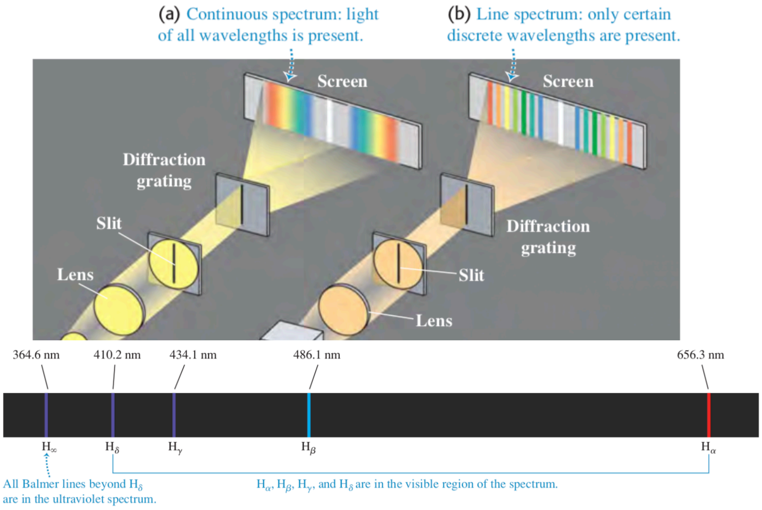


3 Atomic structure

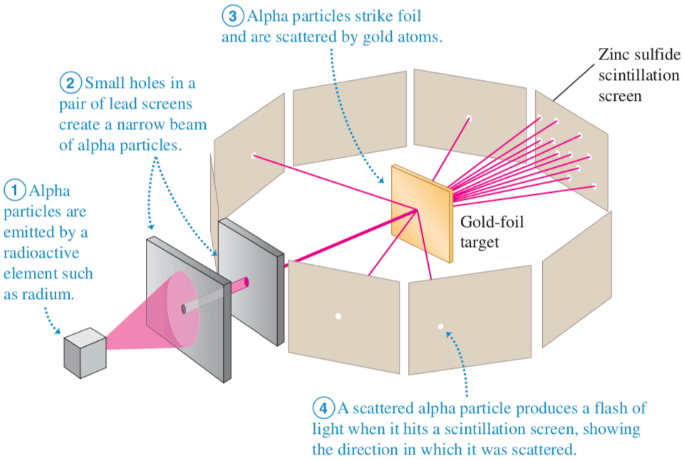
Experiments on gas excited by an electrical discharge showed that the heated gas produced monochromatic lines!! This is not the sort of continuum radiation we are used to seeing from hot material eg coal, electric fire elements etc - blackbody radiation which is what we get from dense material. For gas which is quite dilute, we instead get emission only at very specific energies - lines - e.g. sodium streetlights are yellow because most of the emission is in two distinct lines in the yellow part of the spectrum!

for hydrogen, Balmer found that these lines had a well defined wavelength $\lambda = 363.5[n^2/(n^2-4)]$ nm for $n \geq 3$ integer! so n=3 gives 654nm, n=4 is 468, n=5 is 433nm, as observed! but WHY??

3.1 Models of atoms

Around about the same time there was a revolution in ideas about atomic structrue. The mass and charge of the electron was known, and it was known that most of the mass of an atom was associated with +ve charge not -ve electrons, and that the dimensions of the atom were $\sim 10^{-10}$ m.

Rutherford used a narrow beam of alpha particles (Helium nuclei) on a gold foil target. mass of electron is 1840x less than proton and alpha particle has



2 protons and 2 neutrons so its mass is 7300x larger and electrons cannot appreciably deflect an alpha particle as its momentum is huge in comparison. but some alpha particles were deflected by almost 180 degrees! So they had to be deflected by something much heavier than an electron. The KE of the alpha particles was known, so using the electrostatic potential $V(r) = qQ/(4\pi\epsilon_0 r)$ they found the minimum distance they needed. for He with energy of 4.5MeV=7.27×10^{-13} J then this minimum distance is when we have maximum +ve charge stopping the He nucleus, so $r = qQ/(4\pi\epsilon_0 KE) = 2 \times 79/(4\pi\epsilon_0 7.27 \times 10^{-13}) = 5 \times 10^{-14}$ m, more than 4 orders of magnituyde smaller than the size of the atom.

so this model can explain how large angle scattering can occur, but gives other problems. if we try to bind static -ve electrons to the +ve nucleus then they should simply accelerate towards the attractive charge. So Rutherford proposed that they orbited the nucleus, like planets orbit the Sun in an attractive (gravitational) potential. but circular orbits mean acceleration, and we know from EM that accelerating charges radiate. so the electrons should radiate EM waves and lose energy. so they spiral in! and atoms shouldn't exist.

BUT THEY DO! so the picture is WRONG. electrons are not orbiting around like little planets. electrons are not little billiard balls. they are WAVY. And so they have Heisenburg Uncertainty

$$E_{tot} = KE + PE = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

but $\Delta x \Delta p_x > \hbar/2$ so $p \geq \Delta p = \hbar/(2r)$

$$E_{tot} = \frac{\hbar^2}{8mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

This goes to ∞ as $r \to 0$ so the electron can't collapse into the nucleus.

3.2 Bohr model of the atom

waves have wavelength - and can travel. but waves trapped in a potential interfere with themselves and set up standing waves. standing waves don't travel so don't accelerate so electrons as standing waves don't radiate!!

standing waves can only get set up at certain positions - need the wave to reinforce itself. so then there are only certain distances from the nucleus that the standing wave can exist. and these will be quantised by the number of wavelengths in the standing wave. but distance means energy as the electrostatic potential is $qQ/(4\pi\epsilon_0 r)$ so quantised distances for quantised standing waves means quantised energy. and then we can explain the specific energies of emission/absorption in atoms as the photon energy required to make the transition between 2 different standing wave patterns.

