1. Verify for the particle in a one-dimensional box by explicit integration that the wavefunction 
\[ \psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \]
is normalized.

To verify that \( \psi_2(x) \) is normalized, we have to show that
\[ \int_0^L \psi_2^2(x) \, dx = 1 . \]

Note that the integration range is from \( x=0 \) to \( x=L \) since the particle in a box wavefunctions vanish outside that range. Substituting, the integral becomes
\[ \int_0^L \psi_2^2(x) \, dx = \int_0^L \left( \frac{2}{L} \sin\left(\frac{2\pi x}{L}\right) \right)^2 \, dx = \frac{2}{L} \int_0^L \sin^2\left(\frac{2\pi x}{L}\right) \, dx . \]

The integral that we need can be found, for example, in the CRC or in most any table of integrals:
\[ \int \sin^2 b x \, dx = \frac{x}{2} - \frac{\sin 2b x}{4b} . \]

Setting \( b = \frac{2\pi}{L} \) and substituting, the normalization integral becomes
\[ \int_0^L \psi_2^2(x) \, dx = \frac{2}{L} \int_0^L \sin^2\left(\frac{2\pi x}{L}\right) \, dx = \frac{2}{L} \left[ \frac{x}{2} - \frac{1}{4\left(\frac{2\pi}{L}\right)} \sin^2\left(\frac{4\pi x}{L}\right) \right]_0^L . \]
1. continued

Evaluating the expression at the limits,

\[
\int_0^L \psi_2^2(x) \, dx = \frac{2}{L} \left[ \frac{x}{2} - \frac{1}{4(\frac{2\pi}{L})} \sin\left(\frac{4\pi}{L} x\right) \right]_0^L \\
= \frac{2}{L} \left[ \left( \frac{L}{2} - \frac{L}{8\pi} \sin(4\pi) \right) - \left( 0 - \frac{L}{8\pi} \sin(0) \right) \right] \\
= \frac{2}{L} \left[ \left( \frac{L}{2} - 0 \right) - \left[ 0 - 0 \right] \right]
\]

\[
\int_0^L \psi_2^2(x) \, dx = \frac{2}{L} \left( \frac{L}{2} \right) - 0 = \frac{L}{2} - 0
\]

Therefore, the wavefunction \( \psi_2(x) \) is normalized.
2. Calculate the energy level spacings in Joules between the ground \((n=1)\) and first excited \((n=2)\) levels for the following cases.

a.) An electron confined to a one-dimensional box of width 5 Å.

The energy level spacing \(\Delta E\) between the ground and first excited state is \(\Delta E = E_2 - E_1\). Using the particle in a box energy expression, we can obtain an equation for the energy level spacing,

\[
\Delta E = E_2 - E_1 = \frac{2^2 \hbar^2}{8mL^2} - \frac{1^2 \hbar^2}{8mL^2}
\]

\[
\Delta E = \frac{3\hbar^2}{8mL^2}.
\]

Substituting,

\[
\Delta E = E_2 - E_1 = \frac{3(6.62618 \times 10^{-34} \text{ Js})^2}{8(9.10953 \times 10^{-31} \text{ kg})(5 \times 10^{-10} \text{ m})^2}
\]

\[
\Delta E = E_2 - E_1 = 7.230 \times 10^{-19} \text{ J}.
\]

b.) A baseball with a mass of 140 g confined to a one-dimensional box of width 1 meter.

Using the same expression from part (a) for the energy level spacing, we have

\[
\Delta E = E_2 - E_1 = \frac{2^2 \hbar^2}{8mL^2} - \frac{1^2 \hbar^2}{8mL^2}
\]

\[
\Delta E = \frac{3\hbar^2}{8mL^2}.
\]

Substituting,

\[
\Delta E = E_2 - E_1 = \frac{3(6.62618 \times 10^{-34} \text{ Js})^2}{8(0.1 \text{ kg})(1 \text{ m})^2}
\]

\[
\Delta E = E_2 - E_1 = 1.646 \times 10^{-66} \text{ J}.
\]

Notice how much smaller the energy level spacing is for the macroscopic object. Energy level spacings this small are not measurable, and therefore the energy level spacings are so small as to be effectively continuous for macroscopic objects.
3. An electron in a box of width $L$ undergoes a transition from the lowest energy level ($n=1$) to the first excited level ($n=2$). The wavelength of light absorbed in this transition was determined to be 650 nm. Calculate the width of the box.

