 \; Z \;\; 2 \; / \; (8^{*} \; \mathrm{eps}\_0 \;\; 2 \; h \;\; 2 \; n \;\; 2}$

<- energy of nth state

Plug numbers (for hydrogen $Z = 1$) :

$\boxed{E\_n = - 13.6 \; / \; n \;\; 2 \quad eV}$ <- for H atom

General hydrogen - like :

$E_n = - 13.6 \; Z^2 / n^2 \quad eV$

Energy is negative -> bound state.

$n = 1$ ground state ; $E_1 = - 13.6$ eV

$n = 2$: $E_2 = - 3.4$ eV

$n = inf$: $E = 0$ (ionised)

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Bohr Orbit Diagram (Hydrogen)

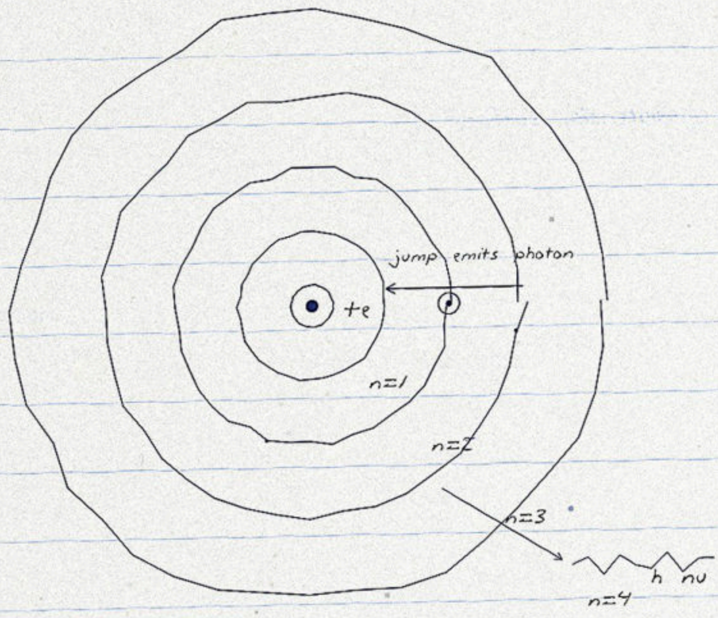


Fig. allowed orbits n = 1, 2, 3, 4 and a transition.

Orbit r__n prop n 2 ; Energy E__n prop -1 / n 2.

Higher n -> bigger orbit and less negative E.

Closest orbit = ground state.

Hydrogen Spectrum - Wavelengths

When electron jumps from higher orbit n_2 to lower orbit n_1 , photon is emitted :

$$h \nu = E_{n2} - E_{n1}$$

$$= 13.6 \ (1 / n_1^2 - 1 / n_2^2) \ \text{eV}$$

Using c = nu lambda and dividing by h c :

$$\boxed{1 / \text{lambda} = R (1 / n\_1 \ 2 - 1 / n\_2 \ 2)}$$

<- Rydberg formula

Rydberg constant

$$R = m e^4 / (8 \varepsilon_0^2 h^3 c)$$

$$\boxed{R = 1.097 \times 10 \ 7 \ m \ -1}$$ <- Rydberg's value

Equivalent form in energy units :

$$R h c = 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J}$$

Series

Each fixed n_1 -> a series of spectral lines as n_2 = n_1 + 1 , n_1 + 2 , . . .

Series limit : n_2 -> infinity .

