Lecture 36
(Atomic Spectra)

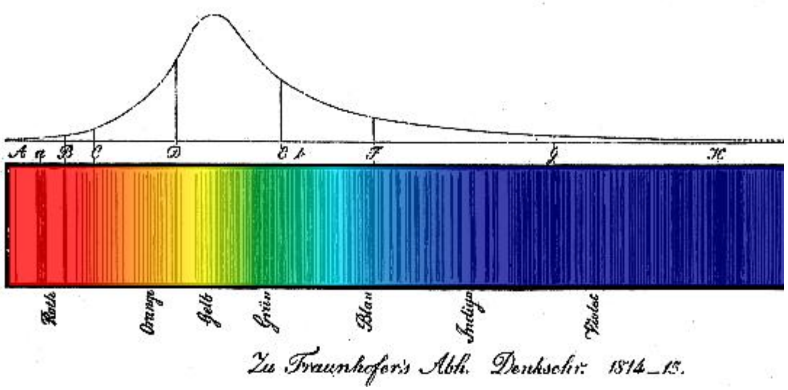
Physics 2310-01 Spring 2020

Douglas Fields

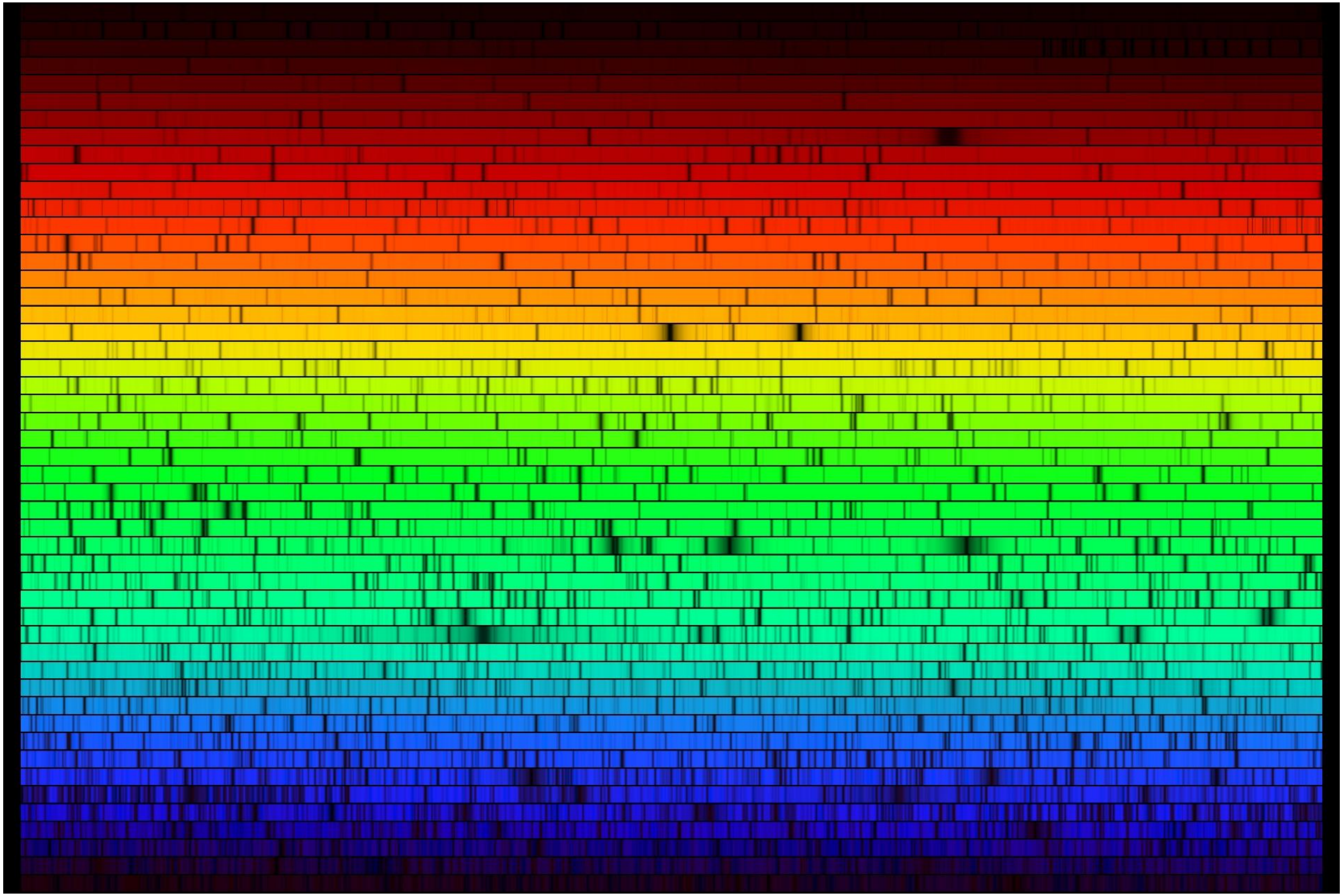
Fraunhofer Lines

- In the late 1700s and early 1800s, one of the premier skills was that of glassmaker. Joseph Fraunhofer became one of the most skilled and sought after glassmakers.
- He discovered a large set of missing colors in the solar spectrum while looking for a bright line instead.

Thus in 1814, Fraunhofer invented the spectroscope. In the course of his experiments he discovered the bright fixed line which appears in the orange color of the spectrum when it is produced by the light of fire. This line enabled him afterward to determine the absolute power of refraction in different substances. Experiments to ascertain whether the solar spectrum contained the same bright line in the orange as that produced by the light of fire led him to the discovery of 574 dark fixed lines in the solar spectrum; millions of such fixed absorption lines are now known. - Wikipedia

