Problem 5.2

In view of Problem 5.1, we can correct for the motion of the nucleus in hydrogen by simply replacing the electron mass with the reduced mass.

- **(a)** Find (to two significant digits) the percent error in the binding energy of hydrogen (Equation 4.77) introduced by our use of m instead of μ.
- **(b)** Find the separation in wavelength between the red Balmer lines ($n = 3 \to n = 2$) for hydrogen and deuterium (whose nucleus contains a neutron as well as the proton).
- **(c)** Find the binding energy of **positronium** (in which the proton is replaced by a positron—positrons have the same mass as electrons, but opposite charge).
- **(d)** Suppose you wanted to confirm the existence of **muonic hydrogen**, in which the electron is replaced by a muon (same charge, but 206.77 times heavier). Where (i.e. at what wavelength) would you look for the "Lyman-α" line ($n = 2 \to n = 1$)?

Solution

Part (a)

A hydrogen atom consists of a proton with mass m_p and an electron with mass m_e. The proton was held fixed at the origin in Chapter 4, but now it's allowed to move like the electron. The Schrödinger equation governs the wave function $\Psi = \Psi(\mathbf{r}_e, \mathbf{r}_p, t) = \Psi(x_e, y_e, z_e, x_p, y_p, z_p, t)$ of this two-particle system's state.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m_e}\nabla_e^2\Psi - \frac{\hbar^2}{2m_p}\nabla_p^2\Psi + V(\mathbf{r}_e, \mathbf{r}_p)\Psi(\mathbf{r}_e, \mathbf{r}_p, t)$$

Since this is a linear and homogeneous partial differential equation, the method of separation of variables can be applied here. Assume a product solution of the form $\Psi(\mathbf{r}_e, \mathbf{r}_p, t) = \psi(\mathbf{r}_e, \mathbf{r}_p)T(t)$ and plug it into the PDE.

$$i\hbar\frac{\partial}{\partial t}[\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)] = -\frac{\hbar^2}{2m_e}\nabla_e^2[\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)] - \frac{\hbar^2}{2m_p}\nabla_p^2[\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)] + V(\mathbf{r}_e, \mathbf{r}_p)[\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)]$$

$$i\hbar\psi(\mathbf{r}_e, \mathbf{r}_p)T'(t) = -\frac{\hbar^2}{2m_e}T(t)\nabla_e^2\psi - \frac{\hbar^2}{2m_p}T(t)\nabla_p^2\psi + V(\mathbf{r}_e, \mathbf{r}_p)\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)$$

Divide both sides by $\psi(\mathbf{r}_e, \mathbf{r}_p)T(t)$ to separate variables.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2m_e}\frac{1}{\psi}\nabla_e^2\psi - \frac{\hbar^2}{2m_p}\frac{1}{\psi}\nabla_p^2\psi + V(\mathbf{r}_e, \mathbf{r}_p)$$

The only way a function of time can be equal to a function of position is if they're equal to a constant.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2m_e}\frac{1}{\psi}\nabla_e^2\psi - \frac{\hbar^2}{2m_p}\frac{1}{\psi}\nabla_p^2\psi + V(\mathbf{r}_e, \mathbf{r}_p) = E$$

As a result of using the method of separation of variables, Schrödinger's equation has reduced to two simpler differential equations.

$$\left.\begin{aligned} i\hbar\frac{T'(t)}{T(t)} &= E \\ -\frac{\hbar^2}{2m_e}\frac{1}{\psi}\nabla_e^2\psi - \frac{\hbar^2}{2m_p}\frac{1}{\psi}\nabla_p^2\psi + V(\mathbf{r}_e, \mathbf{r}_p) &= E \end{aligned}\right\}$$

The solution to the first is $T(t) = e^{-iEt/\hbar}$. The second equation is known as the time-independent Schrödinger equation.

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\psi - \frac{\hbar^2}{2m_p}\nabla_p^2\psi + V(\mathbf{r}_e, \mathbf{r}_p)\psi = E\psi$$

Because the potential energy only depends on the displacement between the proton and electron, the TISE can be simplified by making the change of variables from $\mathbf{r}_e$ and $\mathbf{r}_p$ to $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p$ and $\mathbf{R} = (m_e\mathbf{r}_e + m_p\mathbf{r}_p)/(m_e + m_p)$. As shown in Problem 5.1, this results in the following two equations.

$$\left.\begin{aligned} -\frac{\hbar^2}{2(m_e + m_p)}\nabla_R^2\psi_R + 0\psi_R(\mathbf{R}) &= E_R\psi_R(\mathbf{R}) \\ -\frac{\hbar^2}{2\mu}\nabla_r^2\psi_r + V(\mathbf{r})\psi_r(\mathbf{r}) &= E_r\psi_r(\mathbf{r}) \end{aligned}\right\}$$

μ is the reduced mass of the two-particle system,

$$\mu = \frac{m_e m_p}{m_e + m_p},$$

and the total energy is $E = E_r + E_R$. E_R is the kinetic energy of the electron and proton as if they were one at the center of mass, and E_r is the energy involving the Coulombic attraction between the particles—this is what we want. The equation above for ψ_r is the same one analyzed in Section 4.2 but with μ instead of m_e. The boxed result in Equation 4.70 on page 147 is used here.

$$E_r = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3, \ldots$$

The binding energy of hydrogen is the energy required to remove the ground-state electron from the proton's vicinity, so set $n = 1$.

