The Bohr Model of the Hydrogen Atom

History

- Around 1803, John Dalton resurrects the Ancient Greek idea of atoms after noticing that chemical reactions take place fastest or most efficiently with certain proportions of reactants. The idea gains ground for the rest of the 19^{th} Century, including Dmitri Mendeleev's proposal in 1869 of what we now call the Periodic Table.

- In 1897 at the Cavendish Lab in Cambridge, JJ Thomson discovers that electrons have a negative charge* and proposes that electrons are a fundamental component of all atoms. Since it was known that atoms must be neutral overall (otherwise matter in general would normally have a net charge), there must also be positively-charged material in an atom. This leads Thomson to propose his plum-pudding model in 1898.

- From 1909 to 1911, Ernest Marsden, working under Hans Geiger and Ernest Rutherford at Manchester University, finds that α-particles almost all pass through Gold leaf, and about 1 in 8 000 are deflected back. This means that well over 99% (in fact, $\left(\frac{7\,999}{8\,000}\right)^{3/2} \approx 99.98\%$) of the volume of an atom must be empty space. In 1911, Rutherford proposes a nuclear model of the atom as a refinement of Thomson's model to fit these findings.

- From 1906 to 1913, Robert Millikan performed experiments with charged oil droplets and found evidence that charge is quantised in units of 1.6×10^{-19} C. This was combined with other work to suggest that all electrons carry exactly this amount of charge.

The big question that remained was about how the electrons were arranged in an atom. Rutherford briefly considered a simple solar-system model, but realised this could not be true since an electron in an orbit would be (centripetally) accelerating, and accelerating charges must radiate EM waves. This would mean the electrons would emit photons, lose KE and spiral inwards towards the nucleus within a fraction of a second, meaning normal atomic matter could not exist. Which was a bit of a problem.

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* More precisely, he measured the mass-to-charge ratio ($\frac{m}{e}$) for electrons and showed that this ratio was the same irrespective of what atoms the electrons had come from, suggesting they were fundamental.

Also, it had been known from spectroscopy for decades that all elements emitted spectra with very precisely defined frequencies (thin bright lines) when electrically excited. This suggested that only light of very specific energies ($E = hf$) could be emitted from atoms.

Could all this be explained with one model?

In 1913, Neils Bohr proposed a modification of the solar system model, with these additional assumptions:

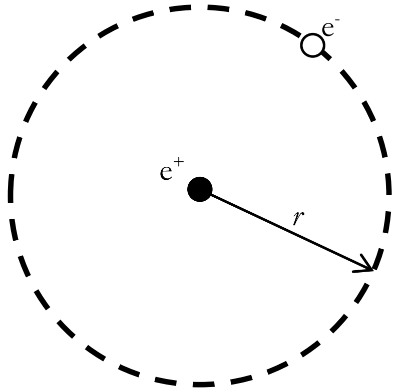
- Each electron can only orbit the nucleus with a very specific orbital radius
- The angular momentum[†] of the electron in an orbit can only be equal to an integer multiple of $\frac{h}{2\pi}$. He had no fundamental theoretical basis for this claim, but then neither did Newton in 1687 when he published his Law of Gravitation[‡].

We can use a decent chunk of A-level Physics to show how Bohr's model fits the known experimental data for Hydrogen.

[†] Remember that Linear momentum = $p = mv$. The rotational equivalent is called Angular momentum = $L = I\omega$ where $I = mr^2$ for a particle in a circular orbit, and $\omega = \frac{v}{r}$.

[‡] When addressing this issue, Newton famously states, at the end of the 1713 second edition of *Principia* (the book in which he published his laws of motion and gravitation), 'hypotheses non fingo' ['I do not feign hypotheses' or, colloquially, 'I don't pretend to know'].

We start by modelling Hydrogen, the lightest and simplest atom. A single electron orbits a single proton in a circular path of radius r:



1) What force provides the centripetal force for the orbit?

2) Give an expression for this force, and set it equal to $\frac{mv^2}{r}$ (for circular motion)

3) Now rearrange this equation to get an expression for the KE $\left(=\frac{1}{2}mv^2\right)$ of the electron in its orbit.

4) Give an expression for the EPE of the electron at distance *r* from the proton.

5) Now add the expressions for KE and PE to find the total energy of the electron in the atom[§].

[§] You should end up with a *negative* value, since the electron is in a *bound* state in the orbit (*i.e.* it needs to be given energy to escape).

We now pause at this stage, and go to Bohr's assumption about the electron only being allowed to be in orbits with certain energies.

6) Take the expressions from the footnote on the second page and get an expression for the angular momentum. Then set it equal to the expression further up the page involving h, using n as a dummy integer value.

7) Now go back to the equation you wrote down in 2) and use it to find an expression for v.

