

Bohr Quantization of Spectra

The problems with the Rutherford model centered on two issues: 1) the stability of atoms and 2) the spectra that atoms emitted and absorbed. It was difficult to imagine a way to make the Rutherford model explain these two phenomena within classical physics. As early as 1885, there were empirical (without explanation) formulae that worked tremendously well in representing the emission lines from hydrogen. The Balmer equation:

$$\lambda = 3646 \frac{n^2}{n^2 - 4}$$

predicted the wavelengths of the first nine lines in the hydrogen spectra to one part in 1000. In 1890, Rydberg generalized this formula for many emission series in hydrogen (and also later for the alkali elements) as

$$k = \frac{1}{\lambda} = R \left[\frac{1}{(m - a)^2} - \frac{1}{(n - b)^2} \right]$$

where, for hydrogen $a = b = 0$ and $R = R_H$ is the Rydberg constant for hydrogen. However, there was still no model for atomic structure that explained these features, much less the fact that atoms were stable at all.

In 1913, Bohr made a series of postulates to explain these experimental observations:

B1) An electron moves in a circular orbit about the nucleus under the influence of the classical Coulomb force.

B2) It is only possible for an electron to move in an orbit where its orbital angular momentum L is an integral multiple of \hbar , i.e., $L = n\hbar$.

B3) An electron moving in such an orbit does not emit radiation despite the fact it is accelerating.

B4) Electromagnetic radiation can be emitted if an electron makes a transition from one allowed orbit to another, with the photon energy being the difference between the energies of the two levels.

Let's examine the consequences of these postulates. Postulate B1 gives us a way to calculate the orbital angular momentum of an electron by knowing the Coulomb force and the resulting acceleration, and, since it is moving in a circular orbit, we can then calculate the velocity, and thus the angular momentum:

$$F = ma = m \frac{v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \Rightarrow$$

$$Ze^2 = 4\pi\epsilon_0 mv^2 r = 4\pi\epsilon_0 \frac{m^2 v^2 r^2}{mr} = 4\pi\epsilon_0 \frac{L^2}{mr} = 4\pi\epsilon_0 \frac{(n\hbar)^2}{mr}$$

where the last step uses now postulate B2. We can now use this relation to calculate the allowed radii, velocities and energies:

$$\begin{aligned}
 r &= 4\pi\epsilon_0 \frac{n^2\hbar^2}{mZe^2} \\
 v &= \frac{n\hbar}{mr} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n\hbar} \\
 E &= T + V = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \\
 &= \frac{1}{2}m \frac{Ze^2}{4\pi\epsilon_0 mr} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{4\pi\epsilon_0 2r} \\
 &= -\frac{mZe^4}{(4\pi\epsilon_0)^2 2\hbar^2} \frac{1}{n^2}
 \end{aligned}$$

So that the radius, velocity and thus the total energy is quantized by quantizing the orbital angular momentum. Now, we use Postulate B4 and calculate the frequency of the radiation emitted in a transition between allowed states:

$$\nu = \frac{E_i - E_f}{h} = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{mZ^2 e^4}{4\pi\hbar^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

or, in terms of the inverse wavelength $k = 1/\lambda = \nu/c$:

$$k = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{mZ^2 e^4}{4\pi\hbar^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_\infty Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

which, for hydrogen ($Z=1$), looks identical to the Rydberg formula with $n_f = 2$. In fact, if one evaluates R_∞ it agrees with the Rydberg constant almost perfectly.

The “almost perfectly” can be accounted for by several omissions by Bohr. The first was that he assumed that the nucleus was stationary as the electron orbited, so that the nucleus carried no orbital angular momentum. This can be correct for by quantizing the total angular momentum and using the reduced mass angular momentum about the system’s center of mass. The second omission was discovered by refining the spectroscopic data to the point where fine splitting of the emission lines were observed. This was treated by Sommerfeld by allowing elliptical orbits, and showing that the Bohr postulates led to another quantum number that dictates the quantization of the allowed elliptical paths. This, in addition to a relativistic treatment of the electrons, led to a very good working model for the energy of electrons in an atom.