Hydrogen Spectral Series

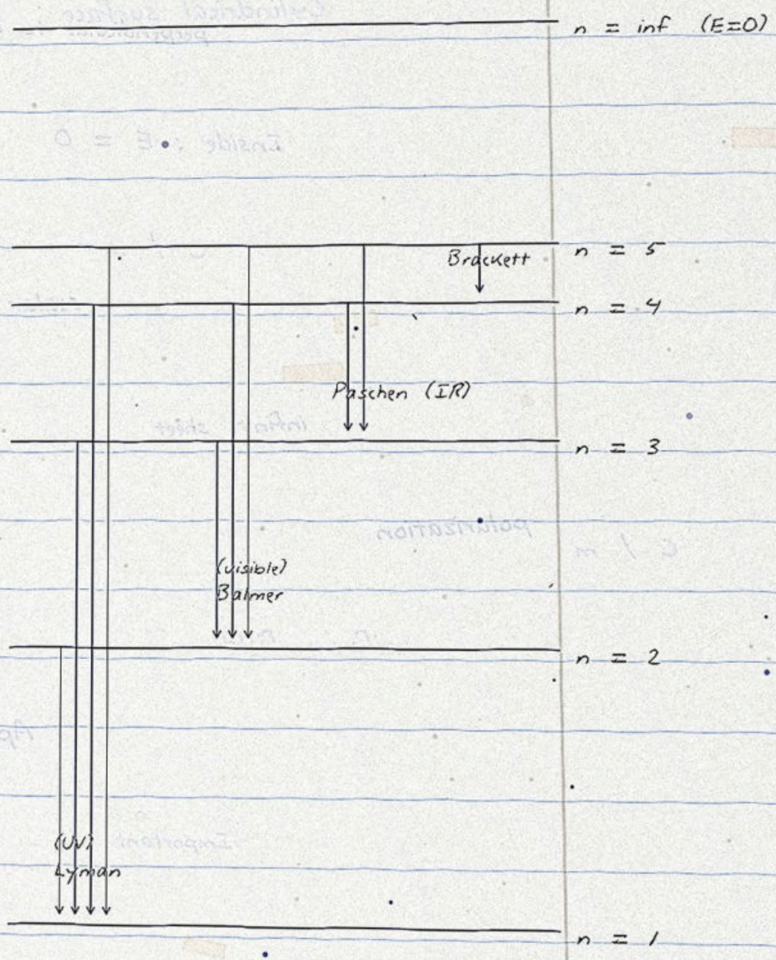


Fig. energy levels + first transitions of each series.

Five series

(1) Lyman $n_1 = 1$ UV

(2) Balmer $n_1 = 2$ visible (H_α, H_β ..)

(3) Paschen $n_1 = 3$ infra - red

(4) Brackett $n_1 = 4$, (5) Pfund $n_1 = 5$ -> far IR

Balmer Series (Visible)

Lines lying in the visible region ; found by Balmer (1885) even before Bohr.

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{n_2^{\,2}}\right)}$$

$\leftarrow$ Balmer ($n_1 = 2$)

First few lines

H_{α} : $n_2 = 3$, $\lambda = 656$ nm (red)

H_{β} : $n_2 = 4$, $\lambda = 486$ nm (blue - gr

H_{γ} : $n_2 = 5$, $\lambda = 434$ nm (violet)

H_{δ} : $n_2 = 6$, $\lambda = 410$ nm (violet)

Series limit

Take $n_2 \to \infty$:

$$\frac{1}{\lambda_{min}} = \frac{R}{4} \;\to\; \lambda_{min} = \frac{4}{R}$$

$$= 364.6 \text{ nm} \quad \text{(near UV edge)}$$

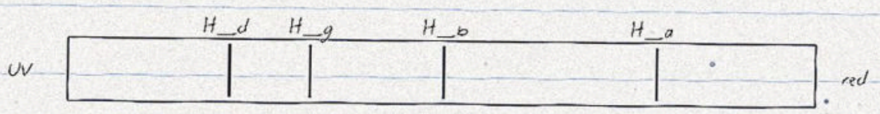


Fig. Balmer lines in visible spectrum.

Wavelengths get closer near the series limit.