For a transition from $n=1$ to $n=2$, the energy difference $\Delta E$ is $\Delta E = E_2 - E_1$. A photon with an energy corresponding to $\Delta E$ would have a frequency given by $E_{\text{photon}} = \Delta E = h\nu$. Since, for light, $\lambda\nu = c$, we can substitute $\nu = \frac{c}{\lambda}$, and obtain an expression for the energy difference,

$$\Delta E = E_2 - E_1 = \frac{hc}{\lambda}.$$

Substituting,

$$\Delta E = E_2 - E_1 = \left(\frac{6.62618 \times 10^{-34} \text{ Js}}{2.99793 \times 10^{8} \text{ ms}^{-1}}\right)\left(680 \text{ nm}\right)\left(10^{-9} \text{ m}\right)$$

$$\Delta E = E_2 - E_1 = 2.9213 \times 10^{-19} \text{ J}.$$

Then, we can use the particle in a box energies to obtain an expression for the energy difference,

$$\Delta E = E_2 - E_1 = \frac{2^2 \hbar^2}{8mL^2} - \frac{1^2 \hbar^2}{8mL^2}$$

$$\Delta E = \frac{3\hbar^2}{8mL^2}.$$

Solving for $L$, the width of the box, yields

$$L = \left(\frac{3\hbar^2}{8m\Delta E}\right)^{1/2}.$$

Substituting,

$$L = \left(\frac{3\hbar^2}{8m\Delta E}\right)^{1/2}$$

$$= \left[\frac{3 \left(6.62618 \times 10^{-34} \text{ Js}\right)^2}{8 \left(9.10953 \times 10^{-31} \text{ kg}\right)\left(2.9213 \times 10^{-19} \text{ J}\right)}\right]^{1/2}$$

$$L = 7.866 \times 10^{-10} \text{ m} \text{ or } 7.866 \text{ Å}.$$
4. Determine the most probable location for the particle in the ground state of the one-dimensional particle in a box. Also determine the most probable location for the first excited state of the particle in a box.

To obtain the most probable value, we must look at the probability density, $\psi^2(x)$. For the ground state of the particle in a box, the probability density is given by

$$\psi_1^2(x) = \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right).$$

A plot of this probability density is shown below.

Note that the maximum of this function occurs at $x = \frac{L}{2}$; this is the most probable value. In this case, the maximum can be found by inspection. For more general situations to get the maximum value, we would have to take the derivative, set it equal to zero, and solve.

For the first excited state of the particle in a box, the probability density is given by

$$\psi_2^2(x) = \frac{2}{L} \sin^2\left(\frac{2\pi x}{L}\right).$$

A plot of this probability density is given below.

For this function, we see from the plot that there are two maxima, each with identical amplitude. By inspection, these maxima occur at $x = \frac{L}{4}$ and $x = \frac{3L}{4}$; these two values are therefore the most probable values.
5. For a particle in a one-dimensional box of width $L$, determine the probability of finding the particle in the right third of the box (between $2/3 \, L$ and $L$) if the particle is in the ground state.

Since the probability is given by $\psi^2(x) \, dx$, if we want the total probability of finding the particle between $2/3 \, L$ and $L$, we must add up the probability for all the points from $2/3 \, L$ to $L$. Since $x$ is a continuous variable, the sum is really an integral from $2/3 \, L$ to $L$,

$$
\text{Probability} = \int_{2L/3}^{L} \psi^2(x) \, dx .
$$

Substituting the particle in a box wavefunction for the ground state, $\psi_1(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{\pi \, x}{L} \right)$, the probability integral becomes

$$
\text{Probability} = \frac{2}{L} \int_{2L/3}^{L} \sin^2 \left( \frac{\pi \, x}{L} \right) \, dx .
$$

This integral can be evaluated using tables. From the CRC Handbook or any other table of integrals, we find the indefinite integral:

$$
\int \sin^2 bx \, dx = \frac{x}{2} - \frac{\sin 2bx}{4b} .
$$

Replacing $b$ with $\frac{\pi}{L}$ yields

$$
\text{Probability} = \frac{2}{L} \left[ \frac{x}{2} - \frac{\sin \left( \frac{2\pi \, x}{L} \right)}{4 \left( \frac{\pi}{L} \right)} \right]_{2L/3}^{L} .
$$

Finally, evaluating the expression at the limits leads to

$$
\text{Probability} = \frac{1}{3} + \frac{1}{2\pi} \sin \left( \frac{4\pi}{3} \right) .
$$

Evaluating the numerical value of the sine function in the expression above, the probability is

$$
\text{Probability} = 0.3333 - 0.1378 = 0.1955 .
$$
6. The 1,3,5-hexatriene molecule is a conjugated molecule with 6 pi electrons. Consider the pi electrons free to move back and forth along the molecule through the delocalized pi system. Using the particle in a box approximation, treat the carbon chain as a linear one-dimensional "box". Allow each energy level in the box to hold 2 pi electrons.

