Lecture 1

Where it all Began

The Bohr Model

Adsorption / Emission spectra for Hydrogen

Johann Balmer (1885) measured line spectra for hydrogen:
364.6 nm (uv), 410.2 nm (uv), 434.1 nm (violet), 486.1 nm (blue), and 656.3 nm (red).

Both absorption and emission spectra consist of discrete lines

$$v = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where $\Re$ is the Rydberg constant (3.29×10^{15} Hz)

Balmer series $n_1=2$ and $n_2=n_1+1$, n_1+2, n_1+3 …..

Other series for $n_1=1$ (Lyman – UV), $n_1=3$ (Paschen – IR) etc.

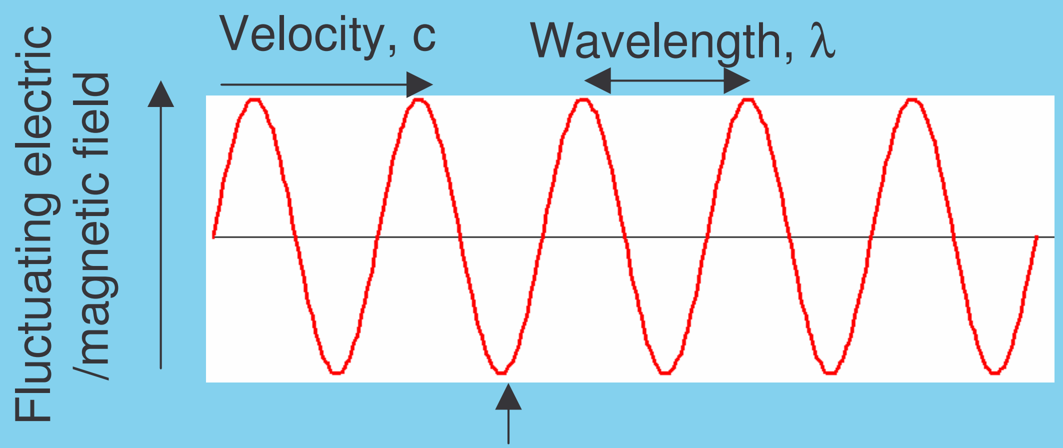
Bohr model of the atom (1913)

Assumptions

1) Rutherford (1912) model of the atom (a 'planetary model' with a central nucleus and orbiting electrons)

2) Planck (1901), Einstein (1905) – 'the energy of electromagnetic waves is quantised' into packets called photons (particle-like property)

$$E = h\nu$$



An stationary observer counts n waves passing per second } frequency = ν

Hz , cycles/sec, sec^{-1}

Bohr model of the atom

Speed of electromagnetic waves (c) is constant (ν and λ vary)

$$c = \nu\lambda, \quad \nu = c/\lambda, \quad E = h\nu, \quad E = hc/\lambda$$

As frequency and energy increases, wavelength decreases.

e.g. radiowaves:	$\lambda = 0.1$ m	X-rays:	$\lambda = 1 \times 10^{-12}$ m
	$\nu = 3 \times 10^{9}$ Hz		$\nu = 3 \times 10^{20}$ Hz
	$E = 2 \times 10^{-24}$ J		$E = 2 \times 10^{-13}$ J

E – energy (J), h – Plancks constant (J s), ν – frequency (Hz), c – speed of light (ms^{-1}), λ – wavelength (m)

Bohr model of the atom

- Classical electrodynamic theory rejected (charged particles undergoing acceleration must emit radiation)
-
- Electron assumed to travel in circular orbits.
- Only orbits with quantised angular momentum are allowed (as observed in spectra)

