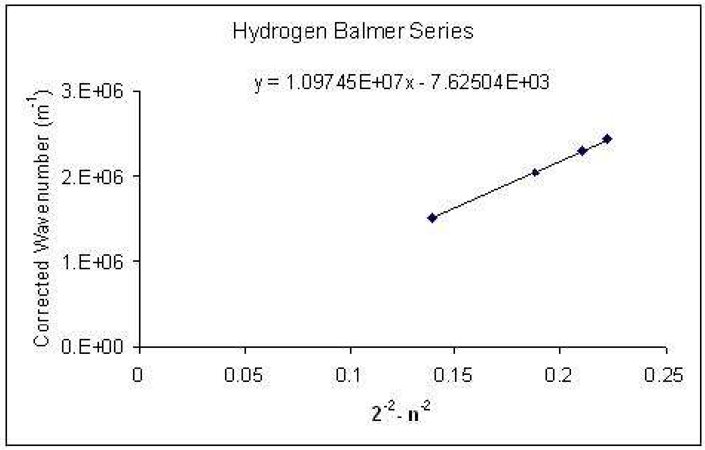
Section 9 - The Bohr Model of Hydrogen

"How could something so wrong [be] so right …?"

- The Casanovas

The Bohr Atom



Explaining the emission lines of the hydrogen atom was one of the big successes of early quantum mechanics. Four such well-defined wavelengths are in the visible range of the spectrum (now known as part of the *Balmer series* and shown in the graph at right), but as spectroscopy advanced, more lines were discovered in the UV and IR. To a very good approximation, the emitted wavelengths follow this formula:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad n_f \text{ and } n_i \text{ are positive integers with } n_i > n_f,$$

where R_H is a constant we will eventually determine theoretically, and the 'f' and 'i' will be explained. For the Balmer series, $n_f = 2$, and the value of R_H can be determined experimentally from the slope of the graph, 1.097×10^7 m^{-1}.

The different series are defined by the value of n_f, with the corresponding n_is running from n_f +1 to infinity.

Series Name	n_f	Range of n_i	
Lyman	1	2, 3, 4, 5, 6, …, ∞	All of these lines are in the UV.
Balmer	2	3, 4, 5, 6, 7, …, ∞	Only 3, 4, 5 & 6 are visible to human eyes. The rest are in the UV.
Paschen	3	4, 5, 6, 7, 8, …, ∞	All of these lines are in the IR.
Bracket	4	5, 6, 7, 8, 9, …, ∞	All of these lines are in the IR.
Pfund	5	6, 7, 8, 9, 10, …, ∞	All of these lines are in the IR.
Humphries	6	7, 8, 9, 10, 11, …, ∞	All of these lines are in the IR.
No names for 7 up	7	8, 9, 10, 11, 12, …, ∞	All of these lines are in the IR.

The model we will use here is *Bohr's planetary model*. The electron orbits the central proton due to the central coulomb force in much the same way that a planet orbits the sun. We will of course make a few assumptions.

DERIVATION 9-1

1) We'll assume that the nucleus is fixed in space[1] and that the electron's orbit is circular.[2]
2) The only interaction between nucleus and electron is the Coulomb force.
3) Classically, an electron accelerated in a circular path should emit electro-magnetic waves, thus losing energy. The electron should therefor spiral down into the nucleus, quite rapidly. We'll assert that this doesn't happen.
4) We'll assume that the angular momentum is conserved and quantized.