Treating 1,3,5-hexatriene as a linear chain, we would have the structure

\[
\text{C}_1 \equiv \text{C}_2 \equiv \text{C}_3 \equiv \text{C}_4 \equiv \text{C}_5 \equiv \text{C}_6
\]

The pi electrons are free to move through the conjugated system; hence, the length of the molecule would represent the "box." We can add up the lengths of the single and double bonds in the molecule to give the width of the box, \( L \). For 1,3,5-hexatriene, this gives

\[
L = 3r_{C-C} + 2r_{C-C}
\]

where \( r \) represents the bond length.

The energy of the pi electrons in the molecule would be represented as

\[
E_n = \frac{n^2 \hbar^2}{8mL^2}, \quad n = 1, 2, 3, \ldots
\]

where \( L \) is the box width defined above and \( m \) is the electron mass.

a.) Calculate the energy of the highest filled level, using 1.54 Å as the carbon-carbon single bond length, and 1.35 Å as the carbon-carbon double bond length.

Using \( r_{C-C} = 1.35 \text{ Å} \) and \( r_{C-C} = 1.54 \text{ Å} \), the width of the box can be calculated from the equation above.

\[
L = 3(1.35 \text{ Å}) + 2(1.54 \text{ Å}) = 7.13 \text{ Å} \quad \text{(or} \quad 7.13 \times 10^{-10} \text{ m})
\]

Using the formula above with \( L = 7.13 \times 10^{-10} \text{ m} \) for the energy leads to the energy diagram shown below.
6 a.) continued

1,3,5-hexatriene has 6 pi electrons. Placing two electrons in each energy level fills the levels up to the \( n=3 \) level, as shown in the figure above. So, \( n=3 \) is the highest filled level. Computing the energy of the highest filled level,

\[
E_3 = \frac{3^2 \left(6.62618 \times 10^{-34} \text{ Js} \right)^2}{8 \left(9.10953 \times 10^{-31} \text{ kg} \right) \left(7.13 \times 10^{-10} \text{ m} \right)^2} = 3^2 \left(1.18511 \times 10^{-19} \text{ J} \right) = 1.0666 \times 10^{-18} \text{ J}
\]

b.) Determine the energy of the lowest unfilled level.

The lowest unfilled level corresponds to \( n=4 \). Calculating the energy of this state gives

\[
E_4 = \frac{4^2 \hbar^2}{8ma^2} = 4^2 \left(1.18511 \times 10^{-19} \text{ J} \right) = 1.8962 \times 10^{-18} \text{ J}
\]

c.) Calculate the wavelength for an electronic transition from the highest filled level to the lowest unfilled level, using your answers from parts a) and b). Compare your result to the experimental ultraviolet absorption maximum of 268 nm.

For an electronic transition from \( n=3 \) to \( n=4 \), the energy difference \( \Delta E \) is \( \Delta E = E_4 - E_3 \). A photon with an energy corresponding to \( \Delta E \) would have a frequency given by \( E_{\text{photon}} = \Delta E = h\nu \). Since, for light, \( \nu c = \lambda \), we can substitute \( \nu = \lambda c \), and solve for the wavelength to give

\[
\lambda = \frac{hc}{\Delta E} = \frac{hc}{E_4 - E_3}.
\]

Inserting numerical values leads to

\[
\lambda = \frac{\left(6.62618 \times 10^{-34} \text{ Js} \right) \left(2.99793 \times 10^8 \text{ ms}^{-1} \right)}{ \left(1.8962 \times 10^{-18} \text{ J} - 1.0666 \times 10^{-18} \text{ J} \right) } = 2.395 \times 10^{-7} \text{ m} \text{ or } \lambda = 239.5 \text{ nm}.
\]

This result is fairly close to the experimental wavelength, \( \lambda_{\text{exp}} = 268 \text{ nm} \) with about an 11% error. This is surprisingly good agreement given the crudeness of the model.
7. Verify, by explicit integration, that \( \psi_2 \) and \( \psi_3 \) for the particle in a one-dimensional box are orthogonal.