$$mvr = n\left(\frac{h}{2\pi}\right)$$

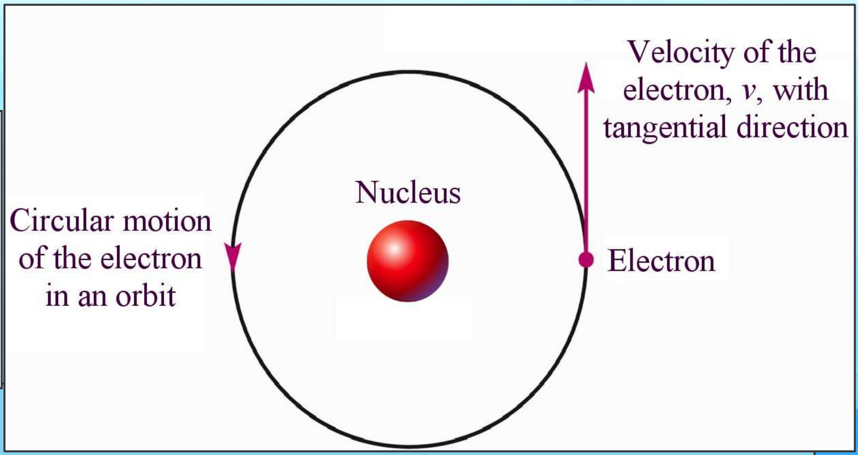
- Electromagnetic radition is adsorbed or emitted only when electrons jump from one orbit to another

$$\Delta E = E_a - E_b$$

where a and b represent the energy of the initial and final orbits

Bohr model

For a H atom an orbit is maintained only when the centrafugal force acting on the electron equals the force of attraction between it and the nucleus



These two forces must be balanced

1) Centrapedal (electrostatic) $F = \dfrac{Ze^2}{4\pi\varepsilon_0 r^2}$ $PE = \dfrac{-Ze^2}{4\pi\varepsilon_0 r}$

2) Centrafugal $F = \dfrac{mv^2}{r}$ $KE = \dfrac{1}{2}mv^2$

Equalize forces

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \Rightarrow mv^2 = \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Resulting energy

$$E = \frac{1}{2}mv^2 + \frac{-Ze^2}{4\pi\varepsilon_0 r} = \frac{-Ze^2}{8\pi\varepsilon_0 r} = -\frac{1}{2}mv^2$$

Z – nuclear charge, e – electron charge, ε_0- permittivity of free space, r - radius of the orbit, m – mass of electron, v – velocity of the electron

Energy levels of Hydrogen

Substitute quantised momentum into energy expression and rearrange in terms of r (radius) (see handout for details if this annoys you !)

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi m Z e^2} \quad = \quad \frac{n^2 a_0}{Z}$$

Radius (r) depends on ***n2*** and $\boldsymbol{\frac{1}{Z}}$

a_0 (Bohr) radius of the 1s electron in Hydrogen 52.9 pm (*n*=1, *Z*=1)

Substitute r back into energy expression give

$$E_n = \frac{-mZ^2 e^4}{8n^2 h^2 \varepsilon_0^2} \quad = \quad \frac{13.6056 \times Z^2}{n^2} \textbf{(in eV)}$$

Energy of 1s electron in H is 13.6056 eV = 0.5 Hartree
(1eV = 1.602×10^{-19} J)

