HYDROGEN-LIKE ATOMS

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.2.

We've seen how the Schrödinger equation for a two-particle system can be split into two one-particle equations if the potential depends only on the separation of the particles. We can apply this to examine some aspects of the hydrogen atom and of hydrogen-like atoms (atoms where we have one positive and one negative particle). The binding energy of the electron in hydrogen in various energy states, and the corresponding spectrum when the electron undergoes a transition between states all depend on the electron mass. The energy levels are, if we use the unadorned electron mass m_e:

$$E_n = -\frac{1}{n^2}\frac{m_e e^4}{2\hbar^2(4\pi\epsilon_0)^2} \tag{1}$$

In the separation of variables solution, we get one equation representing a free particle at the centre of mass and another representing a single particle with the reduced mass of the system moving in the standard Coulomb potential. If we want to replace m_e by the reduced mass $\mu_h = m_e m_p/(m_e + m_p)$ we'll need the masses of the electron and proton. We have

$$m_p = 1.67262158 \times 10^{-27}\text{kg} \tag{2}$$

$$m_e = 9.10938188 \times 10^{-31}\text{kg} \tag{3}$$

$$\mu_h = \frac{m_e m_p}{m_e + m_p} \tag{4}$$

$$= 9.104423456 \times 10^{-31}\text{kg} \tag{5}$$

Plugging in the numbers we find that

$$\frac{m_e - \mu_h}{m_e} \times 100\% = 0.05443\% \tag{6}$$

Since the binding energy depends linearly on the mass, this is the percentage error in the binding energy as well. Thus the error in using the electron mass on its own is quite small.

Now suppose we look at a deuterium atom, which has mass

$$m_d = 3.342674 \times 10^{-27}\text{kg} \tag{7}$$

This gives a reduced mass of

$$\mu_d = 9.1069 \times 10^{-31}\text{kg} \tag{8}$$

The revised Rydberg constants for hydrogen and deuterium are

$$\begin{aligned}
R_h &= \frac{\mu_h}{m_e} R && (9)\\
&= \frac{\mu_h}{m_e} \frac{m_e e^4}{2hc\hbar^2 (4\pi\epsilon_0)^2} && (10)\\
&= 1.0964 \times 10^7 \text{m}^{-1} && (11)\\
R_d &= \frac{\mu_d}{m_e} R && (12)\\
&= 1.0967 \times 10^7 \text{m}^{-1} && (13)
\end{aligned}$$

The wavelength produced by a transition between states with primary quantum numbers n_i and n_f is

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

For hydrogen between states 3 and 2 we get

$$\begin{aligned}
\lambda_h &= \frac{1}{R_h} \left(\frac{1}{2^2} - \frac{1}{3^2} \right)^{-1} && (15)\\
&= \frac{1}{0.139 R_h} && (16)\\
&= 6566.9 \times 10^{-10} \text{ m} && (17)
\end{aligned}$$

For deuterium, we get

$$\begin{aligned}
\lambda_d &= \frac{1}{0.139 R_d} && (18)\\
&= 6565.1 \times 10^{-10} \text{ m} && (19)
\end{aligned}$$

The separation of these two spectral lines is therefore 1.8×10^{-10} m.

We can form another hydrogen-like 'atom' by pairing an electron with a positron, which has the same mass as the electron but a positive charge. In this case, the reduced mass is $\mu_+ = m_e/2$, so the binding energy would be half that of ordinary hydrogen, or -6.8 eV.

Finally, we can pair a proton with a muon, which has a mass of $206.77m_e$, giving a reduced mass of $\mu_\mu = 1692.91 \times 10^{-31}$ kg. The Rydberg constant becomes $R_\mu = \frac{\mu_\mu}{m_e} R = 185.84R = 2.0387 \times 10^9$ m^{-1}. The Lyman-α line (transition from $n = 2$ to $n = 1$) is

$$\lambda_\mu = \frac{1}{0.75R_\mu} = 6.5 \times 10^{-10} \text{ m} \tag{20}$$