Chem 3322 homework #5 solutions

Problem 1 – 10 marks

For a particle in a 1d box, use the normalized wavefunctions derived in class to compute

\[ a) \langle x \rangle \quad b) \langle x^2 \rangle \quad c) \langle p_x \rangle \quad d) \langle p_x^2 \rangle \]

for the ground state. Interpret the results of parts a) [1 mark] and c) [1 mark] physically.

Solution:

\[ \langle x \rangle = \frac{2}{L} \int_0^L x \sin^2 \left( \frac{\pi x}{L} \right) \, dx \]

\[ = \frac{2}{L} \left[ \frac{x^2}{4} - \frac{x \sin(2\pi x/L)}{4\pi/L} - \frac{\cos(2\pi x/L)}{8\pi^2/L^2} \right]_0^L \]

\[ = \frac{2}{L} \left[ \frac{L^3}{4} - \frac{L^3}{8\pi^2} + \frac{L^3}{8\pi^2} \right] = \frac{L}{2} \]

Physically, this makes sense, because the potential energy is symmetric about the middle of the box, so we would not expect to find the particle, on average, in the right hand half of the box: we would expect to find it in the middle, which is another way of saying that we would expect to find the particle as often in the left hand side of the box as in the right hand side of the box.

\[ \langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(\pi x/L) \, dx \]

\[ = \frac{2}{L} \left[ \frac{x^3}{6} - \left( \frac{x^2}{4\pi/L} - \frac{1}{8\pi^3/L^3} \right) \sin(2\pi x/L) - \frac{x \cos(2\pi x/L)}{4\pi^2/L^2} \right]_0^L \]

\[ = \frac{2}{L} \left[ \frac{L^3}{6} - \frac{L^3}{4\pi^2} \right] \]

\[ = L^2 \left( \frac{1}{3} - \frac{1}{2\pi^2} \right) = 0.2827L^2 \]

\[ \langle p_x \rangle = \frac{2}{L}(-i\hbar)\frac{\pi}{L} \int_0^L \sin(\pi x/L) \cos(\pi x/L) \, dx \]

\[ = -i\hbar \frac{2\pi}{L^2} \left[ \frac{L}{2\pi} \sin^2(\pi x/L) \right]_0^L = 0 \]
Physically, this again makes sense because of the symmetry in the potential. On average, we expect to find the particle traveling to the right as often as to the left, making the average velocity zero. Don’t forget that velocity is a vector quantity, which in one dimension means that it carries sign information with it. In fact, if you think about it, you will realize that for this answer to be non-zero means that the box is moving!

\[ \langle p_x^2 \rangle = \frac{2}{L} (-\hbar^2) \int_0^L \sin(\pi x/L) \frac{d^2}{dx^2} \sin(\pi x/L) \]

\[ = \frac{2}{L} \hbar^2 \frac{\pi^2}{L} \int_0^L \sin^2(\pi x/L) \]

\[ = \frac{2\pi^2 \hbar^2}{L^3} \left[ \frac{x}{2} - \frac{1}{4\pi/L} \sin(2\pi x/L) \right]_0^L = \frac{\pi^2 \hbar^2}{L^2} \]  

(11)  

(12)  

(13)

Problem 2 – 4 marks

a) Using the results of Problem 1), determine the standard deviations \( \Delta x \) and \( \Delta p_x \).

Solution:

\[ \Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = 0.181L \]  

(14)

\[ \Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = \frac{\pi \hbar}{L} \]  

(15)

b) Find the value of the product \( \Delta x \Delta p_x \). This kind of product of standard deviations is called an uncertainty product. It can be proved that, for any normalized \( \psi \),

\[ \Delta x \Delta p_x \geq \frac{\hbar}{2} \]  

(16)

known as the Heisenberg Uncertainty Principle. Your result should, of course, be consistent with this inequality. Verify this.

Solution:

\[ \Delta x \Delta p_x = 0.569\hbar \]  

(17)

which is greater than \( \hbar/2 \).

Problem 3 – 4 marks
For the particle in a one dimensional box with quantum number \( n \), work out a) the expected value of the potential energy, b) the expected value of the kinetic energy, and c) compare the sum of these two expected values to the energy value \( E_n \) which we calculated in class.