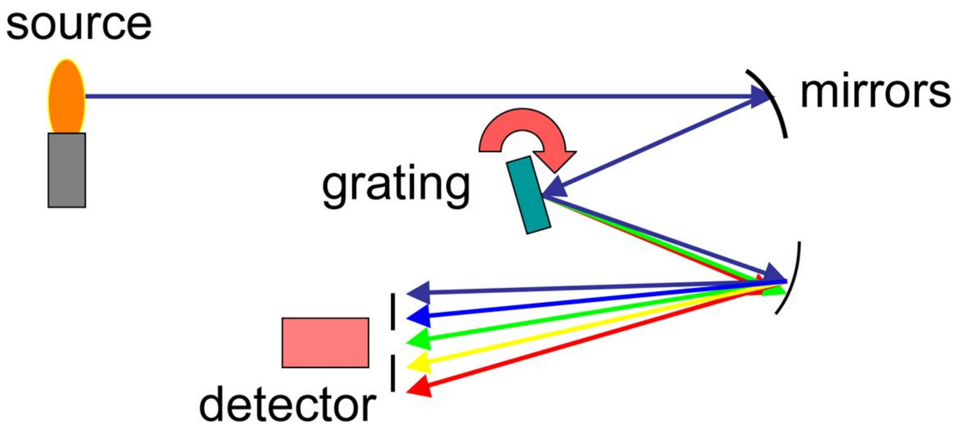


He missed a few…



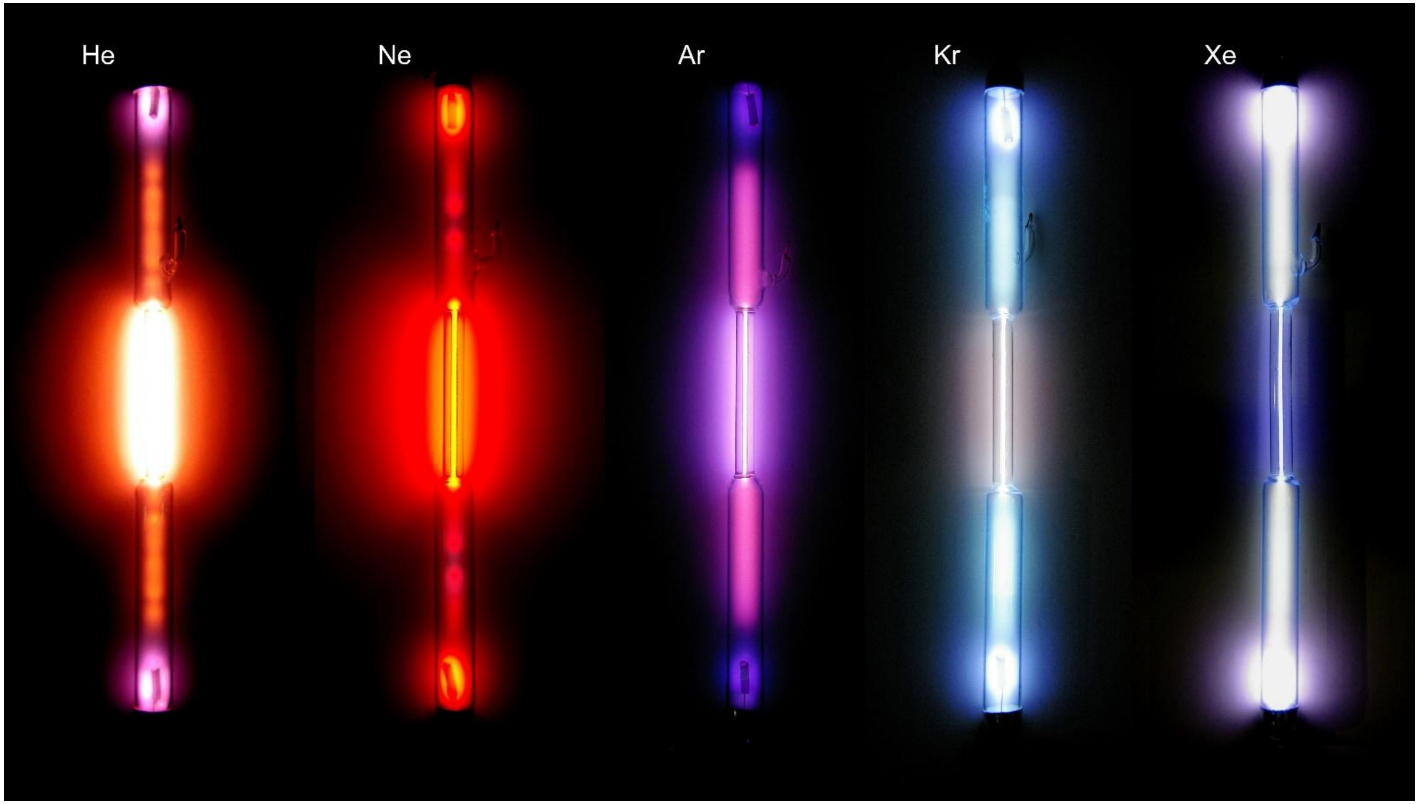
Emission Lines

- About the same time, people were using flame emission spectroscopy to see that different materials emitted light of specific frequencies when heated to high enough temperatures that they became heated gases.



Emission Lines

- Another way to do this is to pass an electric current through a gas, thermally heating it and seeing the spectra of light emission using a diffraction grating.



