

Beyond the Bohr Model

Disclaimer: These lecture notes are not meant to replace the course textbook. The content may be incomplete. Some topics may be unclear. These notes are only meant to be a study aid and a supplement to your own notes. Please report any inaccuracies to the professor.

The Fine Structure Constant

Consider the electron velocity in the Bohr model:

$$v_n = \frac{n\hbar}{m_e r} = \frac{n\hbar}{m_e} \frac{m_e e^2}{4\pi\epsilon_0 n^2 \hbar^2}$$

$$v_n = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0 \hbar}$$

The velocity for an electron in the ground state is:

$$v_1 = (1.6022 \times 10^{-19} \text{ C})^2 (9.0 \times 10^9 \text{ N} \cdot \text{m}^2 \text{C}^{-2}) / (1.055 \times 10^{-34} \text{ J} \cdot \text{s})$$

$$v_1 = 2.2 \times 10^6 \text{ m/s} \approx 0.01c$$

Let us define a dimensionless quantity called the **Fine Structure Constant**:

$$\mathbf{a} \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137}$$

This is an easy to remember number! We can rewrite the Bohr energies and radii in terms of this number:

$$E_n = -\frac{1}{2} m_e c^2 \frac{(Z\mathbf{a})^2}{n^2}$$

$$r_n = \frac{\hbar}{m_e c} \frac{n^2}{(Z\mathbf{a})}$$

These are the expressions for hydrogen-like atoms (H, He⁺, Li⁺⁺, ...) Once again, n is the principal quantum number (which is an integer greater than 0), and Ze is the charge of the nucleus.

The fine structure constant is a measure of the strength of the electromagnetic force, as it depends only on the electron charge, scaled by Planck's constant and the speed of light. We will learn more about the splitting of the spectral lines into "fine structure" when we solve the Hydrogen atom exactly using the Schrodinger Equation. The energy differences between these fine lines are smaller than the coarse structure by about this factor α .

The Correspondence Principle

Classical physics results should be contained as limiting cases of quantum theories. There is nothing wrong with classical physics at the macroscopic scale, only at the atomic scale. When the quantum number n is large, classical and quantum physics should agree.

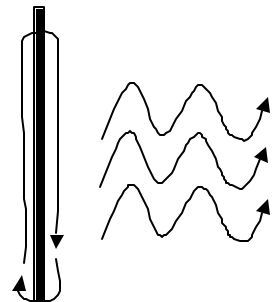
Consider the frequency of radiation in classical electromagnetism. This radiation is caused by charged particles undergoing cyclic motion (like electrons running up and down an antenna). Now imagine viewing edge-on the orbital plane of an electron in a classical orbit about the nucleus. This, too, looks like an electron running up and down an antenna. When the electron completes one orbit, it is back to where it started. So the frequency of the emitted radiation should just be this orbital frequency:

$$f_{\text{classic}} = \frac{v}{2\pi r}$$

From Newtonian circular motion:

$$\begin{aligned} v &= \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}} \\ \Rightarrow f_{\text{classic}} &= \frac{1}{2\pi} \left(\frac{Ze^2}{4\pi\epsilon_0 m_e r^3} \right)^{1/2} \\ &= \frac{1}{2\pi} \left(\frac{Za\hbar c}{m_e r^3} \right)^{1/2} \end{aligned}$$

Antenna



Now if we substitute in the radius from the Bohr formula:

$$r_n = \frac{\hbar}{m_e c} \frac{n^2}{Z a}$$

$$\Rightarrow f_{\text{classic}} = \frac{1}{2p} \left(\frac{Z a \hbar c m_e^3 c^3 Z^3 a^3}{m_e \hbar^3 n^6} \right)^{1/2}$$

$$f_{\text{classic}} = \frac{Z^2 a^2 m_e c^2}{h} \frac{1}{n^3}$$

This is the dependence of the classical frequency on the quantum number n , when we incorporate the Bohr radius.

