

Atomic Spectra, and Bohr's Model for the Hydrogen Atom

The study of the nature of individual atoms comes, almost completely, from studying the radiation that they emit or absorb. Hydrogen is the simplest atom; therefore, earlier attempts to understand materials began with the study of radiation emitted by hydrogen. One can use a prism or diffraction grating to spread out the light emitted; this display is called *the spectrum of the atom*. We quickly learn that the spectrum consists of a number of individual “spectral lines,” which have noticeable intensity in **only** a very narrow band centered around a particular wavelength; therefore, we say that these lines correspond to particular wavelengths.

The studies of hydrogen in the late part of the nineteenth century created a list of spectral lines for hydrogen that as good enough that a Swiss high-school teacher, named Johannes Balmer, was able to devise a “guessed” formula that gave all of their wavelengths:

$$\lambda = \frac{n^2}{n^2 - 4} (364.6 \text{ nm}) , \quad n = 3, 4, 5, 6, \dots . \quad (1)$$

Nowadays this series of spectral lines is referred to as *the Balmer series*.

Somewhat later J.J. Rydberg modified Balmer's formula, in two ways; he wrote it in terms of the inverse of the wavelength:

$$\frac{1}{\lambda} = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right) , \quad n = m + 1, m + 2, m + 3, \dots , \quad (2)$$

where $R \equiv .01097/\text{nm}$ is a constant now referred to as *Rydberg's constant*, and Balmer's original formula is obtained when we take the special case $m = 2$, but Rydberg's formula describes other “series” of spectral lines, for $m = 1$, $m = 3$, etc. [The series $m = 1$ is now called the *Lyman series*, the one with $m = 3$ is called the *Paschen series*, etc., named after their original discoverers.]

Note that Fig. 40-16 in your textbook, p. 994, shows an *energy-level diagram* with all these spectral lines noted on it.

The most immediate question for us, and for the researchers of the time, is to determine a way of understanding these formulae, which were completed empirical; i.e., they were simply good “guesses” that agreed with the experimental data. Around 1913, Niels Bohr, a Danish physicist, completed his Ph.D. and went to England, to work with J.J. Thomson, and then with Ernest Rutherford, born in New Zealand. Both of these men were engaged in experiments to better determine the structure of the atom. An earlier model had been the so-called “plum-pudding” model. By then it was understood that the atom was a neutral object which had positively- and negatively-charged parts, since these could be knocked out. The plum-pudding model visualized the atom as a large mass of positively-charged “stuff” which had the much smaller, negatively-charged electrons embedded into it, in a fixed position, very much in the nature of raisins inside a pudding. [The British of the time were very fond of their plum puddings.] However, Rutherford’s experiments showed that this could not be the case; instead, it showed that a much better model was that the positively-charged “stuff” in the atom was quite small, and near the center of the atom. His experiments did maintain the idea that the electrons also were small and were reasonably far away from the center; this meant, of course, that there was a lot of simply empty space between the electrons and the center. [Nowadays we would refer to that central stuff as *the nucleus of the atom.*]

Since this picture was similar to our understanding of the solar system, with the massive sun at the center and the smaller planets circling around it, with, again, lots of empty space in between, Bohr proposed a similar model for the atom, in which the electrons circulated about the nucleus much like a planet about the sun. The reasons were even very similar, since the planets circulate because of the gravitational force, and the electrons circulated because of the electric force, both of which are proportional to the inverse of the square of the distance between them. However, there was a very serious problem with this model: the electromagnetic theory of moving charged particles says that acceleration would cause those particles to emit radiation—just like the usual sort of radio and TV waves that are now emitted by radio-sending antennas everywhere—which would cause the electron to quite quickly lose all the potential

energy it had and spiral into the nucleus and collapse the atom. It was quite clear that this was not what happened with atoms in the real world!