Other Series of Hydrogen

Lyman series (UV)

$n_1 = 1$, $n_2 = 2, 3, 4, \ldots$

$1 / \lambda = R (1 - 1 / n_2^2)$

First line : $\lambda = 121.5$ nm (Ly - alpha)

Series limit : $\lambda = 1 / R = 91.2$ nm

Paschen series (IR)

$n_1 = 3$, $n_2 = 4, 5, 6, \ldots$

$1 / \lambda = R (1 / 9 - 1 / n_2^2)$

First line : λ 1.875 μm

Brackett series (far IR)

$n_1 = 4$, $n_2 = 5, 6, \ldots$

$1 / \lambda = R (1 / 16 - 1 / n_2^2)$

Pfund series (far IR)

$n_1 = 5$, $n_2 = 6, 7, \ldots$

$1 / \lambda = R (1 / 25 - 1 / n_2^2)$

Summary table

Series	n_1	Region
Lyman	1	UV
Balmer	2	visible
Paschen	3	IR ; Brackett 4 ; Pfund 5

Energy Level Diagram of Hydrogen

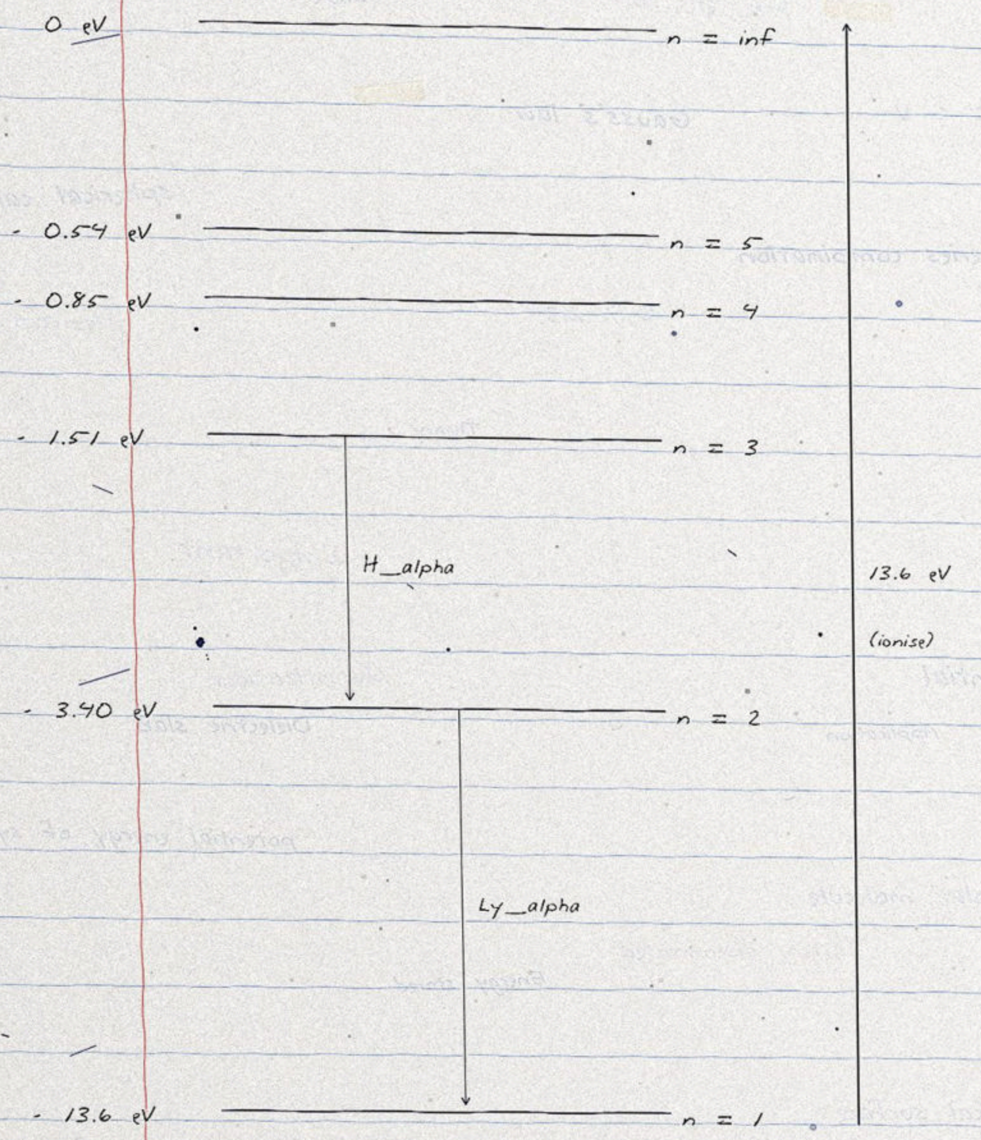


Fig. hydrogen energy ladder with sample transitions.

Ground state -> n = 1 ; E_1 = - 13.6 eV.

Energy gap shrinks rapidly with n.

Ionisation & Excitation

Ionisation energy

Energy needed to remove electron from ground state to $n = \infty$ infinity.

$E_{ion} = 0 - E_1 = 13.6$ eV (for H)

Excitation energy

Energy to lift electron from $n=1$ to a higher level n.

$$E_{ex} = E_n - E_1$$
$$= 13.6 \, (1 - 1/n^2) \text{ eV}$$

$n = 2$: $E_{ex} = 10.2$ eV

$n = 3$: $E_{ex} = 12.09$ eV

$n = 4$: $E_{ex} = 12.75$ eV

Excitation potential

Potential through which electron is accelerated from rest to reach the excitation energy :

$eV = E_{ex} \rightarrow V = E_{ex} / e$