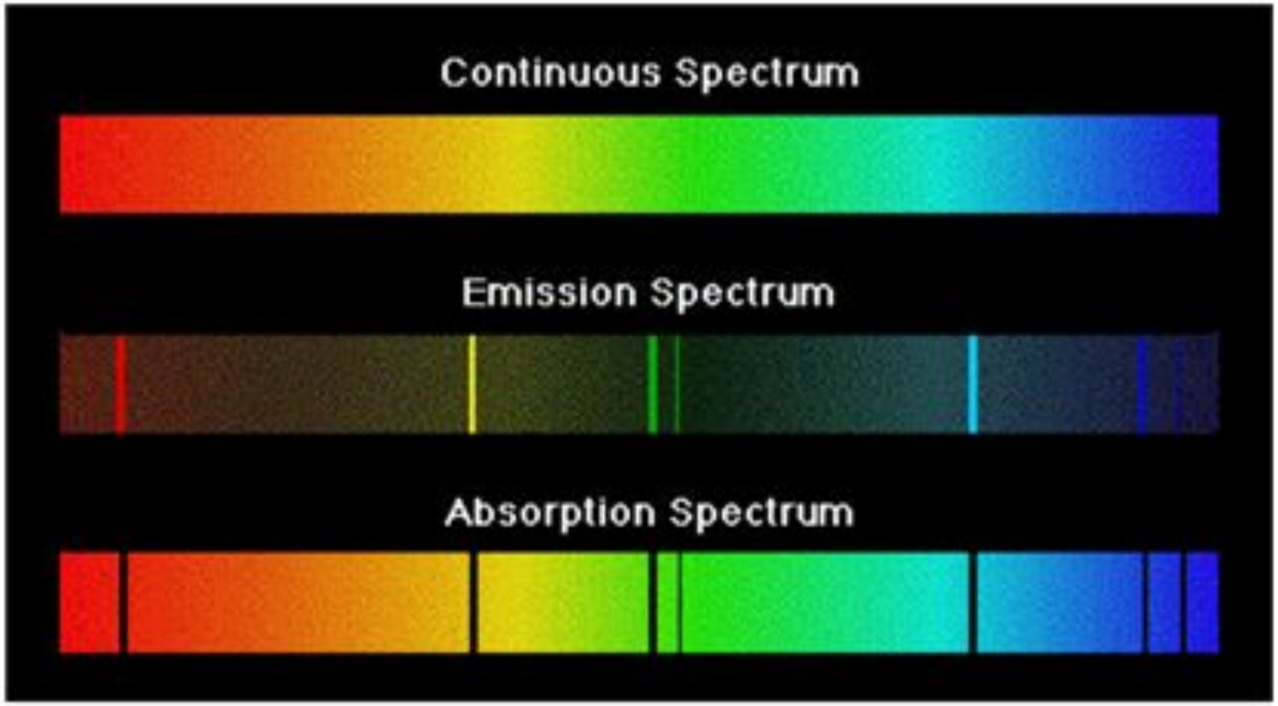
Absorption & Emission

- The other aspect that was noticed is that spectra emitted by an heated element was the same as the spectra of absorption when continuous light was passed through the same cool element (as a gas).
- This confirmed that the spectra were a property of the element.

Blackbody radiator

Heated gas

Blackbody radiation passed through the same cool gas



Hydrogen Energy Levels

- In 1885, Johann Balmer discovered a pattern for the visible emission spectra of hydrogen.

410, 434, 486, and 656 nm

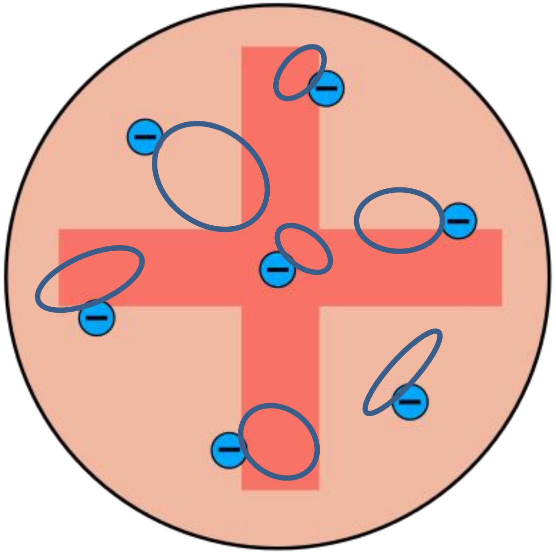
- His formula was: $\lambda = B\left(\frac{n^2}{n^2 - 2^2}\right), \quad B = 364.5nm, \quad n > 2$
- Later, Rydberg reformulated the Balmer formula as:

$$\frac{1}{\lambda} = \frac{4}{B}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad \text{for } n = 3, 4, 5, \ldots$$

$$R_H = 10,973,731.57 \ m^{-1}$$

Thomson Model

- In 1904, J.J. Thomson proposed that atoms were composed of an amorphous positively charged “plum pudding” with embedded electrons.
- The absorption and emission of light could then be accounted for by these electrons having certain natural frequencies of harmonic oscillation.
- One could imagine rings of electrons with different paths, or springs, or some such configuration which would lend each electron with a natural frequency of oscillation, and hence absorb and emit light with those frequencies.

