Assignment 4 Solutions

1. The “red line” in the Balmer series is the photon that results when the H atom changes state from $n = 3$ to $n = 2$. This photon has an energy

$$E_{\text{phot}} = E_3 - E_2 = \frac{-2.18 \times 10^{-18} \text{ J}}{3^2} - \frac{-2.18 \times 10^{-18} \text{ J}}{2^2} = 3.03 \times 10^{-19} \text{ J}.$$ 

This is the energy that the electron in the box will gain when it absorbs the photon. The electron starts in its ground state ($n = 1$, where this $n$ is the particle-in-a-box quantum number—the other $n$ is the H atom principal quantum number), absorbs this energy, and ends in $n = 2$. This energy change is related to the box length $L$ through

$$\Delta E = \frac{\hbar^2}{8m_eL^2} \left(2^2 - 1^2\right) \quad \text{or} \quad L = \sqrt{\frac{3\hbar^2}{8m_e\Delta E}} = 7.73 \times 10^{-10} \text{ m} = 7.73 \text{ Å}.$$ 

2. Problem 77 makes it clear that the symmetry of the wavefunction ensures that the probability of finding the particle between 0 and $L/4$ is 1/4, as the figure below emphasizes.

![Graph showing wavefunction symmetry](image)

The area under the red curve for $\Psi^2$ over the interval $0 \leq x \leq L/4$ (the green bar) is the same as the area over $L/4 \leq x \leq L/2$ or $L/2 \leq x \leq 3L/4$ or $3L/4 \leq x \leq L$. But for $n = 1$, the symmetry changes:

![Graph showing wavefunction symmetry](image)
Here, you can see at a glance that the area under $\Psi^2$ from 0 to $L/4$ is much less than the area from $L/4$ to $L/2$. Thus, the probability of finding the particle anywhere between 0 and $L/4$ is much less than the probability of finding it between $L/4$ and $L/2$. (Note however that symmetry can still be invoked here for some situations. The probability between 0 and $L/4$ is the same as from $3L/4$ to $L$, for instance.) The probability’s numerical value in this case is given by the expression below (and I don’t expect you to know how to do this integral off the top of your head!):

\[
\text{Probability} = \int_0^{L/4} \Psi(x)^2 \, dx = \frac{2}{L} \int_0^{L/4} \sin^2 \left(\frac{\pi x}{L}\right) \, dx = \frac{\pi - 2}{4\pi} = 0.0908 .
\]

3. First, we use the expression in Equation [15.22] to calculate the size of a hydrogen atom ($Z = 1$) in the 3d ($n = 3$, $l = 2$) state:

\[
\overline{r}_{nl} = \frac{n^2a_0}{Z} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right\} = 10.5 \, a_0 .
\]

Then we make a table of $\overline{r}_{nl}$ values for various $n$ and $l$ values for He$^+$ ($Z = 2$):

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$\overline{r}_{nl}/a_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3.00</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.50</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>6.75</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>6.25</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5.25</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>12.00</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>11.50</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>10.50</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>9.00</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>18.75</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>18.25</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>17.25</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>15.75</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>13.75</td>
</tr>
</tbody>
</table>

This table shows that the $n = 4$, $l = 2$ (or 4d) He$^+$ ion has the same average size as the H atom in the 3d state. The He$^+$ 4s and 4p states and all $n > 4$ states are larger than H 3d. Note as well that the average radius does not depend on the $m$ quantum number.

4. First, let’s review the $Z_{\text{eff}}$ calculation. We know the Na first ionization energy: $IE = 8.23 \times 10^{-19}$ J, and we measured the sodium D line wavelength in lab to be about $\lambda = 590$ nm. This wavelength corresponds to a photon energy of
\[ E_{\text{phot}} = \frac{hc}{\lambda} = 3.37 \times 10^{-19} \text{ J} . \]

We can now construct the energy level diagram below for Na:

\[
\begin{array}{c}
E = 0 \\
0 \text{ J} \\
\end{array}
\]

\[
\begin{array}{c}
E_{3p} = -IE + E_{\text{phot}} \\
-4.95 \times 10^{-19} \text{ J} \\
E_{\text{phot}} \\
E_{3s} = -IE \\
-8.23 \times 10^{-19} \text{ J}
\end{array}
\]

From the general expression for the energy of an atomic level in terms of an effective nuclear charge:

\[
E_{n,l} = -\frac{e^4 m_e}{8 \varepsilon_0 h^2} \frac{Z_{\text{eff},n,l}^2}{n^2} Z_{\text{eff},n,l}^2 = -2.18 \times 10^{-18} \text{ J} \frac{Z_{\text{eff},n,l}^2}{n^2}
\]

we can write an expression for \( Z_{\text{eff}} \):

\[
Z_{\text{eff},n,l} = \sqrt{\frac{n^2 E_{n,l}}{-2.18 \times 10^{-18} \text{ J}}}
\]

Our level energies for these two \( n = 3 \) levels give

\[
\begin{align*}
Z_{\text{eff} \ 3s} &= \sqrt{\frac{3^2 E_{3s}}{-2.18 \times 10^{-18} \text{ J}}} = \sqrt{\frac{3^2(-8.32 \times 10^{-19} \text{ J})}{-2.18 \times 10^{-18} \text{ J}}} = 1.85 \\
Z_{\text{eff} \ 3p} &= \sqrt{\frac{3^2 E_{3p}}{-2.18 \times 10^{-18} \text{ J}}} = \sqrt{\frac{3^2(-4.95 \times 10^{-19} \text{ J})}{-2.18 \times 10^{-18} \text{ J}}} = 1.43
\end{align*}
\]

Now we can use Equation [15.25] to calculate average radii for these two orbitals:
Now we can move on to Cs. The analogous transition in Cs involves \( n = 6 \) instead of \( n = 3 \) levels. The Cs atom changes configuration from \([\text{Xe}]6p^1\) to \([\text{Xe}]6s^1\). The 873.5 nm photon that is emitted in this change has an energy \( E_{\text{phot}} = 2.27 \times 10^{-19} \text{ J} \), and with a 6.24 \( \times \) 10\(^{-19} \) J ionization energy, our energy level diagram looks like this:

\[
\begin{align*}
E = 0 & \quad n = \infty \\
0 \text{ J} & \\
E_{6p} = -IE + E_{\text{phot}} & \quad 6p \\
-3.97 \times 10^{-19} \text{ J} & \\
E_{\text{phot}} & \\
E_{6s} = -IE & \quad 6s \\
-6.24 \times 10^{-19} \text{ J} &
\end{align*}
\]

Repeating the effective nuclear charge calculation (with \( n = 6 \)) gives \( Z_{\text{eff}} = 3.21 \) for the 6s level and 2.56 for the 6p level.