First excitation potential of H = 10.2 V.

Ionisation potential of H = 13.6 V.

de Broglie's Explanation

Bohr's quantisation looked 'ad - hoc' until de Broglie (1924) explained it via matter waves.

Standing - wave condition

Electron has wavelength lambda = h / p .
For stable orbit , an integer number of waves must fit the circumference :

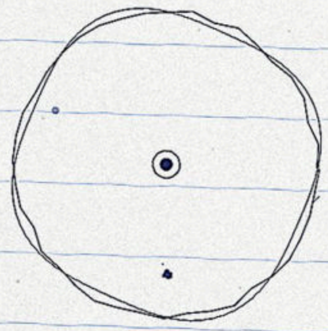
$$\boxed{2 \pi r = n \lambda}$$

<- standing wave
<- on circular orbit

$2 \pi r = n h / p = n h / (m v)$

$\Rightarrow m v r = n h / 2 \pi$. (Bohr's rule ?)

So Bohr's angular - momentum quantisation drops out naturally from wave nature.



n = 4 wave

Non - integer n -> destructive -> not allowed.

Limitations of the Bohr Model

Where it works

Excellent for hydrogen and H - like ions (He^+, Li^{2+}, Be^{3+} . . .)

Predicts wavelengths to 4 - digit accuracy.

Where it fails

(1) Multi - electron atoms : ignores e - e repulsion.

(2) Fine structure : H lines actually split into doublets / triplets ; Bohr predicts a single line.

(3) Zeeman & Stark effects : line splitting in B - or E - fields - not explained.

(4) Cannot predict intensities of spectral lines.

(5) Mixes classical orbit + quantum quantisation - philosophically inconsistent.

(6) Violates Heisenberg uncertainty principle : it assigns exact r ~~along~~ and v at once.

Resolved by full quantum mechanics (Schrodinger).