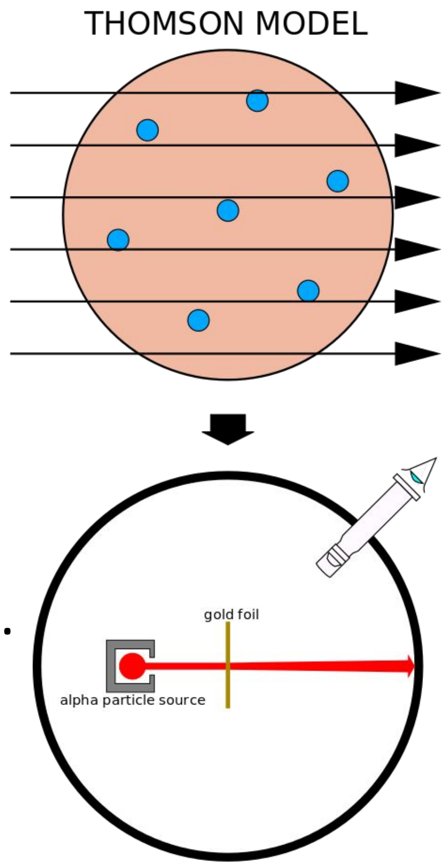


Gold Foil Experiment

- In 1909, Hans Geiger and Ernest Marsden performed an experiment, under the direction of Ernest Rutherford to test Thomson's model of the atom.
- They used a radioactive source that emitted alpha particles (charge = +2) in a tightly collimated beam, onto a gold foil.
- They then looked at the angle through which the alpha particles are scattered.

Gold Foil Experiment

- The alpha particle being relatively heavy (compared to an electron), should pass through an amorphous positively charged (but dilute) object with little deflection.
- What they ***actually saw*** was very large deflections (occasionally) and relatively large deflections more often.
- The only way to explain this was that the positively charged “nucleus” of the atom was much smaller that the size of the atom!



Gold Foil Experiment

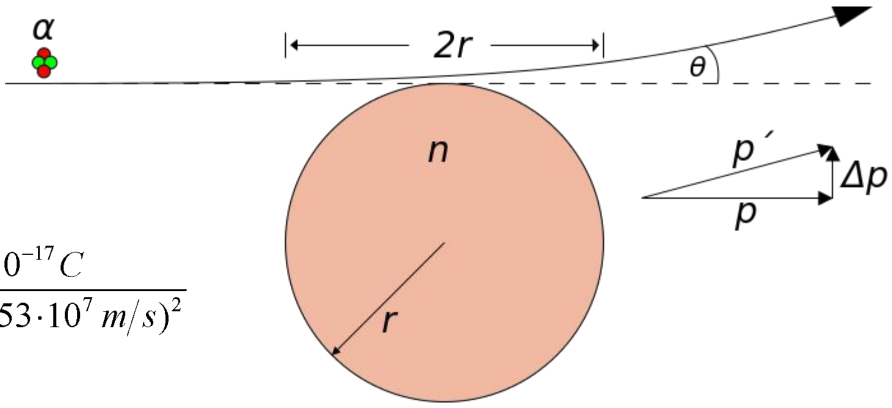
- There are several ways to show the expected results with the Thomson model. The book uses conservation of energy.
- Here, (from Wikipedia) I show using momentum and force, that the expected maximum deviation is quite small.
- Notice that the angle depends on the force (~1/r^2) and the time spent under the force (~r), finally depending on the radius of the positively charged object as 1/r.