Now within the Bohr Model (in which classical radiation does not apply), consider a transition from one level with quantum number $n + 1$ to one with quantum number n . When n is large, the radius is large and the atom should behave classically. Let's see if it does:

$$f_{\text{Bohr}} = \frac{Z^2 E_0}{h} \left(\frac{1}{n^2} - \frac{1}{(n+1)^2} \right)$$

$$= \frac{Z^2 E_0}{h} \left(\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2} \right) = \frac{Z^2 E_0}{h} \frac{(2n+1)}{n^2(n+1)^2}$$

$$\lim_{n \rightarrow \infty} f_{\text{Bohr}} = \frac{Z^2 E_0}{h} \frac{2n}{n^4} = \frac{2Z^2 E_0}{n^3}$$

$$E_0 = \frac{1}{2} m_e c^2 a^2$$

$$\Rightarrow \lim_{n \rightarrow \infty} f_{\text{Bohr}} = \frac{Z^2 a^2 m_e c^2}{h} \frac{1}{n^3} = f_{\text{classic}}$$

Indeed, in the limit of large n , the classical and the quantum result agree. This principle of correspondence was first propounded by Bohr.

The Franck-Hertz Experiment

Although the Bohr model describes an atom in which the electron orbits are quantized, all we really measure is the quantized radiation emitted by the atom. We don't observe the orbits themselves. Perhaps this atomic picture is wrong. Maybe the quantization only applies to the electromagnetic radiation, and not necessarily to the atom.

The validity of the Bohr picture of the atom was supported by the Franck-Hertz experiment, which does not involve electromagnetic radiation at all. In this experiment, electrons are accelerated between a cathode and anode in a tube immersed in a gas like hydrogen. Any energy transfer to the gas atoms must occur via collisions with the electrons, not through light.

If the energy and radius of an atom is really quantized, it shouldn't matter whether it absorbs energy from a photon of light or from the kinetic energy of an electron. In the latter case, we should observe that certain kinetic energies lead to the atom jumping to the next excited state, leaving the electron with a reduced kinetic energy. This is indeed observed! The atom itself really is quantized. The nice thing about the Franck-Hertz experiment is that one does not need a fine optical setup, just some electrical equipment (an ammeter) and the cathode tube.

Mosely and X-ray Spectra

Although the Bohr atom does not apply to multi-electron atoms, it can be used to describe the absorption and emission of x-rays from the inner orbits (shells) of a multi-electron atom.

For example, consider an electron ejected from the innermost shell of a multi-electron atom (the so-called *K*-shell, where $n = 1$). An electron in one of the outer shells may drop from its orbit and fill this inner shell vacancy. However, the remaining electron in the *K*-shell (we haven't learned that yet, but we take it for granted now) will shield one unit of the electric charge of the nucleus, such that the frequency of the transition is given by:

$$f = \frac{E_g}{h} = \frac{E_n - E_1}{h} = cR_\infty (Z - 1)^2 \left(1 - \frac{1}{n^2}\right) \quad \longleftarrow \text{Transitions to K-shell}$$

Since Z can be large for multi-electron atoms, this frequency will typically be in the x-ray spectrum, a region explored by Mosely. Mosely plotted this frequency versus the atomic number Z and was able to verify the above relation (a success of the Bohr model) and also predict new elements that had not yet been discovered.

For vacancies in the *L*-shell ($n = 2$), there are more inner electrons that shield the electric charge of the nucleus. Mosely found that the following relation holds:

$$f = \frac{E_g}{h} = \frac{E_n - E_2}{h} = cR_\infty (Z - 7.4)^2 \left(\frac{1}{4} - \frac{1}{n^2}\right) \quad \longleftarrow \text{Transitions to L-shell}$$

Limitations of the Bohr Model

Despite its successes, the Bohr model of the atom has some serious limitations:

- 1. It can only explain hydrogen-like atomic spectra, not multi-electron atoms like helium, lithium, etc.**
- 2. It can't explain the fine structure of spectral lines**
- 3. It can't explain molecular bonds.**

For these items, we need a full Quantum Mechanical theory. Although Bohr was quite radical in his postulates, he wasn't quite radical enough!