1. Solution to HW#9

(a) The ground state wavefunction for hydrogen:

\[ \psi_{100} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0} \]  

(see Reed table 7.2)

\[ \text{PE is: } V = -\frac{e^2}{4\pi \varepsilon_0 r} \]

\[ \langle PE \rangle = \langle V \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^\ast \psi \rho r^2 \sin \theta \, d\phi \, d\theta \, dr \]

\[ = \int_0^\infty \psi^\ast \psi \, 4\pi r^2 \, dr - \frac{4\pi}{\pi a_0^3} \int_0^\infty e^{-2r/a_0} \left(\frac{e^2}{4\pi \varepsilon_0} r^2 \right) dr \]

\[ = \frac{2e^2}{a_0^3} \]

\[ = -\frac{4}{a_0^3} \left(\frac{e^2}{4\pi \varepsilon_0}\right) \int_0^\infty r e^{-r/a_0} \, dr \]

\[ = -\frac{4}{a_0^3} \left(\frac{e^2}{4\pi \varepsilon_0}\right) \frac{a_0^2}{2} = -\frac{e^2}{4\pi \varepsilon_0} \frac{1}{a_0} \]

\[ \langle PE \rangle = -\frac{e^2}{4\pi \varepsilon_0} \frac{1}{a_0} \]
(b) \[ E_n = -\frac{\mu e^4}{32\pi^2\varepsilon_0 h^2 n^2} \]

So for \( n=1 \)

\[ E = -\frac{\mu e^4}{32\pi^2\varepsilon_0 h^2} \]

Also \( a_0 = \frac{4\pi\varepsilon_0 h^2}{\mu e^2} \)

So, \( \langle PE \rangle = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0} = -\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{\mu e^2}{4\pi\varepsilon_0 h^2} \)

\[ = -\frac{\mu e^4}{16\pi^2\varepsilon_0 h^2} \]

\( \Rightarrow \) Using \( E \) above we find:

\[ E = -\frac{\mu e^4}{16\pi^2\varepsilon_0 h^2} \cdot \frac{1}{2} = \frac{\langle PE \rangle}{2} \quad \checkmark \]

(C) \( \langle KE \rangle = \langle E \rangle - \langle PE \rangle \quad (\text{Note: } \langle E \rangle = E) \)

\[ = \frac{\langle PE \rangle}{2} - \langle PE \rangle = -\frac{\langle PE \rangle}{2} \quad \checkmark \]

So, \( \langle KE \rangle = -\frac{\mu e^4}{32\pi^2\varepsilon_0 h^2} \)

Also note that \( \langle KE \rangle = -\langle E \rangle \).
Problem 7-11

Determine \( \langle r \rangle \) and \( \langle 1/r \rangle \) for a hydrogen atom in the (2,1,0) state. Verify that the most probable value of \( r \) for an electron in this state is \( 4a_0 \). What is the probability of finding the electron between 3.9 and 4.1 Bohr radii from the nucleus?

The relevant wavefunction is

\[
\psi_{210} = \frac{1}{\sqrt{32\pi a_0^{5/2}}} r \cos \theta e^{-r/2a_0}.
\]

Recalling that the volume element in spherical coordinates is given by \( r^2 \sin \theta \, d\phi \, d\theta \, dr \), the mean radial position is given by

\[
\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^3 \psi^2 \sin \theta \, d\phi \, d\theta \, dr = \frac{1}{32\pi a_0^5} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^5 (\sin \theta) (\cos^2 \theta) e^{-r/2a_0} \, d\phi \, d\theta \, dr
\]

\[
= \frac{1}{32\pi a_0^5} \int_0^\infty r^5 e^{-r/2a_0} \, dr \int_0^\pi (\sin \theta) (\cos^2 \theta) d\theta \int_0^{2\pi} d\phi.
\]

The integral over \( \phi \) evaluates immediately to \( 2\pi \). The others proceed as

\[
\int_0^\pi (\sin \theta) (\cos^2 \theta) d\theta = -\frac{1}{3} \left[ \cos^3 \theta \right]_0^\pi = -\frac{1}{3} \left[ -1 - (1) \right] = \frac{2}{3}
\]

and

\[
\int_0^\infty r^5 e^{-r/2a_0} \, dr = 120a_0^6,
\]

hence

\[
\langle r \rangle = \frac{1}{32\pi a_0^5} \frac{2}{3} (2\pi) = 5a_0.
\]
As for \( \langle 1/r \rangle \), we have

\[
\langle 1/r \rangle = \iiint_0^\pi \int_0^{2\pi} \int_0^\infty \left(\frac{1}{r}\right) \psi^2 r^2 \sin \theta \, d\phi \, d\theta \, dr = \frac{1}{32\pi a_o^3} \iiint_0^\pi \int_0^{2\pi} \int_0^\infty r^3 (\sin \theta)(\cos^2 \theta) e^{-r/a_o} \, d\phi \, d\theta \, dr
\]

\[
= \frac{1}{32\pi a_o^3} \int_0^\infty r^3 e^{-r/a_o} \, dr \int_0^\pi (\sin \theta)(\cos^2 \theta) \, d\theta \int_0^{2\pi} d\phi
\]

\[
= \frac{1}{32\pi a_o^3} \left(6a_o^4\right) \left(\frac{2}{3}\right)(2\pi) = \frac{1}{4a_o}.
\]

The most probable radius is that which maximizes the radial probability distribution function, that is, the radial part of \( r^2 R^2 \):

\[
\frac{d}{dr} \left(r^4 e^{-r/a_o}\right) = 0 \Rightarrow 4 - r/a_o = 0,
\]

or \( r_{mp} = 4a_o \).