$$\Delta p = F\Delta t = k \cdot \frac{Q_\alpha Q_n}{r^2} \cdot \frac{2r}{v_\alpha}$$

$$\theta \approx \frac{\Delta p}{p} < k \cdot \frac{2Q_\alpha Q_n}{m_\alpha r v_\alpha^2}$$

$$= 8.998 \cdot 10^9 \frac{N \cdot m^2}{C^2} \times \frac{2 \times 3.204 \cdot 10^{-19} C \times 1.266 \cdot 10^{-17} C}{6.645 \cdot 10^{-27} kg \times 1.44 \cdot 10^{-10} m \times (1.53 \cdot 10^7 \, m/s)^2}$$

$$\theta < 0.000326 \, \text{rad} \ (\text{or} \, 0.0186^\circ)$$

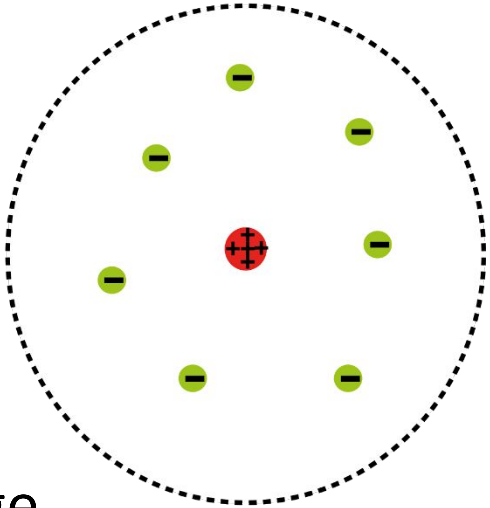


Rutherford Model

- To explain the experimental results, Rutherford needed that the radius of positive charge that was responsible for scattering the alpha particles was roughly 10,000 times smaller than the atomic radius.
- His calculation of the radius was simple, and his interpretation was correct – his alpha particles weren't high enough energy to reach the gold nucleus.

$$\frac{1}{2}mv^2 = \frac{1}{4\pi\varepsilon_0}\cdot\frac{q_1q_2}{b} \Rightarrow$$

$$b = \frac{1}{4\pi\varepsilon_0}\cdot\frac{2q_1q_2}{mv^2} = 2.7\times10^{-14}\,m = 27\,fm$$

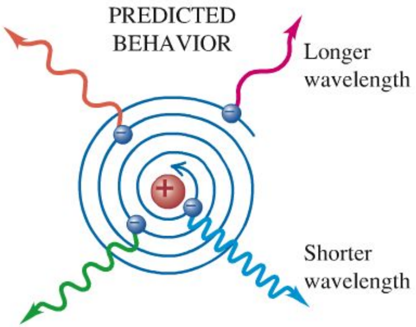


- The actual atomic radius is more like 7.3 fm.
- He noticed that the deviations of the 1/r impulse (from an actual impact) would change the scattering angle distributions, which he didn't see.

Oops

- But there was a reason that Thomson had a plum pudding model.
- Let's pretend again that we are CLASSICAL physicists.
- We have a positive and heavy charge with a small radius, and electrons surrounding it.
- How do they stay separated from each other?
- They must be orbiting: $\frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r^2} = ma \Rightarrow$

$$a = \frac{1}{4\pi\epsilon_0} \cdot \frac{97e^2}{mr^2}$$



- But, since they are accelerating, they must radiate!
- This will lose energy, causing them to fall closer to the positive core…
- In fact, "shortly after Thomson's discovery, Hantaro Nagaoka, a Japanese physicist, predicted a different model for electronic structure. Unlike the plum pudding model, the positive charge in Nagaoka's "Saturnian Model" was concentrated into a central core, pulling the electrons into circular orbits reminiscent of Saturn's rings. Few people took notice of Nagaoka's work at the time, and Nagaoka himself recognized a fundamental defect in the theory even at its conception, namely that a classical charged object cannot sustain orbital motion because it is accelerating and therefore loses energy due to electromagnetic radiation." - Wikipedia

Bohr Model

- In 1913 Rutherford's post-doctoral student, Niels Bohr, proposed a new model of the atom.
- It pre-dated de-Broglie waves by about 11 years, so he didn't yet know about matter waves, but he hypothesized that the electron angular momentum was quantized as:

$$L_n = mv_n r_n = n\hbar$$

- Since it was quantized, there must be a lowest angular momentum, and hence, a lowest energy for the electron.
- This meant that the electrons couldn't radiate at just any energy, and if the electron was in its lowest energy, it couldn't radiate at all.
- It also could explain emission and absorption spectra, since electrons would only emit when changing energy from one quantized state to another.