8) Substitute this expression for v into the expression you gave for question 6) and solve to get an expression for the radius of the orbit, r.

9) When $n = 1$, we should then be able to calculate the theoretical radius of a Hydrogen atom and compare it to reality. The measured value is 52.9 pm**. What is your theoretical value?

10) Nearly there. Now all we need to do is substitute your expression for r (from q8) back into the expression for E (from q5), simplify and then we can check our results against the measured energies from the Hydrogen emission spectrum. Off you go:

** This value is known as the Bohr radius of the Hydrogen atom and is commonly used in nuclear physics

11) Calculate values for E when n = 1, 2 and 3[††]. Convert your values into eV.

Now, if the wavelengths of the emission lines in the Hydrogen spectrum correspond to these energies, than our theory will fit with practice.

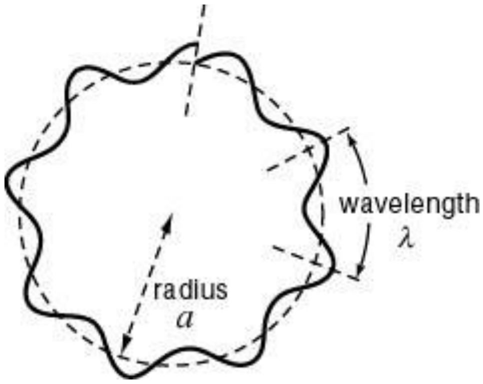
12) Here are some measured frequencies of light emitted by excited Hydrogen atoms: 91.4 nm, 365 nm and 823 nm[‡‡].
Show that these wavelengths correspond to the same Energy values you just calculated in question 11 and shout Hip Hip Hooray.

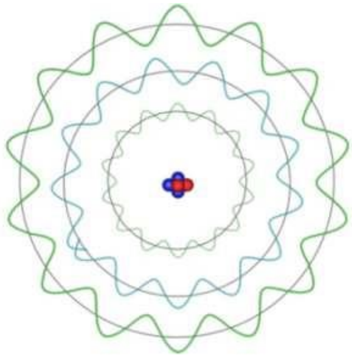
†† Your calculator may not like the powers of ten involved in this. You need to go Old School, and calculate the powers of ten separately – just add and subtract as required – then do the numbers (or *mantissae* as we used to call them) and then put it all together.

‡‡ These are actually the shortest wavelength lines from each of the Lyman, Balmer and Paschen series (respectively) of Hydrogen emission lines. Since the *shortest* wavelength will correspond to the *biggest* Energy gaps (because $\Delta E \propto \frac{1}{\lambda}$), these three lines are therefore caused by electrons de-exciting from an unbound state (*i.e.* ionized) to the lowest three energy levels of a Hydrogen atom.

At this stage, everyone got very excited. Spectral lines, which had been observed for decades, finally had a theoretical model to explain them. Sadly, the excitement was short-lived. The Bohr model gave no explanation for why some spectral lines were much brighter than others, for example, and it also gave false predictions of the wavelengths of spectral lines for atoms more complex than Hydrogen.

Over the next 20 or so years, further refinements were made to the model. In 1923, de Broglie proposed that all particles with momentum have an associated wavelength $\left(\lambda = \frac{h}{p}\right)$, which gave a justification for Bohr's electrons only being permitted to orbit with specific radii. The permitted orbits occur when an integer multiple of the electron's wavelength fits into the orbital circumference. The idea was that some sort of constructive superposition 'allowed' the orbit to occur:





Later in the 1920s, Werner Heisenberg and Erwin Schrödinger generalised Quantum Theory to give a fuller theory which could be applied to a wider range of systems. Wolfgang Pauli then added ideas about two electrons not being able to be in the same energy state at the same time (1925), and Heisenberg formulated the Uncertainty Principle (1927) which showed that it would be impossible to simultaneously know an electron's position and momentum to a certain degree of accuracy $\left(\Delta p \Delta x \geq \frac{h}{2\pi}\right)$: we were starting to see that electrons in atoms were nowhere near as straightforward as normal matter as we encounter it.

Finally, we ended up with a purely statistical description which showed how electrons only can be said to have a certain *probability* of being in a certain place at a certain time. This makes little intuitive sense, but it fits with all other theories and gives the 'right answers' in the way that the – intuitively nicer – solar system model doesn't. Despite this, nearly 100 years later, we still rather stubbornly want to think of atoms behaving like mini solar systems and often end up confusing ourselves as a result.

Summary

Explaining what atoms are and what happens within them was one of the great intellectual triumphs of the early 20th Century. In less than 50 years, we had gone from simple solid indivisible atoms to atoms which didn't behave like anything we had ever suspected could even exist. In Physics, we call this Progress.