Solution:

a) [1 mark] \( < V > = 0 \)

b) [2 marks]

\[
< K > = -\frac{\hbar^2}{2m} \int_0^L \psi_n^* \frac{d^2}{dx^2} \psi_n \tag{18}
\]

\[
= -\frac{\hbar^2}{2m} \int_0^L \psi_n^* \left( -\frac{n\pi}{L} \right)^2 \tag{19}
\]

\[
= \left( \frac{n\pi}{L} \right)^2 \frac{\hbar^2}{2m} \tag{20}
\]

from orthonormality.

c) [1 mark]

\[
< V > + < K > = \frac{n^2\pi^2\hbar^2}{2mL^2} = E_n \tag{21}
\]

Problem 4 – 7 marks

Recall the harmonic oscillator model has potential energy \( V(x) = m\omega^2x^2/2 \). For the ground state,

\[
\psi_0(x) = \left( \frac{2\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2} \tag{22}
\]

where \( \alpha = m\omega/2\hbar \), work out a) the expected value of the potential energy, b) the expected value of the kinetic energy, and c) compare the sum of these two expected values to the energy \( E_0 \) which we calculated in class.

Solution:

a) [3 marks]

\[
< V > = m\omega^2 \frac{2\alpha}{\pi} \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx \tag{23}
\]

\[
= \frac{1}{2} \frac{m\omega^2}{\pi^{1/2}} \left( \frac{\alpha}{\pi} \right)^{1/2} \frac{\pi^{1/2}}{2(2\alpha)^{3/2}} = \frac{1}{4} \hbar \omega \tag{24}
\]
b) [3 marks]

\[ <K> = \frac{\hbar^2}{2m} \left( \frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-i\hbar \frac{d}{dx}\right)^2 e^{-\alpha x^2} dx \]  

\[ = -\frac{\hbar^2}{2m} \left( \frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} (4\alpha^2 x^2 - 2\alpha) e^{-2\alpha x^2} dx \]  

\[ = -\frac{\hbar^2}{2m} \left( \frac{2\alpha}{\pi} \right)^{1/2} \left[ \frac{4\alpha^2 \pi^{1/2}}{2(2\alpha)^{3/2}} - 2\alpha \frac{\pi^{1/2}}{(2\alpha)^{1/2}} \right] = \frac{1}{4} \hbar \omega \]  

(27)

c) [1 mark]

\[ <V> + <K> = \frac{1}{4} \hbar \omega + \frac{1}{4} \hbar \omega = \frac{1}{2} \hbar \omega = E_0 \]  

(28)

**Problem 5 – 5 marks**

Consider the operator

\[ \hat{A} = x \frac{d}{dx} - \frac{d}{dx} x \]  

(29)

What does this operator do to a function \( f(x) \)? Based on your answer, express this operator in a simpler form. Hint: the \( x \) at the very end of Eq. 29 must be interpreted as an operator, so that the \( d/dx \) preceding it cannot act on it directly since an operator doesn’t take, as its argument, another operator (but rather a function).

Solution:

\[ \hat{A} f(x) = \left( x \frac{d}{dx} - \frac{d}{dx} x \right) f(x) \]  

\[ = x f'(x) - \frac{d}{dx} (xf(x)) = xf'(x) - (f(x) + xf'(x)) = -f(x) \]  

from which we conclude that \( \hat{A} = -1 \). Namely the operator \( A \) acts on a function by multiplying the function by \(-1\).

**Problem 6**

Do problem 6-21 from your textbook.

**Problem 7**

Do problem 6-30 from your textbook.
6-20. Calculate the probability that a hydrogen 1s electron will be found within a distance 2\(a_0\) from the nucleus.

This problem is similar to Example 6-10. The wave function for the 1s orbital of hydrogen is

\[
\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\sigma}
\]

where \(\sigma = r/a_0\), and the probability that the electron will be found within a distance 2\(a_0\) from the nucleus is

\[
\text{prob} = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^{2a_0} dr \ r^2 \frac{1}{\pi} \left(\frac{1}{a_0}\right)^{3} e^{-2\sigma}
\]

\[
= 4 \left(\frac{1}{a_0}\right)^{3} \int_0^{2a_0} dr \ r^2 e^{-2\sigma}
= 4 \int_0^{2} d\sigma \sigma^2 e^{-2\sigma}
\]

\[
= 4 \left(\frac{1}{4} - \frac{13}{4} e^{-4}\right) = 1 - 13e^{-4} = 0.762
\]

6-21. Calculate the radius of the sphere that encloses a 50% probability of finding a hydrogen 1s electron. Repeat the calculation for a 90% probability.