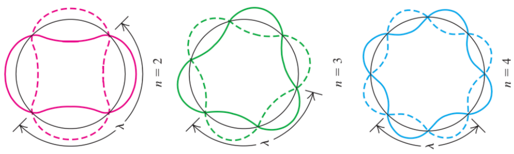
if the electrons are orbiting in a plane then we have $2\pi r_n = n\lambda$ and combine with $\lambda = h/p = h/(mv_n)$ so

$2\pi r_n = nh/(mv_n)$ so $mv_n r_n = nh/(2\pi) = n\hbar = L_n$ - angular momentum is quantised!!

the observation that atoms are stable means that each atom has a lowest level - ground state. levels with higher energy are called excited states.

Bohr postulated that

1) electrons move in circular orbits under coulomb attraction



2) these are stable orbits where the electrons do not radiate

3) these stable orbits have angular momentum $L_n = mv_nr_n = nh/(2\pi) = n\hbar$

4) transitions from orbit of energy E_i to E_f are accompanied by emission of radiation $hf = E_i - E_f$

So lets work this out - for a hydrogen-like ion we have forces on circular orbits

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

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

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

$$v_n n\hbar = \frac{Ze^2}{4\pi\epsilon_0}$$

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} = \frac{Ze^2}{2\epsilon_0 nh}$$

and then we can solve for $r_n = n\hbar/(mv_n)$

$$r_n = n\hbar \frac{2\epsilon_0 nh}{Ze^2 m} = n\frac{h}{2\pi}\frac{2\epsilon_0 nh}{Ze^2 m}$$
$$= \frac{\epsilon_0 n^2 h^2}{m\pi Ze^2} = a_0 n^2/Z$$

where $a_0 = \epsilon_0 h^2/(m\pi e^2) = 5 \times 10^{-11}$ m

so now we know KE and PE as

$$K = \frac{1}{2}mv_n^2 = \frac{1}{2}m\frac{(Ze^2)^2}{(2\epsilon_0 nh)^2} = \frac{mZ^2e^4}{8\epsilon_0 n^2 h^2}$$

$$U_n = -\frac{Ze^2}{4\pi\epsilon_0 r_n} = -\frac{Ze^2 \times Ze^2 m\pi}{4\pi\epsilon_0\epsilon_0 n^2 h^2}$$

$$= -\frac{Z^2e^4m}{4\epsilon_0^2 n^2 h^2}$$

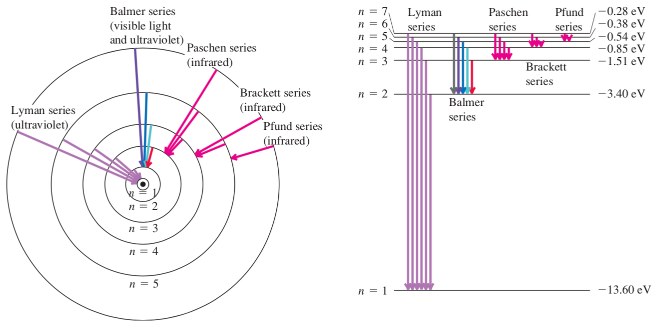
total energy

$$E_n = K_n + U_n = -\frac{Z^2e^4m}{8\epsilon_0^2 n^2 h^2}$$

energy difference between levels.

$$hf = E_i - E_f = -\frac{Z^2e^4m}{8\epsilon_0^2 h^2}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

Example: for hydrogen, $Z = 1$ and the constant is 2.18×10^{-18} but $hf = hc/\lambda$ so $1/\lambda = 1.1 \times 10^7 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$



(a) Permitted orbits of an electron in the Bohr model of a hydrogen atom (not to scale). Arrows indicate the transitions responsible for some of the lines of various series.

(b) Energy-level diagram for hydrogen, showing some transitions corresponding to the various series

so for transitions from $n_i = 1$ we have the Lyman series n=1-2 is $\lambda = 1.21 \times 10^{-7}$ m $= 121$ nm, and $n = 1 - 3$ is 102 nm and $n = 1 - 4$ is 97.0 mn. But these are all in the UV region of the spectrum where instruments were not so developed as in the optical.

if instead we look at transitions to $n_i = 2$ then this is called the Balmer series. so we have

$$\frac{1}{\lambda} = 1.1 \times 10^7 \left[\frac{1}{4} - \frac{1}{n_f^2}\right]$$

so $n = 2 - 3$ is 654 nm. $n = 2 - 4$ is 484 nm... and we can re-arrange

$$\frac{1}{\lambda} = 1.1 \times 10^7 \left[\frac{1}{4} - \frac{1}{n_f^2}\right]$$

$$\lambda = 363.5 \frac{n_f^2}{n_f^2 - 4} \; nm$$

which is the Balmer series formula that had been discovered by experiment!!

3.3 limitations of Bohr model

Its amazing that it gets the transition energies right!! but its some horrid mixture of classical and quantum concepts - we got here by assuming electrons were wavy but then we treated them as if they had KE and position like a particle, which doesn't mkae sense with the uncertainty principle!

and it actually violates the uncertainty principle much more directly - it assumes that the electron moves in a plane around the nucleus. Let's call this the xy-plane, so the z-axis is perpendicular to the plane. Hence the Bohr model says that an electron is always found at $z = 0$ AND that its z-momentum, p_z, is always zero (the electron does not move out of the xy-plane). But this implies that there are no uncertainties in either z or p_z, which directly contradicts $\Delta z \Delta p_z \geq \hbar/2$. so it fundamentally can't be correct. but it gives such a good match to reality that it must encompass something fundamental about reality!