Bohr's response, to his own question, was to suppose that perhaps the classical theory did NOT apply to electrons inside atoms. Making the same sort of logical leaps that Planck, and Einstein, had already been making in the previous decade, Bohr decided to make some (very small number of) non-classical assumptions, and see they would then allow one to create a model that fit the experimental data. The most important difficulty with the planetary model was that the atom would be completely unstable, and decay within microseconds. Therefore, Bohr's *two assumptions* were designed explicitly to prevent this from happening:

- (1.) *Electrons inside an atom can exist in any of some number of stable states of fixed energy, without radiating. (We can label these states by some integers, say n ; they may therefore be considered as “quantum states.”)*
- (2.) *An atom emits, or absorbs, radiation at a fixed frequency when an electron in that atom moves from one of its stable quantum states to another:*

$$E_{n_i} - E_{n_f} = hf . \tag{3}$$

We immediately see the second assumption is influenced by the earlier work concerning photons; however, the first assumption has no basis whatsoever, except for the fact that it is necessary in order to create a theory based on accelerated motions of (charged) electrons.

In order to be able to use these “postulates” to describe the radiation being emitted by the atom, Bohr also inserted a “reasonableness” principle, that this, presumably more correct, theory should be able to reproduce the earlier, classical theory in the limit when the values of the quantum numbers, n , became very large, so that the “jumps” in energy because of these quantum effects would be incredibly small. This principle, following Bohr's thinking, is

now known as *the correspondence principle*, and is widely taken as a necessary part of more advanced theories. Bohr eventually used it to derive the value of the Rydberg constant. However, before we proceed to that derivation, we want now to compare these assumptions to Rydberg's original, empirical formula.

Since Rydberg's formula gives values for $1/\lambda$, if we multiply it by hc , we will acquire a formula for the energy of the photons, namely

$$hf_{mn} = \left(\frac{-hcR}{n^2} \right) - \left(\frac{-hcR}{m^2} \right), \quad (4)$$

where we have inserted the minus signs in the formula above so that it looks like Rydberg's formula. It required $n > m$, so we have written it to have the form where the result is positive when $n > m$. Since Bohr's second assumption wants the energy of the emitted photon to be equal to the difference of the energies of two allowed, quantum states of the electron, then it is very reasonable to suppose that this formula already gives us the individual energies of those states—since it gives the energy of the photon as the difference of two terms of the form of energies:

$$E_n = -\frac{hcR}{n^2}. \quad (5)$$

The fact that this means that the individual energies of the (quantum) states of the electron are negative is exactly what we actually want. This is because the electron and the nucleus are bound together to form the atom; the binding energy given by the Coulomb attraction between oppositely-charged particles is in fact negative! One could also look at the fact that it's negative as saying that one must do (positive) work in order to take the electron apart from the atom, i.e., away from the nucleus.

We suppose that the values of n in the equation for the energy begin with 1, and take on all integer values, beginning there and increasing. (Obviously we do not want to allow n to take on the value 0; on the other hand, allowing negative values would give the same results as positive values, so that we might as well just stick with the positive ones.) This then labels

the various states that the electron is allowed to reside in, in a stable configuration, inside the atom.

Derivation of the Energy Formula

Unfortunately, while the formula above for the energy is the correct one, it has not yet been obtained by a complete theoretical derivation, but, rather, by using our new modes of thought and comparing with Rydberg's empirical formula. In particular, it still contains the Rydberg constant, R , which was determined experimentally instead of in terms of fundamental principles and fundamental constants. Our task, now, is to follow through a careful, rigorous derivation of the value of this constant.

In fact Bohr followed quite a complicated logical path, first using Coulomb's law to determine the angular frequency of the electron as it follows a presumed circular path around the nucleus, and then using the **correspondence principle** to say that this angular frequency has to agree with the equations from classical mechanics for very large quantum numbers, n . The algebra is a bit involved. So we will use a somewhat simpler approach; however, our approach will be one that was evolved a few years after Bohr, involving the thinking of Prince Louis de Broglie, and the de Broglie wavelengths we have already been talking about, so far only for more or less free electrons, instead of those bound inside some system, like our atom.

We first presume that the electron actually travels in a circular orbit around the nucleus, like a planet around the sun. Therefore, the centripetal force required for an object to move along a circular path must be provided by some force. In this case that force is the (attractive) Coulomb force between the nucleus and the electron:

$$F_{Coulomb} = \frac{ke^2}{r^2} = \frac{mv^2}{r} = F_{centripetal} \quad (5)$$

which implies that $mv^2r = ke^2$.