Let's get the action integral out of the way, since it's again very simple:

$$\oint \mathrm{L}\, d\theta = \mathrm{nh}\,,$$

and just like the rotator above, L is conserved (the coulomb force is a central force, so the torque is zero and $d\mathrm{L}/dt = 0$), so

$$\mathrm{L} \oint d\theta = \mathrm{nh} \quad \rightarrow \quad \mathrm{L} = \frac{\mathrm{nh}}{2\pi} = \mathrm{n}\hbar.$$

Consider Coulomb's law; here, Q is the charge of the proton and q is the absolute value of the charge of the electron (both equal e, the elementary charge).

$$F_E = \frac{k_e Q|q|}{r^2} = \frac{k_e \mathrm{e}^2}{r^2}\,.$$

So, first we have that the potential energy U(r) is given by

$$\mathrm{U} = \frac{\mathrm{k_e Qq}}{\mathrm{r}} = -\frac{\mathrm{k_e e^2}}{\mathrm{r}}.$$

We have two expressions for the kinetic energy. The first comes from Newton's second law, treating the kinetic energy as due to translation:

$$\mathrm{F_E} = \frac{\mathrm{k_e e^2}}{\mathrm{r^2}} = \mathrm{ma_C} = \mathrm{m}\frac{\mathrm{v^2}}{\mathrm{r}} = \frac{2\mathrm{K}}{\mathrm{r}} \rightarrow \mathrm{K} = \frac{\mathrm{k_e e^2}}{2\mathrm{r}}\,.$$

The second comes from treating the electron's kinetic energy as due to rotation about the nucleus:

$$\mathrm{K} = \frac{1}{2}\mathrm{I}\omega^2 = \frac{\mathrm{L^2}}{2\mathrm{I}} = \frac{\mathrm{L^2}}{2(\mathrm{mr^2})}\,.$$

These two expressions should be equivalent, so

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[1] This is equivalent to making the nucleus have infinite mass. For the gravitational two body problem, we expect both objects to orbit their common center of mass. Same here. We'll discuss corrections to the Bohr model later in this section.

[2] Remember that elliptical orbits would also be allowed for a central $1/r^2$ force.

$$\frac{L^2}{2(mr^2)} = \frac{k_e e^2}{2r} \quad \rightarrow \quad r_n = \frac{L^2}{k_e e^2 m} = \frac{n^2\hbar^2}{k_e e^2 m}.$$

That is, only certain radius orbits will be allowed, and these of course correspond to particular electron energies:

$$E = U + K = -\frac{k_e e^2}{r} + \frac{k_e e^2}{2r} = -\frac{k_e e^2}{2r}.$$

$$E_n = -\frac{k_e e^2}{2r_n} = -\frac{k_e e^2}{2\left(\frac{n^2\hbar^2}{k_e e^2 m}\right)} = -\frac{1}{n^2}\frac{{k_e}^2 e^4 m}{2\hbar^2}.$$

The lowest energy level for an electron in hydrogen will be when n = 1, so $E_1 \approx -13.6$ eV; the rest follow the relationship $E_n = -13.6\ \text{eV}/n^2$. The smallest radius (the *Bohr radius*, symbol a_o) will then be 0.53Å, roughly the same order for the size of an atom as determined by our other attempts! The other orbital radiuses follow the relationship $r_n = n^2 a_o$.

EXERCISE 9-1

Show that we can arrive at the expression for allowed radiuses using the De Broglie notion. Like the square well above (Example 8-1), we might expect that the wave around the circumference of the electron's orbit must form a standing wave, lest it experience destructive interference. Constructive interference will occur if the circumference is a (positive) integer number of De Broglie wavelengths:

So, how to explain the emission lines? Classically, a charge orbiting a proton will lose energy through electro-magnetic radiation and spiral down into the nucleus quite quickly. Here we assume that the electron maintains its energy and orbit without emitting radiation. It must emit, that is shed, energy, if the electron drops from one allowed energy level to a lower one; this bit actually works out to be a fairly good match with observation.