The probability that a 1s electron will be found within a distance \(D a_0\) of the nucleus is given by

\[
\text{prob}(D) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^{D a_0} dr \ r^2 \frac{1}{\pi} \left(\frac{1}{a_0}\right)^{3} e^{-2\sigma}
\]

\[
= 4 \int_0^{D} d\sigma \sigma^2 e^{-2\sigma} = 1 - e^{-2D(2D^2 + 2D + 1)}
\]

We find that \(D = 1.3\) for \(\text{prob}(D) = 0.50\) and \(D = 2.7\) for \(\text{prob}(D) = 0.90\), so the 50% and 90% probability spheres have radii of 1.3\(a_0\) and 2.7\(a_0\), respectively.

6-22. Many problems involving the calculation of average values for the hydrogen atom require evaluating integrals of the form

\[
I_n = \int_0^{\infty} r^n e^{-\beta r} \, dr
\]

This integral can be evaluated readily by starting with the elementary integral

\[
I_0(\beta) = \int_0^{\infty} e^{-\beta r} \, dr = \frac{1}{\beta}
\]

Show that the derivatives of \(I(\beta)\) are

\[
\frac{dI_0}{d\beta} = -\int_0^{\infty} re^{-\beta r} \, dr = -I_1
\]

\[
\frac{d^2I_0}{d\beta^2} = \int_0^{\infty} r^2e^{-\beta r} \, dr = I_2
\]
6–28. Calculate the value of \( \langle r \rangle \) for the \( n = 2, \ l = 1 \) state and the \( n = 2, \ l = 0 \) state of the hydrogen atom. Are you surprised by the answers? Explain.

The average value of \( r \), \( \langle r \rangle \), is given by

\[
\langle r \rangle = \int d\tau \psi_\alpha^*(r, \theta, \phi) \psi_\alpha(r, \theta, \phi)
\]

We use the wave functions in Table 6.6 to find

\[
\langle r \rangle_{20} = \frac{4\pi}{32\pi a_0^3} \int_0^\infty dr \, r^3 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}
\]

\[
= \frac{a_0}{8} \int_0^\infty dx \, x^3 (2-x)^2 e^{-x} = \frac{a_0}{8} (4.3! - 4.4! + 5!)
\]

\[
= 6a_0
\]

and

\[
\langle r \rangle_{21} = \frac{2\pi}{32\pi a_0^3} \int_0^\infty d\theta \, \sin \theta \cos^2 \theta \int_0^\infty dr \, r^3 \left( \frac{r}{a_0} \right)^2 e^{-r/a_0}
\]

\[
= \frac{a_0}{16} \left( \frac{2}{3} \right) \int_0^\infty dx \, x^5 e^{-x}
\]

\[
= \frac{a_0}{16} \left( \frac{2}{3} \right) (5!) = 5a_0
\]

These results show that an electron in the \( 2s \) orbital is farther from the nucleus (on average) than an electron in the \( 2p \) orbital. This is surprising, as we might expect the reverse to be true from our studies of multi-electron systems in general chemistry; note, however, that a one-electron hydrogen-like wave function differs from multi-electron wave functions (Chapter 8).

6–29. In Chapter 4, we learned that if \( \psi_1 \) and \( \psi_2 \) are solutions of the Schrödinger equation that have the same energy \( E_n \), then \( c_1 \psi_1 + c_2 \psi_2 \) is also a solution. Let \( \psi_1 = \psi_{210} \) and \( \psi_2 = \psi_{211} \) (see Table 6.5). What is the energy corresponding to \( \psi = c_1 \psi_1 + c_2 \psi_2 \) where \( c_1^2 + c_2^2 = 1 \)? What does this result tell you about the uniqueness of the three \( p \) orbitals, \( p_x \), \( p_y \), and \( p_z \)?

Recall that the energy of the hydrogen atom depends only on the value of \( n \). Therefore, \( \psi_{211} \) and \( \psi_{210} \) have the same energy, \( E_2 \), and so (Chapter 4) the energy corresponding to \( \psi = c_1 \psi_1 + c_2 \psi_2 \) where \( c_1^2 + c_2^2 = 1 \) is also \( E_2 \). The three \( p \) orbitals \( (p_x, p_y, \text{and} \ p_z) \), therefore, are not a unique representation of the three degenerate orbitals for \( n = 2 \) and \( l = 1 \).