From this requirement it is straightforward to determine all the relevant quantities in terms of just one (unknown) one. We will follow this approach and write out the formulas for the

velocity, the (orbital) angular momentum, the kinetic energy, the potential energy, and the total energy, **in terms of the radius r , and also the constants m and e^2 :**

$$\begin{aligned}
 v &= \sqrt{\frac{ke^2}{mr}} , & f &= v/(2\pi r) = \sqrt{\frac{ke^2}{4\pi^2 mr^3}} , & p &= mv = \sqrt{\frac{ke^2 m}{r}} , \\
 L &= mvr = \sqrt{ke^2 mr} , \\
 K &= \frac{1}{2}mv^2 = \frac{ke^2}{2r} , & U &= -\frac{ke^2}{r} , & E &= -\frac{ke^2}{2r} .
 \end{aligned} \tag{6}$$

At this point we need some requirement that will specify a quantum state label, i.e., a label to define the allowed states that Bohr insists the electron is allowed to be in. As already noted, Bohr—never having heard, at that time, of de Broglie’s work (which came in 1924, 11 years later)—required that the angular frequencies be consistent with the predictions of classical physics, at least for very large values of this quantum number for which we are now searching. On the other hand, we will here take de Broglie’s approach, and require that the electron must have a wavelength, and that it must revolve in a circular orbit, then we have a requirement exactly like the requirement on a guitar string; namely the length of the guitar string must be an exact integer multiple of the wavelength.

Since our electron must “fit” on a circle of radius r , we now require the reasonable requirement that the circumference of that circle must be an integer number of wavelengths:

$$2\pi r = n \lambda = nh/p \implies L = rp = n (h/2\pi) . \tag{7}$$

As soon as we start considering angles and circular motions, we find the combination $h/2\pi$ to be incredibly common; therefore, it has been common for very many years now to introduce a slightly modified symbol, so that this ratio does not have to be written out so much:

$$\hbar \equiv \frac{h}{2\pi} = 6.582 \times 10^{-16} \text{ eV-s} = 197.3 \text{ Mev-f/c} . \tag{8}$$

This brings us to the very simple statement that the (orbital) angular momentum of our electron in a “Bohr orbit” must simply be an integer multiple of \hbar . We may now go back and insert this statement into the equations above for the speed, the orbital radius, etc., and, finally, the

energy, to obtain their dependence on this integer n . Of course we do hope we already know the dependence of the energy on n ; however, the calculation will show that, firstly this n is the same as the one there, and, secondly, will also tell us the value of the Rydberg constant in terms of more fundamental physical constants. Although we could do that right away, and the algebra is simple, it is very useful to first introduce a couple of relevant combinations of constants:

$$\begin{aligned} \alpha &\equiv ke^2/\hbar c = 1/137 \quad \text{—the fine structure constant [dimensionless],} \\ a_0 &\equiv \frac{\hbar}{m\alpha} = \frac{\hbar^2}{ke^2m} = 52.92 \text{ pm} \quad \text{—the Bohr radius.} \end{aligned} \tag{9}$$

We may write out the following relationships for the Bohr model of the electron:

$$\begin{aligned} v &= \alpha c/n, \quad L = n\hbar, \quad r = n^2 \frac{\hbar}{\alpha mc} = n^2 a_0, \\ E &= -K = U/2 = -\frac{1}{2}mc^2\alpha^2/n^2 = -13.6 \text{ eV}/n^2. \end{aligned} \tag{10}$$

These quantized energies are in fact the correct energies—at least to 3 significant figures. The model, that the electron revolves in something like a circular orbit, is no longer consistent with what we would say today is an accurate picture of the behavior of the electron in a hydrogen atom, although it is true that the *Bohr radius*, a_0 , above is a remarkably useful and convenient unit to describe atomic systems. Nonetheless the theory was surprisingly successful in analyzing the electromagnetic radiations emitted by hydrogen. [It should also be noted that it can also be applied to many other atoms if we replace, everywhere, the structure constant α by $Z\alpha$, where Z is the number of positive charges within the nucleus of that atom.] On the other hand, it does not provide any basis to calculate which among the many allowed radiations are more likely to be emitted, nor does it tell us anything about how to create molecular bonds between hydrogen and other atoms. Lastly, it also tells us (almost) nothing about the wave structure of the electron in the atom. That wave structure was provided, even later, in 1927 and 1925, by Erwin Schrödinger and Werner Heisenberg. We will spend a little time looking at it somewhat later in the course.

adapted from RKH4, Chapter 51.