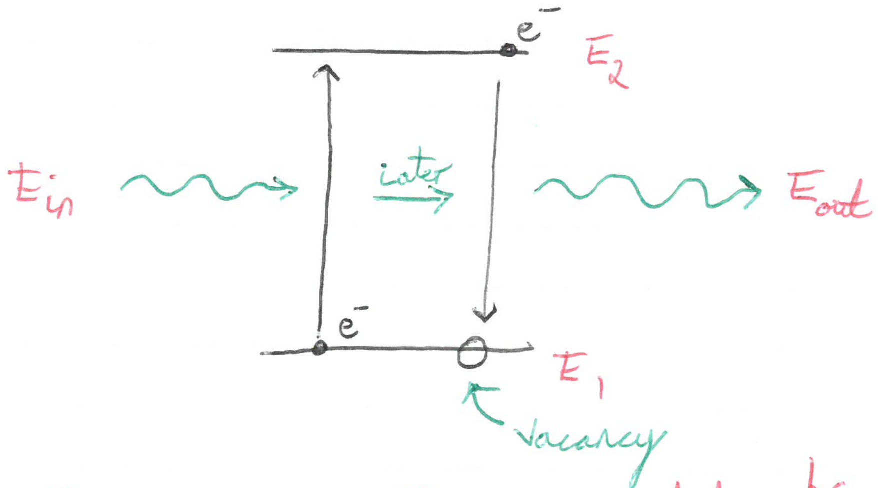
L4 Atomic Energy Levels and Spectra

- From Bohr model thinking:

  Light can only be emitted/absorbed when electrons move between certain set energy levels.

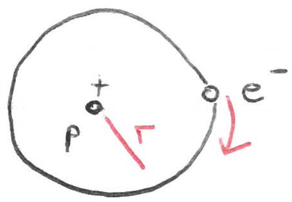


$$E_{in} = E_{out} = \underbrace{E_2 - E_1}_{E_\gamma \rightarrow \text{Photon}} = hf = \frac{hc}{\lambda}$$

|| Emission spectra examples

- Simplest case: Atomic hydrogen

(Bohr picture)



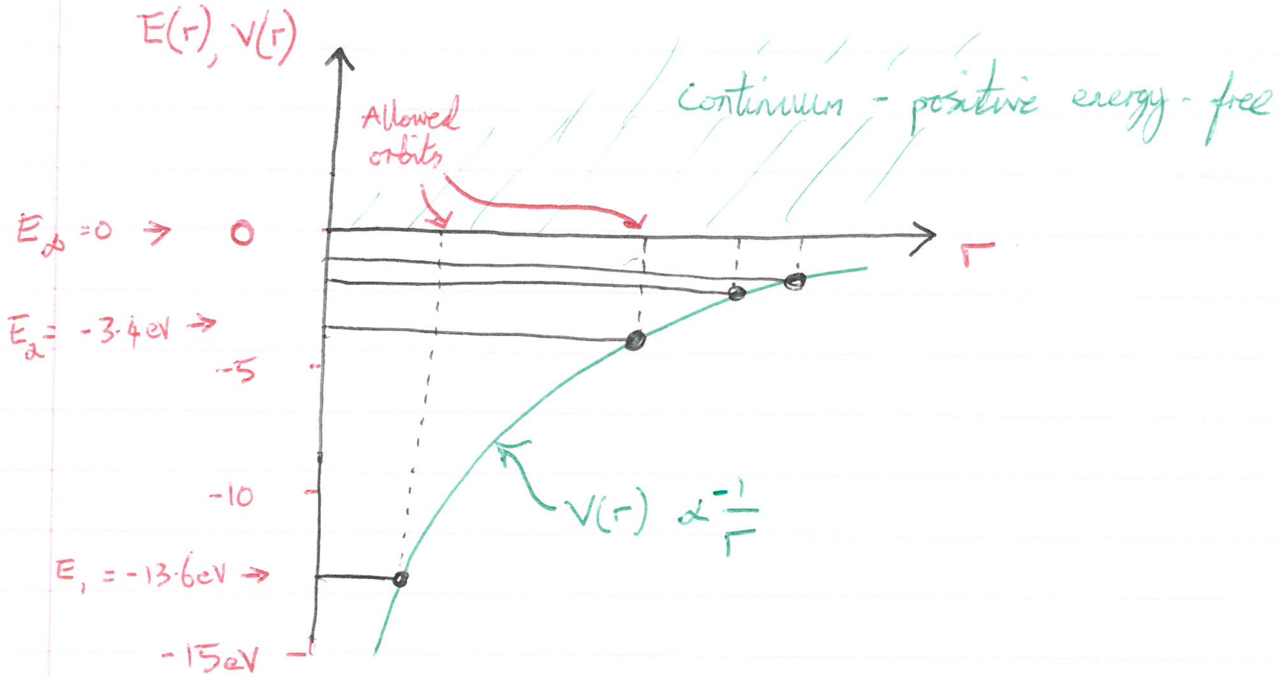
$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

Negative potential energy (trapped in potential well)

$$\underbrace{E}_{} = \overset{K.E.}{T} + \overset{P.E.}{V}$$

+ve   -ve

If total is -ve, electron is bound.
(Give it enough KE and it will escape)