6–30. Show that the total probability density of the \( 2p \) orbitals is spherically symmetric by evaluating \( \sum_{m=-1}^{1} \Psi_{21m}^3 \). (Use the wave functions in Table 6.6.)
\[ \sum_{m=-1}^{1} \psi_{21m}^2 = \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^3 \sigma^2 e^{-r/\sigma} \left( \cos^2 \theta + \sin^2 \theta \cos^2 \phi + \sin^2 \theta \sin^2 \phi \right) \]
\[ = \frac{Z^3 \sigma^2 e^{-r/\sigma}}{32\pi a_0^3} \left[ \cos^2 \theta + \sin^2 \theta \left( \cos^2 \phi + \sin^2 \phi \right) \right] \]
\[ = \frac{Z^3 \sigma^2 e^{-r/\sigma}}{32\pi a_0^3} \left( \cos^2 \theta + \sin^2 \theta \right) \]
\[ = \frac{Z^3 \sigma^2 e^{-r/\sigma}}{32\pi a_0^3} \]

The sum depends only on the variable \( r \) (through \( \sigma \)), so the total probability density of the \( 2p \) orbitals is spherically symmetric.

---

6–31. Show that the total probability density of the \( 3d \) orbitals is spherically symmetric by evaluating \( \sum_{m=-2}^{2} \psi_{32m}^2 \). (Use the wave functions in Table 6.6.)

\[ \sum_{m=-2}^{2} \psi_{32m}^2 = \frac{1}{8127\pi} \left( \frac{Z}{a_0} \right)^3 \sigma^4 e^{-2r/\sigma} \left[ \frac{(3 \cos^2 \theta - 1)^2}{6} + 2 \sin^4 \theta \cos^2 \theta \cos^2 \phi \right. \]
\[ + 2 \sin^2 \theta \cos^2 \theta \sin^2 \phi + \frac{\sin^4 \theta \cos^2 \phi}{2} + \frac{\sin^4 \theta \sin^2 2\phi}{2} \right] \]
\[ = \frac{Z^3 \sigma^4 e^{-2r/\sigma}}{8127\pi a_0^3} \left[ \frac{(3 \cos^2 \theta - 1)^2}{6} + 2 \sin^2 \theta \cos^2 \theta \left( \sin^2 \phi + \cos^2 \phi \right) \right. \]
\[ + \frac{\sin^4 \theta \left( \cos^2 2\phi + \sin^2 2\phi \right)}{2} \right] \]
\[ = \frac{Z^3 \sigma^4 e^{-2r/\sigma}}{(81)^2 6\pi a_0^3} \left[ (3 \cos^2 \theta - 1)^2 + 12 \sin^2 \theta \cos^2 \theta + 3 \sin^4 \theta \right] \]

Now substitute \( \sin^2 \theta = 1 - \cos^2 \theta \) into the above expression to get

\[ \sum_{m=-2}^{2} \psi_{32m}^2 = \frac{Z^3 \sigma^4 e^{-2r/\sigma}}{(81)^2 6\pi a_0^3} \left[ 9 \cos^4 \theta - 6 \cos^2 \theta + 1 + 12(1 - \cos^2 \theta) \cos^2 \theta + 3(1 - \cos^2 \theta)^2 \right] \]
\[ = \frac{Z^3 \sigma^4 e^{-2r/\sigma}}{(81)^2 6\pi a_0^3} \left[ 9 \cos^4 \theta - 6 \cos^2 \theta + 1 + 12 \cos^2 \theta - 12 \cos^4 \theta + 3 - 6 \cos^2 \theta + 3 \cos^4 \theta \right] \]
\[ = \frac{4Z^3 \sigma^4 e^{-2r/\sigma}}{(81)^2 6\pi a_0^3} = \frac{2Z^3 \sigma^4 e^{-2r/\sigma}}{(81)^2 3\pi a_0^3} \]

The sum depends only on the variable \( r \) (through \( \sigma \)), so the total probability density of the \( 3d \) orbitals is spherically symmetric.

---

6–32. Show that the sum of the probability densities for the \( n = 3 \) states of the hydrogen atom is spherically symmetric. Do you expect this to be true for all values of \( n \)? Explain.

In Problem 6–31 we showed that the sum of the probability densities of the \( 3d \) orbitals is spherically symmetric. The probability density of the \( 3s \) orbital is also spherically symmetric, and so we need only show that the sum of the probability densities of the \( 3p \) orbitals is spherically symmetric. The