Energy (E) depends on $\frac{1}{n^2}$ and $\boldsymbol{Z^2}$

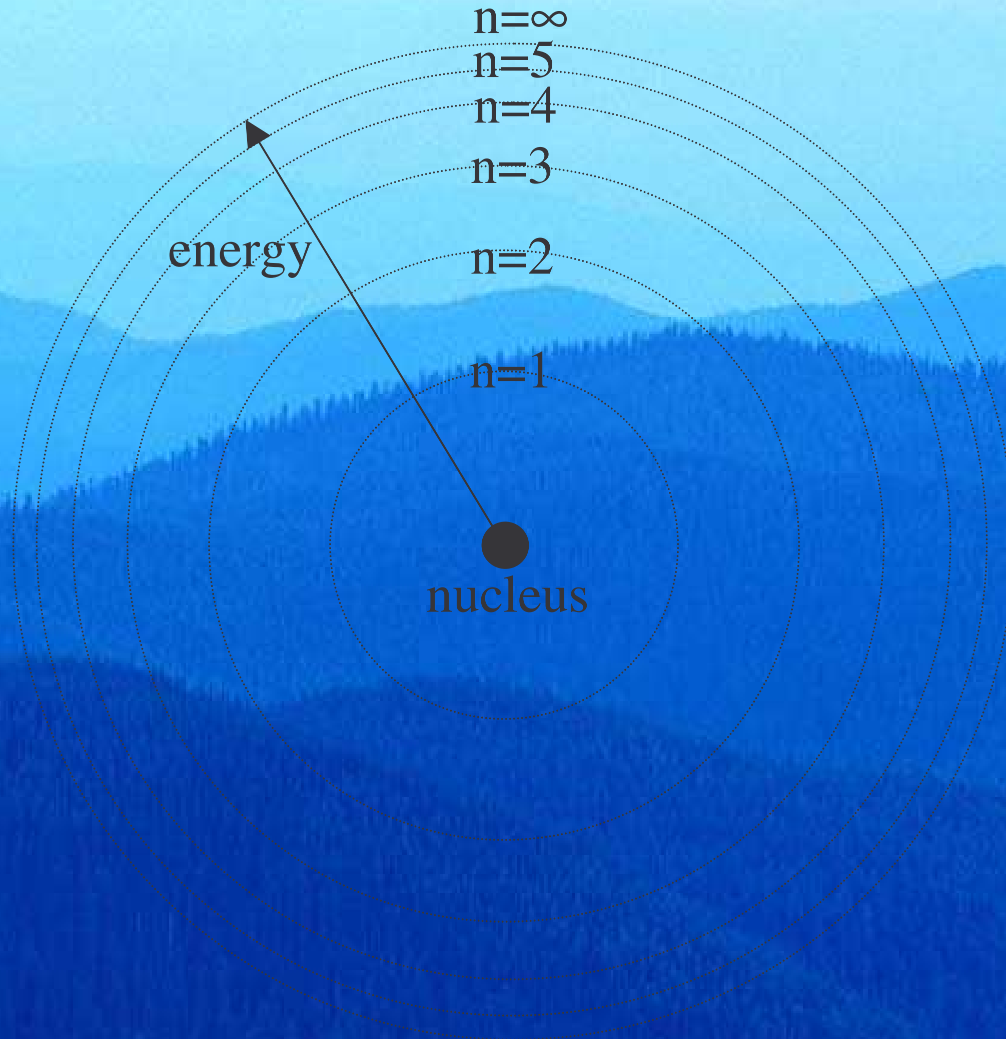
Energy levels of Hydrogen

For hydrogen (Z=1)

$r = n^2 a_0$ $\qquad$ $E_n = \dfrac{-13.6056}{n^2}$

n	energy (eV)
1	-13.6056
2	-3.4014
3	-1.5117
4	-0.8504
5	-0.3779
∞	0.0000

Ionization energy = -13.6056 eV



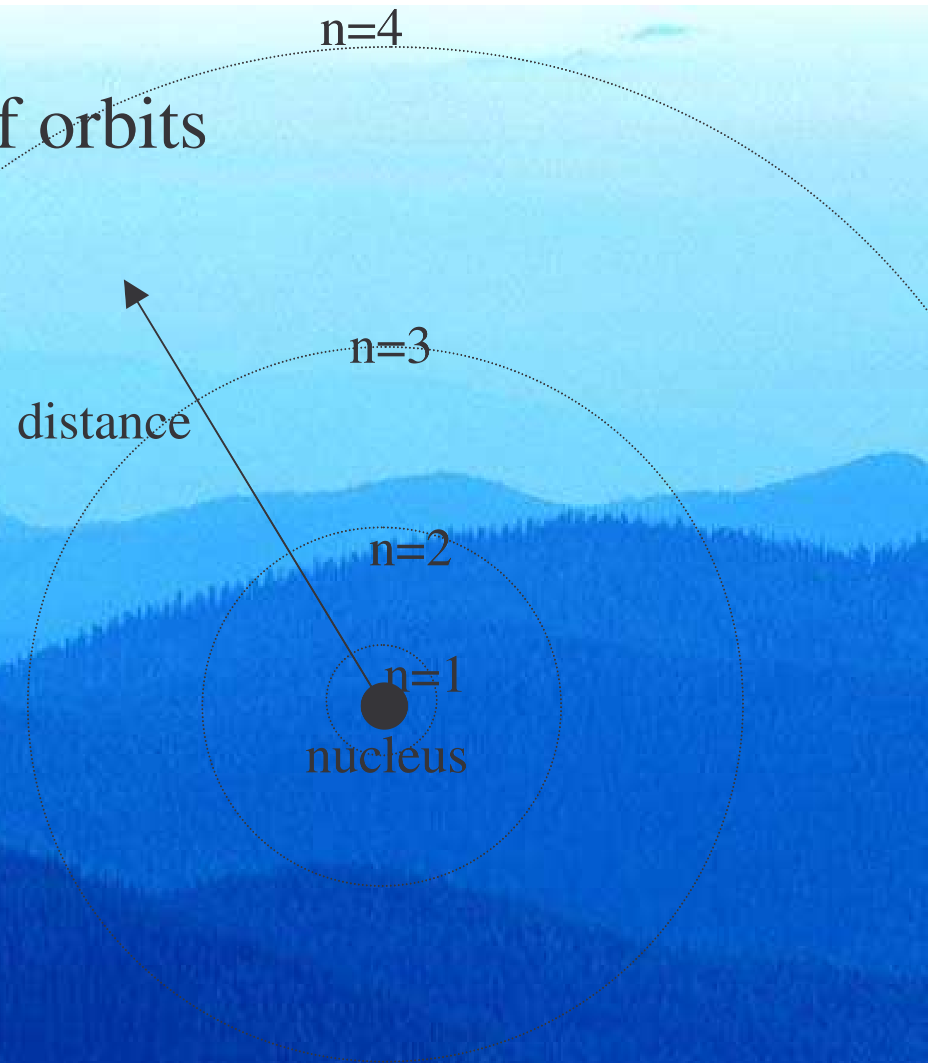
Note. The spacing reflects the energy not the radius of the orbit.

