

## HYDROGEN ATOM - SPECTRUM

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Section 4.2.2 & Problem 4.16.

In the (relatively) simple model of the hydrogen atom we've been looking at, the energy levels depend only on the quantum number  $n$ . (In reality, the energy *does* depend on the other quantum numbers  $l$  and  $m$  as well, but we'll get to that in due course.)

Although the wave functions corresponding to the various states are stationary, if the atom is bumped or prodded in some way, transitions between the states can be made to happen. If an atom is excited (moved from a lower to a higher energy state), it must absorb the energy difference between the two states; similarly, if an atom in an excited state decays to a lower state, it emits a photon whose energy is the difference in energy levels.

Thus hydrogen (well, any atom, really) can have an *absorption spectrum* if light is shone on it and some of the photons are absorbed to excite the atoms, or an *emission spectrum* if excited atoms decay and emit photons. The energies of these photons are easily calculated from the Bohr energy formula:

$$E_n = -\frac{1}{n^2} \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} \quad (1)$$

For transitions from or to the ground state, we calculate  $E_n - E_1$  for  $n = 2, 3, \dots$ . The series of energies so obtained is called the Lyman series, named after the Harvard physicist Theodore Lyman, who discovered them experimentally in the years 1906 - 1914. Their energies are

$$E_{n1} = E = \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} \left(1 - \frac{1}{n^2}\right) \quad (2)$$

This energy can be related to the wavelength of the photon emitted or absorbed by using Planck's formula

$$E = h\nu \quad (3)$$

Note that this formula uses the bare Planck constant  $h$  and not  $\hbar = h/2\pi$ . The relation between frequency  $\nu$  and wavelength  $\lambda$  is  $\lambda = c/\nu$  where  $c$  is the speed of light, so we can find  $\lambda$  as

$$\frac{1}{\lambda} = \frac{\nu}{c} \quad (4)$$

$$= \frac{E}{hc} \quad (5)$$

$$= \frac{me^4}{2hc\hbar^2(4\pi\epsilon_0)^2} \left(1 - \frac{1}{n^2}\right) \quad (6)$$

We can rewrite the constant in the last equation as

$$R = \frac{me^4}{2hc\hbar^2(4\pi\epsilon_0)^2} \quad (7)$$

$$= \frac{me^4}{4\pi c\hbar^3(4\pi\epsilon_0)^2} \quad (8)$$

$$= 1.097 \times 10^7 m^{-1} \quad (9)$$

This constant is known as the Rydberg constant, named after Johannes Rydberg, a Swedish physicist who devised a formula for predicting the wavelengths of photons emitted by hydrogen atoms in 1888. Clearly, as Rydberg's formula predates quantum mechanics by several decades, his formula was based on experimental measurements rather than quantum theory. He couldn't have derived the theoretical form of the constant given here; rather he would have come up with the numerical value.

For other transitions, the formula is very similar. In general, if an atom makes a transition between an initial state  $i$  and a final state  $f$ , the wavelength of the photon involved is

$$\frac{1}{\lambda} = R \left| \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \right| \quad (10)$$

We've used the absolute value since the wavelength is always positive. Depending on the initial and final states, the difference in this formula could be positive or negative, depending on whether the photon is absorbed or emitted.

The series of wavelengths resulting from transitions to and from  $E_2$  are known as the Balmer series, named after Johann Balmer, a Swiss physicist who devised an empirical formula for these lines in 1885.

The series resulting from  $E_3$  is called the Paschen series, from  $E_4$  we get the Brackett series, from  $E_5$  the Pfund series and from  $E_6$  the Humphreys series. Higher series are so far unnamed, so if you fancy a go at fame in physics you could try to get your name attached to one of them.

By plugging in the numbers, we find that the Lyman series is entirely in the ultraviolet, the Balmer series is in the visible region, and all higher series are in the infrared.

We can work out similar series for any 'hydrogen-like' atom, that is, an atom with  $Z$  protons in the nucleus and a single electron. The idea is that the positive charge in the hydrogen atom changes from  $e$  to  $Ze$  so the change needs to be propagated through all the various formulas. Since the elementary charge  $e$  occurs only in the form  $e^2$  (or the square of this) we need to replace every occurrence of  $e^2$  with  $Ze^2$ . We get (using the subscript  $H$  to indicate values for the hydrogen atom, that is, for  $Z = 1$ ):

$$E_n = Z^2 E_{nH} \quad (11)$$

$$a = \frac{a_H}{Z} \quad (12)$$

$$R = Z^2 R_H \quad (13)$$

The revised Bohr radius follows from the original formula for hydrogen  $a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ .

For  $Z = 2$ , the energy levels are all four times those for hydrogen, so the ground state is  $E_1 = 4 \times (-13.4) = -53.6 \text{ eV}$ .

The Lyman series is the set of spectral lines generated by transitions to the ground state, where the wavelengths are found from

$$\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (14)$$

with  $n_f, n_i$  being the final and initial states respectively. Since the Rydberg constant is  $Z^2$  times that for hydrogen, the frequencies of the spectral lines will be  $Z^2$  those for hydrogen, and the wavelengths  $1/Z^2$  those of hydrogen.

For  $Z = 2$ , the longest Lyman wavelength is  $303.86 \text{ \AA}$  which is well into the ultraviolet area. For  $Z = 3$ , the longest Lyman wavelength is  $135 \text{ \AA}$ , even further into the ultraviolet.

Note that we can't derive anything for cases where the number of *electrons* is greater than 1 by any such simple method, since we then have several separate negative charges, which will interact with each other as well as with the nucleus, making the potential much more complex. Such problems do not have any exact solutions, and need to be tackled either numerically or approximately.

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