

## 7.4: The Bohr Model of Hydrogen-like Atoms

The model proposed in 1913 by the Danish physicist Niels Bohr (and later further developed by Arnold Sommerfeld) to describe the hydrogen spectrum was of great importance in the historical development of atomic theory. Even though it is very different from the modern description of an atom, it is difficult to avoid a summary of it in any introductory description of spectroscopy. In the simplest form, we could describe a model of an electron moving around a proton in a circular orbit. Here, however, we shall include in the theory such hydrogenlike atoms as  $\text{He}^+$ ,  $\text{Li}^{++}$ ,  $\text{Be}^{+++}$ , etc. Furthermore, we shall not suppose that the electron moves around the nucleus; rather we assume that the nucleus has a charge  $Ze$  ( $Z$  = atomic number) and mass  $M$ , and the electron has a mass  $m$ , and the electron and nucleus move around their common centre of mass.

In Bohr's original model it was assumed that the electron could move round only in certain circular orbits (he and Sommerfeld later included the possibility of elliptic orbits in order to explain fine structure) such that the angular momentum is an integral multiple of Planck's constant divided by  $2\pi$ . [The symbol  $\hbar$  is short for  $h/(2\pi)$  and is a quantum unit of angular momentum.] This was an empirical assumption made only because it correctly predicted the appearance of the hydrogen spectrum.

Let us suppose that the hydrogen-like atom has a nucleus of charge  $+Ze$  and mass  $M$ , and the electron has charge  $-e$  and mass  $m$ , and that the distance between them is  $a$ . The distance of the nucleus from the centre of mass is  $ma/(M+m)$  and the distance of the electron from the centre of mass is  $Ma/(M+m)$ . We'll suppose that the speed of the electron in its orbit around the centre of mass is  $v$ . It may not be immediately obvious, and the reader should take the trouble to derive it, that the angular momentum of the system is  $mva$ . Bohr's first assumption, then is that

$$mva = n\hbar, \quad (7.4.1)$$

where  $n$  is an integer.

The Coulomb force on the electron is equal to its mass times its centripetal acceleration:

$$\frac{Ze^2}{4\pi\epsilon_0 a^2} = \frac{mv^2}{Ma/(M+m)}. \quad (7.4.2)$$

If you eliminate  $v$  from these, you obtain an expression for the radius of the  $n$ th orbit:

$$a = \frac{4\pi\epsilon_0 \hbar^2 n^2}{Ze^2 \mu}, \quad (7.4.3)$$

where

$$\mu = \frac{mM}{m+M}. \quad (7.4.4)$$

The quantity represented by the symbol  $\mu$  is called the *reduced mass* of the electron. It is slightly less than the actual mass of the electron. In the hydrogen atom, in which the nucleus is just a proton, the ratio  $M/m$  is about 1836, so that  $\mu = 0.99946m$ . For heavier hydrogen-like atoms it is closer to  $m$ .

Notice that the radius depends on  $n^2$ , so that, for example, the radius of the  $n = 2$  orbit is four times that of the  $n = 1$  orbit. The reader should now calculate the radius of the first Bohr orbit for hydrogen. It should come to about 0.053 nm, so that the diameter of the hydrogen atom in its ground state is a little over one angstrom. Logically, I suppose, the symbol  $a_1$  should be used for the first Bohr orbit, but in practice the usual symbol used is  $a_0$ . If you wish to calculate the radius of the first Bohr orbit for some other hydrogen-like atom, such as D, or  $\text{He}^+$ , or muonic hydrogen, note that for such atoms the only things that are different are the masses or charges or both, so there is no need to repeat the tedious calculations that you have already done for hydrogen. It would also be of interest to calculate the radius of the orbit with  $n = 109$ , in view of the observation of the radio line 109 $\alpha$  mentioned in section 7.3.