Suppose that the electron emits a photon of energy $E = hf$ when it drops from one level to another; that energy should equal the difference in the energy levels within the atom.

$$E_{PHOTON} = hf = -\Delta E_{ELECTRON} = -(E_f - E_i),$$

$$\frac{hc}{\lambda} = -\frac{1}{n_i^2}\frac{{k_e}^2 e^4 m}{2\hbar^2} - -\frac{1}{n_f^2}\frac{{k_e}^2 e^4 m}{2\hbar^2},$$

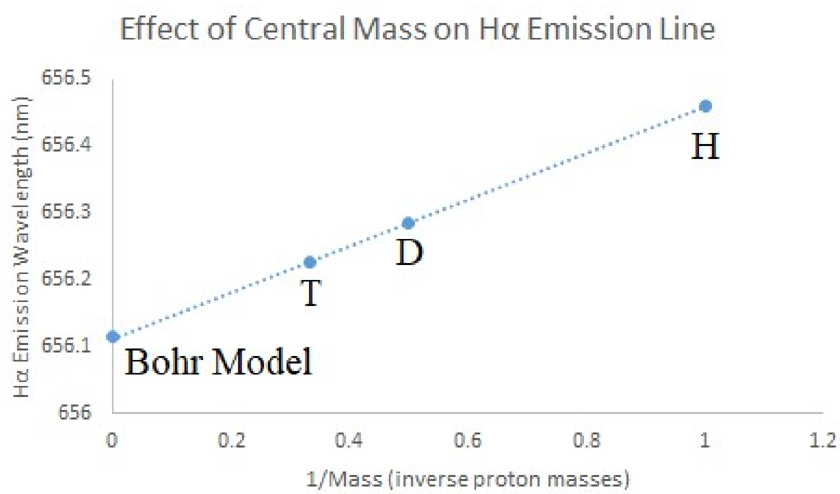
$$\frac{1}{\lambda} = \left(\frac{{k_e}^2 e^4 m_e}{4\pi c\hbar^3}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

This is the same formula found empirically for the emission lines of hydrogen. The collection of constants equals $1.097\times10^7\ \text{m}^{-1}$, and is known as the *Rydberg constant*, R_H. Note that this value agrees fairly well with that we obtained from the observation above.

HOMEWORK 9-1

Find the wavelength of light emitted by a hydrogen atom when its electron moves from the n = 4 orbit to the n = 1 orbit. The light is emitted as a photon; how much energy does this photon carry away?

Corrections to the Bohr Model



The Bohr model is quite successful, but spectroscopy in the early twentieth century was already a mature art, and there are some small discrepancies between the predicted emission wavelengths and the observed wavelengths. We made some assumptions in the derivation above that in fact lead to disagreement between the theory and experiment. One such was that the proton at the center of the atom is stationary, or if you prefer, has infinite mass. This is obviously not the case. Luckily, we can observe this effect, since there are three 'common' types of hydrogen, each with a different mass. *Protium* (H) has one proton at the center of the atom, *deuterium* (D)[3] has just about twice the mass of protium, and *tritium* (T) three times the mass. Chemically, they are identical. The graph shows the measured Hα emission lines (n=3 to n=2) of H, D, and T. Extrapolation back to 'infinite mass' at the left edge of the graph predicts an agreement with the Bohr model.

Rather than simply acknowledge a problem with the Bohr model, it would be nice to find a modification to the model that accounts for this effect. You may have discussed the *reduced mass* in Semester One, perhaps in terms of orbital motion. Mathematically, we can make the central mass act as if it were infinite if we reduce the orbiting mass by a factor $M_C/(M_C + M_O)$. The emission wavelengths for hydrogen then change to

$$\frac{1}{\lambda} = \left(\frac{{k_e}^2 e^4 m_e m_P}{4\pi c\hbar^3 (m_e + m_P)}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

Balmer line	Measured Wavelength (in vacuum)	Bohr Model (infinite mass)	Bohr Model (reduced mass)	Disagreement
Hα	656.458 nm	656.112 nm	656.470 nm	0.0017 %
Hβ	486.268 nm	486.009 nm	486.274 nm	0.0013 %

[3] This was in fact how deuterium was discovered, through the observation of a set of faint 'ghost lines' of slightly shorter wavelengths than those of hydrogen.