To determine the probability of finding the electron within 3.9 to 4.1 Bohr radii of the nucleus, we integrate the probability distribution \( \psi^2 \) over all possible angles between the radii of interest, say \( r_1 \) and \( r_2 \):

\[
P(r_1, r_2) = \frac{1}{32\pi a_o^3} \int_{r_1}^{r_2} r^3 e^{-r/a_o} \, dr \int_0^\pi (\sin \theta)(\cos^2 \theta) \, d\theta \int_0^{2\pi} d\phi = \frac{1}{24 a_o^3} \int_{r_1}^{r_2} r^4 e^{-r/a_o} \, dr,
\]

where we have used the values of the angular integrals quoted above. Since the range of \( r \) is small (\( \Delta r = r_2 - r_1 = 0.2 \, a_o \)), we can approximate this integral as

\[
P(r_1, r_2) \approx \frac{1}{24 a_o^3} r^4 e^{-r/a_o} \Delta r,
\]

with \( r = (r_1 + r_2)/2 = 4 \, a_o \). Hence

\[
P(r_1, r_2) = \frac{1}{24 a_o^3} \left(4a_o\right)^4 e^{-4\, a_o} \left(0.2 \, a_o\right) = 0.0391.
\]

There is about a 3.9% chance of finding the electron in the given range of radii.
3. Reed: Chapter 7

Problem 7-13
For a hydrogen atom in the (1,0,0) state, what value of $r$ corresponds to a cumulative probability of 50% of finding the electron “within” $r$?

From section 7.5.1 we need to find the value of $r$ that gives $P = 0.50$ in the expression

$$P_{100}(\leq r) = 1 - e^{-2r/a_o} [2(r/a_o)^2 + 2(r/a_o) + 1].$$

Defining $z = (r/a_o)$ and setting $P = 0.50$ means that we must have

$$e^{-2z} (2z^2 + 2z + 1) - 0.5 = 0.$$

This can only be solved numerically, and yields $z = 1.3370$. Compare this result to Figure 7.5.

$$e^{-2z} (2z^2 + 2z + 1) - 0.5$$

The value of $z$ (x-axis) where this function (y-axis) is equal to zero is for $z=1.337$
Problem 7-21

Using the angular momentum operators developed in Chapter 6, verify that \( \langle L_x \rangle = 0 \) for the (2,1,1) state of hydrogen. Refer to the results of problem 6–7.

The (2,1,1) wavefunction for hydrogen can be written as

\[
\psi_{211} = K e^{-r/2a_0} \sin \theta e^{i \phi},
\]

where

\[
K = \frac{1}{8 \sqrt{\pi} a_0^{3/2}}.
\]

From problem 6-7, the operator for the \( x \)-component of angular momentum in spherical coordinates is

\[
L_x = i \hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right).
\]

We wish to compute

\[
\langle L_x \rangle = \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{211}^* (L_x \psi_{211}) r^2 \sin \theta \, dr \, d\theta \, d\phi.
\]

We first compute \( (L_x \psi_{211}) \). Since \( L_x \) operates only on the angular part of wavefunctions, any radial terms can be factored out immediately:

\[
L_x (\psi_{211}) = \hbar (K e^{-r/2a_0}) \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) (\sin \theta e^{i \phi})
\]

\[
= \hbar (K e^{-r/2a_0}) (\cos \theta) (\sin \phi + \cot \phi) e^{i \phi}.
\]

Hence

\[
\langle L_x \rangle = K^2 \langle \hbar \rangle \int_0^\infty r^4 e^{-r/2a_0} \, dr \int_0^\pi \cos \theta \sin^2 \theta \, d\theta \int_0^{2\pi} (\sin \phi + \cot \phi) \, d\phi.
\]

Both terms in the integral over \( \phi \) vanish, hence \( \langle L_x \rangle = 0 \).
5. Reed: Chapter 7

Problem 7-23

Using the rules developed in the text for interpreting plots of $|\psi|$, how many and what type of nodes would you expect to find in the case of $(n, \ell, m) = (6,2,1)$? Check your conclusions against the image below.

![Image of a plot with radial and angular nodes.]

With $m \neq 0$, we expect $(\ell-m+1) = 2$ angular nodes, which agrees with the figure. Since $\ell \neq 0$, we expect a central radial node and a total of $n-\ell = 4$ radial nodes, including the central radial node. This also agrees with the figure.