Bohr Model (Pre-Matter Waves)

- Let's get a bit more quantitative. We will examine an electron in the hydrogen atom (Z=1), and start by using classical forces and accelerations:

$$F = ma = m\frac{v^2}{r}$$

- And now solve for the nth radius and the nth velocity using Bohr's quantization:

$$L_n = mv_n r_n = n\hbar \Rightarrow$$

$$r_n = \frac{n\hbar}{mv_n}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n^2} = m\frac{v_n^2}{r_n} \Rightarrow$$

$$v_n^2 = \frac{1}{4\pi m\varepsilon_0}\frac{e^2}{r_n} = \frac{1}{4\pi m\varepsilon_0}\frac{e^2 m v_n}{n\hbar} \Rightarrow$$

$$v_n = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{n\hbar} \Rightarrow \quad r_n = 4\pi\varepsilon_0\frac{n^2\hbar^2}{me^2} = n^2 a_0$$

Bohr radius: $$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} = 5.29\times 10^{-11}\,m$$

Bohr Model (Pre-Matter Waves)

- And now, we can ask, what is the energy difference between the first two energy levels?

$$E_n = KE_n + U_n = \frac{1}{2}mv_n^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n}$$

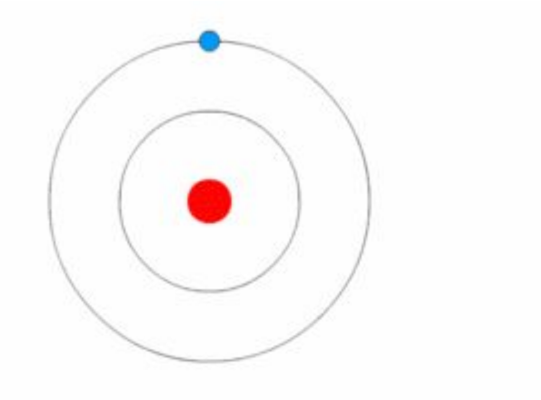
$$= \frac{1}{2}m\left(\frac{1}{4\pi\varepsilon_0}\frac{e^2}{n\hbar}\right)^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left(4\pi\varepsilon_0\frac{n^2\hbar^2}{\pi me^2}\right)}$$

$$= \frac{1}{2}\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{n^2\hbar^2} - \frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{n^2\hbar^2}$$

$$= \frac{-1}{2}\frac{m}{(4\pi\varepsilon_0)^2}\frac{e^4}{n^2\hbar^2}$$

$$= \frac{-1}{2}\frac{k^2me^4}{n^2\hbar^2} = \frac{-13.6}{n^2}eV, \text{ where } k = \frac{1}{4\pi\varepsilon_0}$$

NOTE!!! Different k!



$$E_2 - E_1 = \frac{-13.6eV}{2^2} - \frac{-13.6eV}{1^2} = 10.2eV$$

Hydrogen Energy Levels

- What frequency and wavelength does this correspond to?