Example 1 - Wavelength of H_alpha

Q. Find the wavelength of the H_alpha line of the Balmer series (n_2 = 3 -> n_1 = 2).
Take R = 1.097 x 10 7 m -1.

Solution

Use Rydberg formula :

$$1 / \lambda = R (1 / n\_1^2 - 1 / n\_2^2)$$
$$= R (1 / 4 - 1 / 9)$$
$$= R (9 - 4) / 36$$
$$= 5 R / 36$$

$$1 / \lambda = 5 . (1.097 \times 10^7) / 36$$
$$= 1.524 \times 10^6 \text{ m}^{-1}$$

$$\lambda = 1 / (1.524 \times 10^6)$$
$$= 6.563 \times 10^{-7} \text{ m}$$

$\boxed{\text{lambda} = 656.3 \text{ nm} \quad \text{(red)}}$

<- answer

Matches the experimental H_alpha line.
This is the prominent ~~blue~~ red line
of the hydrogen spectrum.

Example 2 - Energy of $n = 2$

Q. Find the energy, orbital radius and speed of the electron in $n = 2$ state of hydrogen.

Energy

$E_n = -13.6 / n^2$ eV

$E_2 = -13.6 / 4$

$$\boxed{E_2 = -3.40 \text{ eV}}$$

Radius

$r_n = 0.529\ n^2 / 2$ Angstrom

$r_2 = 0.529 \cdot 4 = 2.116$ Angstrom

$$\boxed{r_2 = 2.12 \times 10^{-10} \text{ m}}$$

Speed

$v_n = (2.19 \times 10^6)\ 2 / n$ m/s

$v_2 = 2.19 \times 10^6 / 2$

$$\boxed{v_2 = 1.09 \times 10^{6} \text{ m/s}}$$

All three drop on going from $n = 1 \to 2$: energy less negative, orbit 4x larger, speed halved.

Example 3 - Balmer series limit

Q. Find the series limit (shortest wavelength) of the Balmer series.

Solution

Series limit -> $n_2 \to$ infinity.

$$1/\lambda_{min} = R(1/4 - 0)$$
$$= R/4$$

$$\lambda_{min} = 4/R = 4/(1.097 \times 10^7)$$
$$= 3.646 \times 10^{-7}\ m$$

$$\boxed{\text{lambda\_min} = 364.6\ nm\ \text{(near UV)}}$$

<- Balmer limit

Energy of the limit photon

$$E = hc/\lambda_{min}$$
$$= (1240\ eV\ nm)/(364.6\ nm)$$
$$= 3.40\ eV$$

Matches $E_2 = 3.40$ eV exactly :
photon from n = infinity -> $n = 2$ carries the full binding energy of $n = 2$.
(makes physical sense ?)

Chapter Summary

Models in sequence

1. Thomson - uniform + sphere with embedded e -
   Failed : alpha - scattering at large angles.

2. Rutherford - tiny dense + nucleus + orbiting e -
   Failed : instability + continuous spectrum.

3. Bohr - quantised orbits + jumps emit h nu
   Worked for H ; failed for multi - e atoms.

Master formulae

$r_n = 0.529\ n^2 / 2$, Angstrom

$v_n = 2.19 \times 10^6 \cdot 2 / n$ m / s

$E_n = -13.6\ 2^2 / n^2$ eV

$1 / \lambda = R (1 / n_1^2 - 1 / n_2^2)$

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

$L = m v r = n h / 2 \pi$

Key numbers

Bohr radius a_0 = 0.529 Angstrom

Ionisation E of H = 13.6 eV

Ground - state E_1 = - 13.6 eV ; E_2 = - 3.4 eV

Fine - struct. alpha = 1 / 137 .

Quick Revision Points

Conceptual

(i) Atom is mostly empty space.

(ii) Mass / + charge in a tiny dense nucleus.

(iii) Allowed orbits = quantised L.

(iv) Photon emission -> jump down ; absorption -> jump up.

Trends with n

r prop n^2 (orbit gets bigger)

v prop $1/n$ (slower in outer orbits)

E prop $-1/n^2$ (less bound)

T prop n^3 (longer period)

Trends with Z

r prop $1/Z$; E prop Z^2

Heavier H - like ions are smaller and more tightly bound.

Spectral - line counting

If atom is excited to level n , number of possible spectral lines emitted :

$$\boxed{N = n(n-1)/2}$$ <- useful trick