By eliminating  $a$  rather than  $v$  from equations 7.4.1 and 7.4.2 you could get an explicit expression for the speed of the electron in its orbit. Alternatively you can simply calculate  $v$  from equation 7.4.2 now that you know  $a$ . You should, for interest, calculate  $v$ , the speed of the electron in the first Bohr orbit, and see how large a fraction it is of the speed of light and hence to what extent our nonrelativistic analysis so far has been. You should also calculate the frequency of the orbital electron - i.e. how many times per second it orbits the nucleus. The explicit expression for  $v$  is

$$v = \frac{MZe^2}{4\pi\epsilon_0(M+m)\hbar n}. \quad (7.4.5)$$

The energy of the atom is the sum of the mutual potential energy between nucleus and electron and the orbital kinetic energies of the two particles. That is:

$$E = -\frac{Ze^2}{4\pi\epsilon_0 a} + \frac{1}{2}mv^2 + \frac{1}{2}M\left(\frac{mv}{M}\right)^2. \quad (7.4.6)$$

If we make use of equation 7.4.2 this becomes

$$\begin{aligned} E &= -\frac{m(M+m)v^2}{M} + \frac{1}{2}mv^2 + \frac{1}{2}\frac{m^2}{M}v^2 \\ &= -\frac{1}{2}m\left(\frac{M+m}{M}\right)v^2. \end{aligned}$$

Then, making use of equation 7.4.5, we obtain for the energy

$$E = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \cdot \frac{1}{n^2}. \quad (7.4.7)$$

In deriving this expression for the energy, we had taken the potential energy to be zero at infinite separation of proton and nucleus, which is a frequent convention in electrostatics. That is, the energy level we have calculated for a bound orbit is expressed relative to the energy of ionized hydrogen. Hence the energy of all bound orbits is negative. In tables of atomic energy levels, however, it is more usual to take the energy of the ground state ( $n = 1$ ) to be zero. In that case the energy levels are given by

$$E = \frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \cdot \left(1 - \frac{1}{n^2}\right). \quad (7.4.8)$$

Further, as explained in section 7.1, it is customary to tabulate *term values*  $T$  rather than energy levels, and this is achieved by dividing by  $hc$ . Thus

$$T = \frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2 hc} \cdot \left(1 - \frac{1}{n^2}\right). \quad (7.4.9)$$

The expression before the large parentheses is called the *Rydberg constant* for the atom in question. For hydrogen ( $^1\text{H} : Z = 1$ ), it has the value  $1.09679 \times 10^7 \text{ m}^{-1}$ .

If we put  $Z = 1$  and  $\mu = m$  the resulting expression is called the *Rydberg constant for a hydrogen nucleus of infinite mass*; it is the expression one would arrive at if one neglected the motion of the nucleus. It is one of the physical constants whose value is known with greatest precision, its value being

$$R_\infty = 1.097\,373\,153\,4 \times 10^7 \text{ m}^{-1}.$$

(The gravitational constant  $G$  is probably the least precisely known.)

The term value equal to  $1.097\,373\,153\,4 \times 10^7 \text{ m}^{-1}$ , or the corresponding energy, which is  $2.1799 \times 10^{-18} \text{ J}$  or  $13.61 \text{ eV}$ , is called a *rydberg*.

We can use equation 7.4.9 now to calculate the term values for the hydrogen atom. We use, of course, the Rydberg constant for the real hydrogen atom, not for infinite mass. We obtain:

$n$	$T \text{ (}\mu\text{m}^{-1}\text{)}$
$\infty$	10.9679
6	10.6632
5	10.5292
4	10.2824
3	9.7492
2	8.2259
1	0.0000

Notice the large gap between  $n = 1$  and  $n = 2$ , which corresponds to the line Lyman- $\alpha$  75% of the way from the ground level ( $n = 1$ ) to the ionization limit ( $n = \infty$ ). The level  $n = 3$  is 89% of the way, and  $n = 4$  is 94% of the way.