$$E_2 - E_1 = hf = 10.2eV \Rightarrow$$

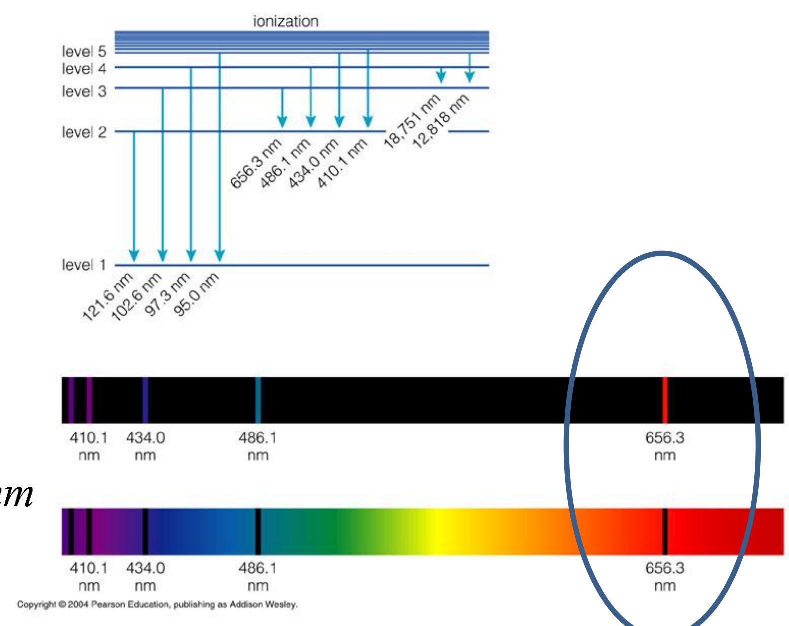
$$f = \frac{10.2eV}{4.136\times10^{-15}\,eV\cdot s} = 2.468\times10^{15}\,Hz$$

$$\lambda = \frac{c}{f} = \frac{3\times10^{8}\,m/s}{2.468\times10^{15}\,s^{-1}} = 121.6nm$$

- Unfortunately, this is outside of the visible.
- But, if we look at the transitions between the third and second energy levels:

$$E_3 - E_2 = \frac{-13.6eV}{3^2} - \frac{-13.6eV}{2^2} = 1.89eV$$

$$\lambda = \frac{hc}{\Delta E} = \frac{\left(4.136\times10^{-15}\,eV\cdot s\right)\cdot\left(3\times10^{8}\,m/s\right)}{1.89eV} = 656.5nm$$



Pontification on constants…

- Remember the Rydberg constant that was extracted from the hydrogen spectra and Rydberg's reformulation of the Balmer formula?

$$E_n = -\frac{1}{2}\frac{k^2 m e^4}{n^2 \hbar^2} = -\frac{1}{n^2} R_H \Rightarrow$$

$$R_H = \frac{k^2 m e^4}{2\hbar^2} = \frac{1}{2}\frac{k^2 e^4 m c^2}{\hbar^2 c^2} = \frac{1}{2}\frac{k^2 e^4}{\hbar^2 c^2} m c^2 = \frac{1}{2}\alpha^2 \left(mc^2\right)$$

$$\alpha = \frac{ke^2}{\hbar c} = \frac{1}{137} \quad \left[\text{here, } k = \frac{1}{4\pi\varepsilon_0}\right]$$

- Alpha is called the fine structure constant and it plays an important role as the coupling constant determining the strength of the interaction between electrons and photons!

There is a most profound and beautiful question associated with the observed coupling constant, *e* – the amplitude for a real electron to emit or absorb a real photon. It is a simple number that has been experimentally determined to be close to 0.08542455. (My physicist friends won't recognize this number, because they like to remember it as the inverse of its square: about 137.03597 with about an uncertainty of about 2 in the last decimal place. It has been a mystery ever since it was discovered more than fifty years ago, and all good theoretical physicists put this number up on their wall and worry about it.) Immediately you would like to know where this number for a coupling comes from: is it related to pi or perhaps to the base of natural logarithms? Nobody knows. It's one of the greatest damn mysteries of physics: a magic number that comes to us with no understanding by man. You might say the "hand of God" wrote that number, and "we don't know how He pushed his pencil." We know what kind of a dance to do experimentally to measure this number very accurately, but we don't know what kind of dance to do on the computer to make this number come out, without putting it in secretly!

— *Richard Feynman, Richard P. Feynman (1985). QED: The Strange Theory of Light and Matter. Princeton University Press. p. 129. ISBN 0-691-08388-6.*