Hγ	434.166 nm	433.937 nm	434.173 nm	0.0017 %
Hδ	410.285 nm	410.070 nm	410.294 nm	0.0021 %

The table lists data for the four visible hydrogen emission lines; similar information could be developed for other lines as well, but these four should make the point sufficiently. The first column lists the actual measured wavelengths of the emission lines as seen in vacuum. The next column is the predicted wavelengths assuming that the central proton is infinitely massive, an assumption that we've already shown to be a source of error. The third column makes use of the reduced mass approach to take into account that the nucleus wiggles around as the electron 'orbits' it. The final column compares the wavelengths predicted using the reduced mass to the actual measured wavelengths. Note that there is still a difference and that it is about the same size and in the same direction for all four lines (the photons carry away more energy than predicted). One might think that there is another correction that should be made. What other effects should we think about?

HOMEWORK 9-2

Find the speed of the electron in the n = 2 orbit. Remember that in the Bohr atom derivation, K = -E. How does this compare with c? Was a non-relativistic calculation O.K?

HOMEWORK 9-3

Estimate (roughly as an order of magnitude) the correction necessary to the Bohr model when relativistic effects are considered. Remember from Section One that the relativistic kinetic energy of a 'slow' object is

$$K \approx \left(\frac{1}{2}\left(\frac{v}{c}\right)^2 + \frac{3}{8}\left(\frac{v}{c}\right)^4 + \cdots\right) m_o c^2$$

and from the Bohr derivation that E = -K. You might, for example, divide the first expansion term by the Newtonian expression:

$$\text{Shift in Energy due to relativity} \approx \frac{\frac{3}{8}\left(\frac{v}{c}\right)^4 m_o c^2}{\frac{1}{2}\left(\frac{v}{c}\right)^2 m_o c^2} \approx \left(\frac{v}{c}\right)^2.$$

If the velocity is v << c, then the emitted wavelengths should show a fractional shift of about the same order of magnitude. Compare your result here to the information in the table above. Does relativity explain the residual difference in the Bohr model (reduced mass) and the actual emitted wavelengths?

Other Atoms: Highly Ionized Atoms and Hydrogen-like Metals

Strictly speaking, this result is valid for one electron orbiting one proton, but we can extend its usefulness a bit for some special cases. For example, one electron only orbiting any nucleus with Z protons can be described just as well by substituting the charge Q = Ze of that nucleus.

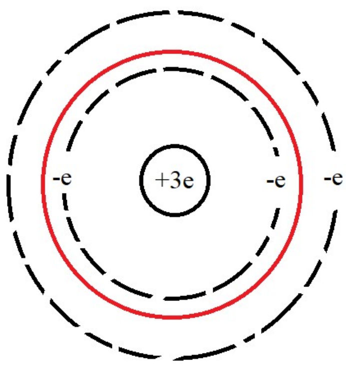
$$E_n = -\frac{1}{n^2}\frac{{k_e}^2 Z^2 e^4 m}{2\hbar^2}$$

So, He^{+1} (or really any $Z^{+(Z-1)}$) should follow the same general behavior.

HOMEWORK 9-X

Find the wavelength emitted by the electron in He^{+1} as it transitions from the n=4 state to the n = 3 state.

Somewhat less so, atoms of elements from Column I with a single outlying electron should behave similarly, if we consider Gauss's law. For example, the two inner electrons of lithium, together with the three protons in the nucleus inside of a Gaussian surface, look very much like a single proton to the outermost electron. The inner electrons form a roughly spherical shape that combines with, or 'screens,' the positive nucleus. We might expect the energies of the outermost electrons of Column I atoms to be about the same.



Element	Ionization Energy (eV)
H	13.12
Li	5.20
Na	4.96
K	4.18
Rb	4.03
Cs	3.76

Strangely enough, these energies are about the same, <u>except</u> for our prototype, hydrogen. The hydrogen is now thought to be a single proton and so spherically symmetric, but we would expect the outside electron to affect through repulsion the charge distribution on the inner electrons in the other elements, so the Gaussian sphere model mentioned above is probably not applicable. However, whatever shielding <u>does</u> occur seems to work the same way for each of the heavier atoms.