You can now calculate the vacuum wavenumbers (and standard air or vacuum wavelengths) for all the series. The lower level for the Lyman series is  $n = 1$ , so the wavenumbers of the lines are just equal to the term values of the higher levels. The vacuum wavelengths of the Lyman lines, as well as the series limit, are therefore:

Ly $\alpha$	121.57 nm
Ly $\beta$	102.57
Ly $\gamma$	97.25
Ly $\delta$	94.97
Ly $\epsilon$	93.78
Limit	91.18

The Lyman series limit corresponds to an ionization potential of 13.59 volts.

The lower level of the Balmer series is  $n = 2$ , so you can now verify the wavelengths and wavenumbers given in section 7.2. In a similar manner, you can calculate the wavelengths of the several infrared series.

Should you wish to calculate the wavelengths of corresponding lines in the spectra of other hydrogenlike atoms, such as D, or  $\text{He}^+$  or muonic hydrogen, all you need do is to put the appropriate values of  $Z$  and  $\mu$  in the expression for the Rydberg constant (see equation 7.4.9). The wavelengths of corresponding lines in the spectrum of deuterium are close to, but not exactly equal to, those of  $^1\text{H}$ . The reader is strongly urged to calculate the term values for  $\text{He}^+$ . Then draw two energy level diagrams, to scale, side-by-side, for H and  $\text{He}^+$ , positioning them so that  $n = 1$  for H is at the same horizontal level as  $n = 2$  for  $\text{He}^+$ . Please do this - it will take only a few minutes with pencil and paper, but it would take me all day to try and do it on this computer. In any case, you will understand it far better if you do it yourself. You will find that, for  $\text{He}^+$ ,  $n = 1$  lies a long, long way below  $n = 2$ . The wavelength of the line, which corresponds to Ly  $\alpha$ , is 30.38nm. You will find that the ionization potential for  $\text{He}^+$  is 54.4 volts. You will find that the levels  $n = 2, 4, 6$  of  $\text{He}^+$  nearly coincide with the levels  $n = 1, 2, 3$  of H, but that the odd-numbered levels of  $\text{He}^+$  fall in between. The He II series whose lower level is  $n = 3$  is called the Fowler series, and the wavelength of its first member is 468.6 nm. (The reference in which I looked this up did not say whether this was the vacuum or the standard air wavelength. Please, always, when you are writing your scientific material, be absolutely explicit about this; you cannot expect the reader to guess. For the time being, however, you have enough information to calculate the term values for  $\text{He}^+$  and hence to calculate the vacuum wavenumber and the standard air wavelength yourself.) The series for which the lower level is  $n = 4$  is called the Pickering series. You should be able to calculate the following standard air wavelengths:

656.02 nm
541.16
485.94
454.17
433.87
419.99
410.01

You will notice that half of these coincide closely with lines in the Balmer series of H I. These lines are important in the spectra of O stars.

The Bohr theory has been remarkably successful in enabling you to calculate the energy levels, wavelengths and series limits for hydrogenlike atoms, and consequently no apology need be offered for discussing it in such detail. Yet it has its limitations. It does not explain the fine structure (which we have yet to describe) that can be observed in hydrogenlike spectra, and is inadequate to deal with the spectra of more complex atoms, in which the "fine structure" is by no means as "fine" as it is in hydrogen. True, Bohr and Sommerfeld managed to refine the theory with some success by including the possibility of elliptical orbits. Yet a more unsatisfying aspect of Bohr theory is not so much its weakness in dealing with fine structure, but is the somewhat arbitrary and *ad hoc* nature of its assumptions. In classical electromagnetic theory, an electron in orbit around a proton will radiate away energy and will rapidly spiral in towards the nucleus. And the assumption that the only orbits possible are those in which the angular momentum of the system is an integral number of times  $h/(2\pi)$ , while it successfully predicts the spectrum, hardly explains it.

The development of wave mechanics not only copes better with fine structure, but the quantization of energy levels appears naturally and without the need for *ad hoc* assumptions.

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