Radius of orbits

For hydrogen (Z=1)

$r = n^2 a_0$ $\qquad E_n = \dfrac{-13.6056}{n^2}$

n	energy (eV)	r (pm)
1	-13.6056	52.9
2	-3.4014	211
3	-1.5117	476
4	-0.8504	847
5	-0.3779	1322
∞	0.0000	∞



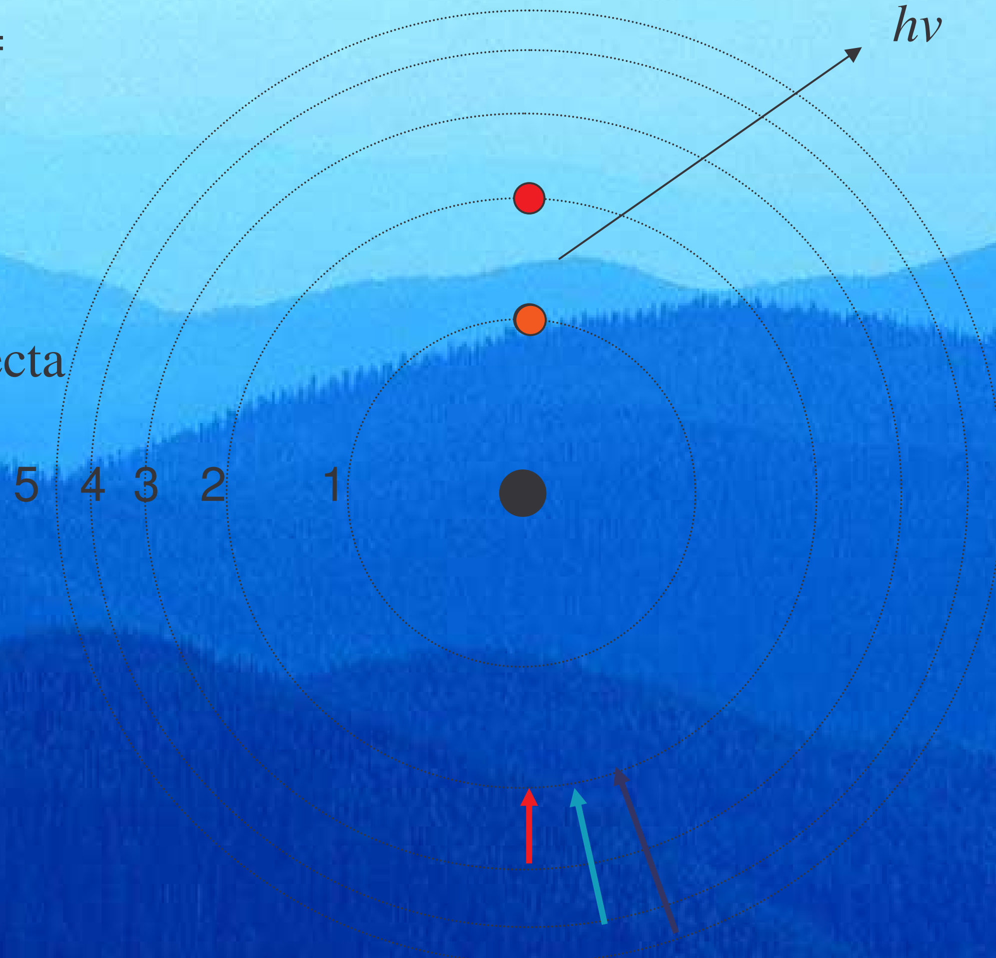
Note. The spacing reflects the radius of the Orbit – not the energy.