$$\begin{aligned} E_{r1} &= -\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \\ &= -\frac{m_e m_p}{2(m_e + m_p)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \\ &\approx -13.5983 \text{ eV} \end{aligned}$$

The percent error of $E_1 \approx -13.6057$ eV (given in Equation 4.77 on page 148) compared to E_{r1} is

$$\begin{aligned}
\text{Percent Error} &= \frac{\text{Approximate Value} - \text{Actual Value}}{\text{Actual Value}} \times 100\% \\
&= \frac{E_1 - E_{r1}}{E_{r1}} \times 100\% \\
&= \frac{-\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 + \frac{m_e m_p}{2(m_e+m_p)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2}{-\frac{m_e m_p}{2(m_e+m_p)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2} \times 100\% \\
&= \frac{1 - \frac{m_p}{m_e+m_p}}{\frac{m_p}{m_e+m_p}} \times 100\% \\
&= \frac{(m_e + m_p) - m_p}{m_p} \times 100\% \\
&= \frac{m_e}{m_p} \times 100\% \\
&\approx 0.054\%.
\end{aligned}$$

This means that E_1 is about 0.054% higher than E_{r1}: $E_1 \approx 1.00054 E_{r1}$.

Part (b)

When a hydrogen atom transitions from $n = 3$ to $n = 2$, a photon is emitted with energy $E_\gamma = h\nu$.

$$\begin{aligned}
E_\gamma &= E_{r3} - E_{r2} \\
h\nu &= -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{3^2} + \left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{2^2} \\
(2\pi\hbar)\left(\frac{c}{\lambda}\right) &= \frac{5}{36}\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] \\
\frac{1}{\lambda} &= \frac{5}{72\pi\hbar c}\left[\frac{m_e m_p}{2(m_e + m_p)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]
\end{aligned}$$

Inverting both sides gives the wavelength of the hydrogen line.

$$\lambda_{\text{H}} = \frac{144\pi(m_e + m_p)\hbar^3 c}{5 m_e m_p}\left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \approx 6.56469606 \times 10^{-7} \text{ m}$$

Deuterium is similar to hydrogen except that it has a neutron with mass m_n in addition to the proton and electron. Since the neutron is electrically neutral and has practically the same position as the proton, the analysis is the same as above except that m_p is replaced with $m_p + m_n$.

$$\lambda_{\mathrm{D}} = \frac{144\pi[m_e + (m_p + m_n)]\hbar^3 c}{5m_e(m_p + m_n)} \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \approx 6.56290818 \times 10^{-7} \text{ m}$$

Therefore, the separation between the hydrogen and deuterium lines for an $n = 3 \to n = 2$ transition is

$$\begin{aligned}
\Delta\lambda &= \lambda_{\mathrm{H}} - \lambda_{\mathrm{D}} \\
&= \frac{144\pi(m_e + m_p)\hbar^3 c}{5m_e m_p} \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 - \frac{144\pi[m_e + (m_p + m_n)]\hbar^3 c}{5m_e(m_p + m_n)} \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \\
&= \frac{144\pi\hbar^3 c}{5m_e} \left[\frac{m_e + m_p}{m_p} - \frac{m_e + (m_p + m_n)}{m_p + m_n}\right] \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \\
&= \frac{144\pi\hbar^3 c}{5m_e} \left[\frac{m_e m_n}{m_p(m_p + m_n)}\right] \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \\
&= \frac{144\pi m_n \hbar^3 c}{5m_p(m_p + m_n)} \left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \\
&\approx 1.78788 \times 10^{-10} \text{ m.}
\end{aligned}$$

Part (c)

Positronium is similar to hydrogen except that it has a positron with mass m_e in place of the proton. The positron has the same charge as the proton, so the analysis is the same as in part (a) except that m_p is replaced with m_e. The binding energy of positronium is therefore

$$\begin{aligned}
E_{r1} = -\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -\frac{m_e m_e}{2(m_e + m_e)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -\frac{m_e}{4\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 &= \frac{E_1}{2} \\
&\approx -1.08994 \times 10^{-18} \text{ J} \\
&\approx -6.80285 \text{ eV.}
\end{aligned}$$

Part (d)

Muonic hydrogen is similar to hydrogen except that it has a muon with mass $206.77m_e$ in place of the electron. The muon has the same charge as the electron, so the analysis is the same as in part (a) except that m_e is replaced with $206.77m_e$.

$$E_r = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3, \ldots$$

$$= -\left[\frac{(206.77m_e)m_p}{2[(206.77m_e) + m_p]\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

When a muonic-hydrogen atom transitions from $n = 2$ to $n = 1$, a photon is emitted with energy $E_\gamma = h\nu$.

$$E_\gamma = E_{r2} - E_{r1}$$

$$h\nu = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{2^2} + \left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{1^2}$$

$$(2\pi\hbar)\left(\frac{c}{\lambda}\right) = \frac{3}{4}\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]$$

$$\frac{1}{\lambda} = \frac{3}{8\pi\hbar c}\left[\frac{206.77m_e m_p}{2(206.77m_e + m_p)\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]$$

Inverting both sides gives the wavelength of the muonic-hydrogen line.

$$\lambda_{\mu\mathrm{H}} = \frac{16\pi(206.77m_e + m_p)\hbar^3 c}{620.31m_e m_p}\left(\frac{4\pi\epsilon_0}{e^2}\right)^2 \approx 6.53793 \times 10^{-10}\ \mathrm{m}$$