Other Atoms (of any Type)

For other, larger atoms, the number of electrons inside the 'Gaussian surface' will change as the electron changes orbit. A reasonably useful fitting function for this situation is

$$\frac{1}{\lambda} = \frac{R}{Z^2}\left(\frac{Z_f^2}{n_f^2} - \frac{Z_i^2}{n_i^2}\right).$$

The two Zs in the numerators reflect the charge 'seen' by the electron when in each of its orbits, that is, the number of protons minus the number of electrons in orbits inferior to that of the electron of interest.

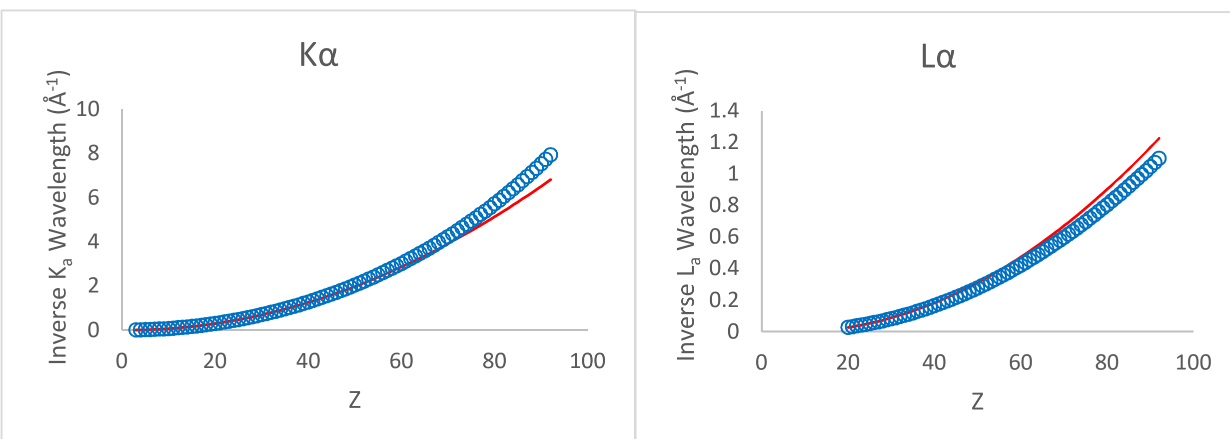
Here's a question. How do we know Z for a particular element? The elements were initially defined by how their electrons interact with those of other atoms, but electrons can be gained or lost. It's the number of protons that determines the identity of an element. Let's consider some experiments conducted by Moseley, and see if we can make sense of them. The experiment measured the wavelengths of the X-Ray Kα and Lα lines[4] for a number of different elements. Moseley used a different fitting form than the one mentioned above and asserted that[5]

$$\frac{1}{\lambda_{K\alpha}} \sim (Z-1)^2 \quad \frac{1}{\lambda_{L\alpha}} \sim (Z-7.4)^2$$

are reasonably good fits. We know <u>now</u> that the Kα line is the result of an n = 2 to n = 1 electron transition, while the Lα is the n = 3 to n = 2 transition. One possible simplified explanation for these results follows. We would expect that prior to the Kα transition, there is one electron in the n = 1 orbit, plus an empty place for another one from n = 2 to fall into. The single n = 1 electron cancels out the effect of one of the protons, leaving the central charge as Z-1. Similarly for the Lα line, although we might naïvely expect nine electrons to be available for screening; somewhere between 7 and 8 electrons provide a degree of screening of the nucleus, slightly changing the energy levels and therefor the emission line wavelengths.

$$\frac{1}{\lambda_{K\alpha}} = R_H\,(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) \qquad \frac{1}{\lambda_{L\alpha}} = R_H\,(Z-7.4)^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right).$$

However, if we take more recent data for lithium through uranium (bluer points),[6] it is clear neither



fit (red curves) is particularly good for high Z nuclei. One problem with this analysis is that the kinetic energies of the electrons will increase as Z increases, necessitating the use of relativistic expressions. In a class like this one, we use the rule that relativity is necessary when v > 0.1c. Let's do a rough calculation for n = 1:

[4] We talked about Kα and Kβ lines several sections back.
[5] Moseley, H.G.J., "The high frequency spectra of the elements," *Phil. Mag.* (1913) p1024.
[6] Bearden, J. A., *Rev. Mod. Phys*. **39**, (1967) p78.

$$\beta = 0.1 \quad \gamma = \frac{1}{\sqrt{1-\beta^2}} = 1.005 \quad K_{n=1} = (\gamma - 1)m_o c^2 = 0.005 m_o c^2 = 2500 \text{ eV}.$$

$$K_{n=1} \sim Z^2 13.6 \text{ eV} \quad \text{and so, } Z < 14.$$

We should expect that the fit will begin to diverge from reality for elements heavier than silicon. So, it's no surprise there is some disagreement between the simple Bohr model and reality here for even moderately high values of Z.[7]

HOMEWORK 9-4

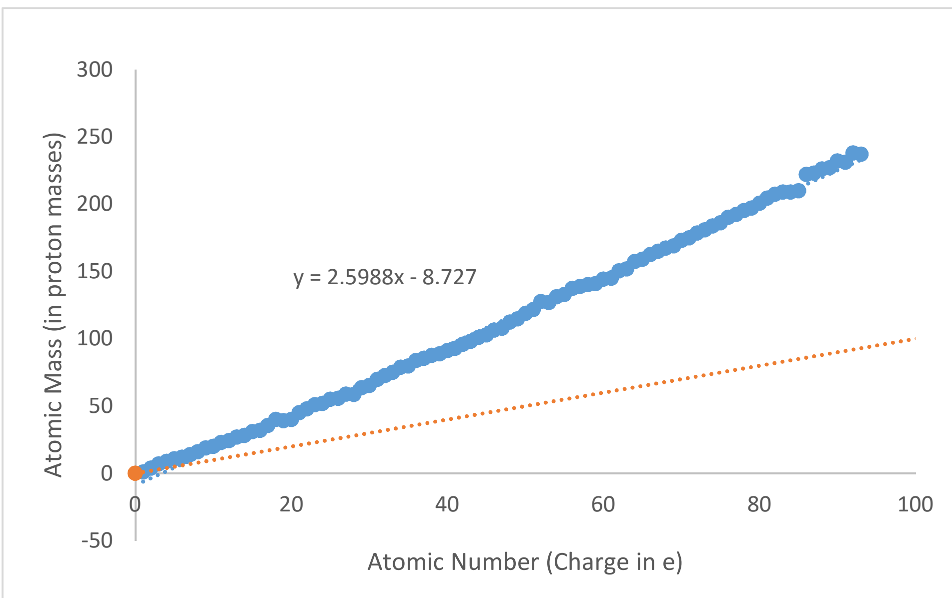
The Lα line of some metal is 1.39121 Å. Identify the metal.

FYI, here is an alternate and reasonably useful fitting function for this situation:

$$\frac{1}{\lambda} = \frac{R}{Z^2}\left(\frac{Z_f^2}{n_f^2} - \frac{Z_i^2}{n_i^2}\right).$$

The two Zs in the numerators reflect the charge 'seen' by the electron when in each of its orbits. However, the values of Z_f and Z_i must be adjusted for each element and for each energy level with each type of element.

Here is another interesting result from Moseley's data. Once we identify the hydrogen nucleus as a proton, we would expect the mass of the nucleus in proton masses to be equal to its charge in fundamental units, e. However, this is not the case; indeed, the masses of most nuclei are a bit more than double what we expect. So, what is this extra mass? Stay tuned!



Summary

We've used the 'old' quantum mechanics, based on the Wilson-Sommerfeld quantization rule for cyclic processes, to take a first look at several important system. In a later section, we'll use the Schrödinger picture to examine this system more carefully.

[7] This doesn't detract from Moseley's accomplishment, ordering the elements correctly by Z value.