Emission spectra

Energy of emission is $E_{initial}$ - E_{final}=

$$\Delta E = 13.6056\left(\frac{1}{n_{inital}^2} - \frac{1}{n_{final}^2}\right)$$

Same form as fitted to emission specta



Balmer series (→ n=2)

n=3 → n=2 → λ = 656 nm

n=4 → n=2 → λ = 486 nm

n=5 → n=2 → λ = 434 nm

$\Re$ = 13.6056 eV / c = 3.29×10^{15} Hz

Note. The spacing reflects the energy not the radius of the orbit.

Problems with the Bohr Model

- Only works for 1 electron systems
  - E.g. H, He^{+}, Li^{2+}
- Can not explain splitting of lines in a magnetic field
  - Modified Bohr-Sommerfield (elliptical orbits - not satisfactory)
- The model cannot interpret the emission spectra of complex atoms
- Electrons were found to exhibit wave-like properties
  - e.g. can be diffracted as they pass through a crystal (like x-rays)
  - considered as classical particles in Bohr model

Bohr model – calculating the energy and radius

- Energy

$$\frac{-Ze^2}{8\pi\varepsilon_0 r} = -\frac{1}{2}mv^2$$

- Quantised angular momentum

$$mvr = n\left(\frac{h}{2\pi}\right)$$

- Combining the two

$$\frac{-Ze^2}{8\pi\varepsilon_0 r} = -\frac{1}{2}mv^2 = \frac{-(mvr)^2}{2mr^2} = \frac{-n^2h^2}{8\pi^2 mr^2}$$

- Rearranging to give r

$$\frac{r^2}{r} = \frac{-n^2h^2}{8\pi^2 m}\frac{8\pi\varepsilon_0}{\left(-Ze^2\right)} \qquad r = \frac{n^2h^2\varepsilon_0}{\pi mZe^2}$$

- Substitute r into energy gives

$$\frac{-Ze^2}{8\pi\varepsilon_0 r} = \frac{-mZ^2e^4}{8n^2h^2\varepsilon_0^2}$$

- Energy is dependent on n^2 and Z^2 (for one electron systems 2s and 2p energies are the same)

Wave / particle duality

de Broglie (1923)

proposed that particles could have wave properties (wave/particle duality). Particles could have an associated wavelength (λ)

It was accepted that electromagnetic radiation can have wave and particle properties (photons)

$$E = mc^2, \quad E = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{h}{mc}$$

No experimental at time.

1925 Davisson and Germer showed electrons could be diffracted according to Braggs Law (used for X-ray diffraction)

Numerically confirm de Broglie’s equation

Introducing Wave Mechanics

- For waves: it is impossible to determine the position and momentum of the electron simultaneously – Heisenberg 'Uncertainty principle'

- Use probability of finding an electron from $\boldsymbol{\psi^2}$ (actually $\psi^*\psi$ – but functions we will deal with are real)

  Where $\boldsymbol{\psi}$ is a solution of the Schrödinger equation (1927) and is a wavefunction.

  The time-independent form of the Schrödinger equation for the hydrogen atom is and needs to be solved in 3-dimensional space:

$$\underbrace{\boxed{\frac{-h^2}{8\pi^2 m}\nabla^2}}_{\text{Kinetic energy}}\Psi \quad \underbrace{\boxed{\frac{-e^2}{4\pi\varepsilon_0 r}}}_{\text{Potential energy}}\Psi = \underbrace{\boxed{E}}_{\text{Total energy}}\Psi \qquad \nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Solutions of the Schrödinger equation for H

- Schrödinger equation can only be solved exactly for one electron systems
  - Solved by trial and error manipulations for more electrons

- **Solutions of the equation naturally give rise to 3 quantum numbers describing a three dimensional space called an atomic orbital:**

- *n, l, m* (and spin quantum number describing the electron s)

n = principal quantum number, defines the orbital size with values 1 to ∞

l = azimuthal or angular momentum quantum number, defines shape. For a given value of n, l has values 0 to (n-1).

m_l = magnetic quantum number, defines the orbital orientation. For a given value of l, m_l has values from $+l$ through 0 to $-l$.