In L8 we will derive, from the Bohr model

$$E_n = \frac{-13.6\text{eV}}{n^2} \qquad n = 1, 2, 3 \ldots \infty$$

Emission / absorption occurs when we move between 2 different E_n energy levels $(m \to n)$

$$E_\gamma = E_n - E_m = 13.6\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{eV}$$

$$\frac{hc}{\lambda} = 13.6\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{eV}$$

$$\frac{1}{\lambda} = \frac{13.6\ \text{eV}}{hc}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Rydberg constant $R = 1.096776 \times 10^{7}\ \text{m}^{-1}$

Check! Don't forget to × the eV value by 1.6×10^{-19} to get it into SI units to match h, c

The 'Balmer Series' happen to be at visible wavelengths

|| Balmer series

To find these, we can just set m (or n!) $= 2$

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$ (see labs!)

For $n = 3$ $(3 \to 2)$ "Balmer alpha" H_α line:

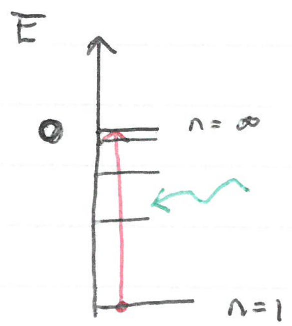
$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \Rightarrow \lambda = 656.3\ \text{nm}$$

Note: visible spectrum ~ 400 - 700 nm

Blue (400), Red (low energy) (700)

- Ionisation energy of H

Defined as energy to kick an electron out of ground state into freedom (just!)



Electron is juuust free (no KE to spare, exactly 0 energy), when $n=\infty$

Put $m=1$, $n=\infty$:

$$\frac{1}{\lambda} = R\left(\frac{1}{1} - \frac{1}{\infty}\right) = R(1-0) = R$$

→ Rydberg constant is the ionisation energy of hydrogen

Note: The energy levels can be very sharp - and don't change. Used for eg atomic clocks, gravity sensing (UoB)...

|| Cold Atoms

L4

- What about bigger atoms...?

Bigger Atoms

- If they have only <u>one</u> electron, we are ok → Bohr Model with a bigger +ve charge on the nucleus

$$E_n = Z^2 \left(\frac{-13.6 \text{ eV}}{n^2} \right)$$

Atomic number, = charge on nucleus

eg $He^+ \rightarrow Z=2$
$Li^{2+} \rightarrow Z=3$ (ions)

- If we have multiple electrons... not so ok!
  → No general formula

  (Electrons interact with each other, can't share same orbitals...)

  → Energy levels are split into sublevels/orbitals:

  $n=1 \rightarrow 1s$
  $n=2 \rightarrow 2s, 2p$
  $n=3 \rightarrow 3s, 3p, 3d$

- Electrons have an intrinsic property called 'spin'. They are spin-$\frac{1}{2}$ ('Fermions') which means they have...

2 spin states $\uparrow e^-$ $\downarrow e^-$

UP DOWN

('spin' is a very quantum thing - don't try to imagine a physical classical picture too much!)

- Maximum occupancy of each level is

$$2n^2$$

2 spin states, $\uparrow$ and $\downarrow$

$n=1 \rightarrow 2e^-$

$n=2 \rightarrow 8\ e^-$

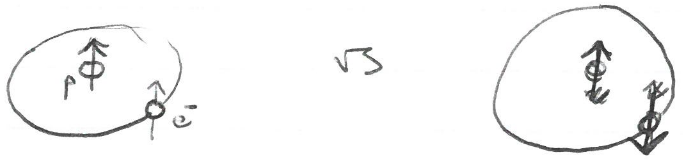
$n=3 \rightarrow 18\ e^-$

Gives the periodic table its shape!

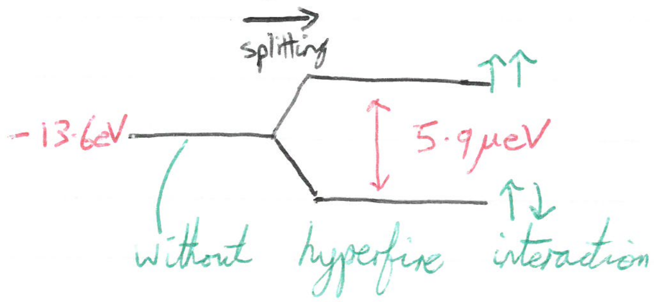
So, e.g. Sodium, $Z=11$, fills $n=1$ and $n=2$ and has 1 electron in $n=3$ (3s)

- More complexity!
  - 'Fine splitting' - electrons are moving too (non-zero angular momentum)
    ↳ Moving charge → magnetic field
      ↳ changes energy of other electrons (charged particle in a field)
  - 'Hyperfine splitting'
    Both the nucleus and the electron have spin

Parallel vs Antiparallel



→ Two configurations have (slightly) different energy.



Upper state decays, half-life 10 million years

... but there is so much H in the galaxy that radio astronomers can use this!

L4

- Conclusions

  → Looked at atomic emission / absorption

  → Bohr model lets us predict energies for H or single-e^- ions, it works

  → In general, energy levels very complex

  → Sharp spectra observed are evidence again of quantised energies