For a particle in a 1D box, the wavefunctions are given by

\[
\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right).
\]

To show that \( \psi_2 \) and \( \psi_3 \) are orthogonal, the integral of the product of the two functions (including the complex conjugate of one of the functions if they are not real functions) must be zero. Evaluating the integral (in this case, both functions are real), we have

\[
\int_0^L \psi_2^*(x) \psi_3(x) \, dx = \frac{2}{L} \int_0^L \sin \left( \frac{2\pi x}{L} \right) \sin \left( \frac{3\pi x}{L} \right) \, dx.
\]

Note that the integration range is from \( x=0 \) to \( x=L \) since the particle in a box wavefunctions vanish outside that range. The indefinite integral that we need can be found, for example, in the CRC or in most any table of integrals:

\[
\int \sin mx \sin nx \, dx = \frac{\sin(m-n)x}{2(m-n)} - \frac{\sin(m+n)x}{2(m+n)}.
\]

Setting \( m = \frac{2\pi}{L} \) and \( n = \frac{3\pi}{L} \), we have \( m-n = -\frac{\pi}{L} \) and \( m+n = \frac{5\pi}{L} \). Substituting,

\[
\int_0^L \psi_2^*(x) \psi_3(x) \, dx = \frac{2}{L} \left[ -\frac{L}{2\pi} \sin \left( -\frac{\pi x}{L} \right) - \frac{L}{10\pi} \sin \left( \frac{5\pi x}{L} \right) \right]_0^L.
\]

Using the identity \( \sin(-x) = \sin x \), and evaluating the integral at the limits yields

\[
\int_0^L \psi_2^*(x) \psi_3(x) \, dx = \frac{2}{L} \left[ \frac{L}{2\pi} \sin \pi - \frac{L}{10\pi} \sin 5\pi \right] - \frac{2}{L} \left[ \frac{L}{2\pi} \sin 0 - \frac{L}{10\pi} \sin 0 \right].
\]

Since \( \sin \pi = \sin 5\pi = \sin 0 = 0 \), the integral simplifies to

\[
\int_0^L \psi_2^*(x) \psi_3(x) \, dx = 0.
\]

Therefore, the functions \( \psi_2(x) \) and \( \psi_3(x) \) are orthogonal.
8. Determine the average value of the position $x$ for the ground state of the one-dimensional particle in a box. Compare your result with the most probable location.

The average value of the position is given by

$$\langle x \rangle = \int_0^L \psi^*_1(x) \hat{x} \psi_1(x) \, dx = \int_0^L \psi^*_1(x) x \, \psi_1(x) \, dx,$$

where the definition of the position operator, $\hat{x} = x$, has been used. In addition, the limits of the integral are $x=0$ to $x=L$ because the wavefunction vanishes outside this range.

The ground state wavefunction for the particle in a box is given by

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right).$$

Upon substitution, the expression for the average value of the position becomes

$$\langle x \rangle = \int_0^L \psi^*_1(x) x \, \psi_1(x) \, dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) x \cdot \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \, dx$$

$$= \frac{2}{L} \int_0^L x \sin^2 \left( \frac{\pi x}{L} \right) \, dx.$$

From the CRC Handbook (or handout of integrals),

$$\int x \sin^2 \alpha x \, dx = \frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2}.$$

Replacing $\alpha$ by $\frac{\pi}{L}$, the average value becomes

$$\langle x \rangle = \frac{2}{L} \left[ \frac{x^2}{4} - \frac{x \sin \left( \frac{2\pi x}{L} \right)}{4\left( \frac{\pi}{L} \right)} - \frac{\cos \left( \frac{2\pi x}{L} \right)}{8\left( \frac{\pi}{L} \right)^2} \right]_0^L.$$
8. continued

Evaluating the expression at the limits yields the \textbf{average value of the position} for the ground state of the particle in a box:

\[
\langle x \rangle = \frac{2}{L} \left[ \frac{L^2}{4} - \frac{L^2}{4\pi} \sin(2\pi) - \frac{L^2}{8\pi^2} \cos(2\pi) \right] - \frac{2}{L} \left[ 0 - 0 \cdot \sin(0) - \frac{L^2}{8\pi^2} \cos(0) \right]
\]

\[
= \frac{2}{L} \left[ \frac{L^2}{4} - 0 - \frac{L^2}{8\pi^2} \right] - \frac{2}{L} \left[ 0 - 0 - \frac{L^2}{8\pi^2} \right]
\]

\[
\langle x \rangle = \frac{L}{2}.
\]

For the ground state of the particle in a box, the average value and most probable value of \(x\) are identical (the most probable value of \(L/2\) was found in problem 4). This will not always be the case, as we will see in next problem.
9. Repeat problem 8 for the first excited state of the particle in a box. Does your result agree this time with the most probable location for this state?

For the first excited state of the particle in a box, the wavefunction is

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi x}{L} \right).$$

Thus, the average value of $x$ for this state is

$$\langle x \rangle = \int_0^L \psi_2^*(x) \cdot x \cdot \psi_2(x) \, dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi x}{L} \right) \cdot x \cdot \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi x}{L} \right) \, dx$$

$$= \frac{2}{L} \int_0^L x \sin^2 \left( \frac{2\pi x}{L} \right) \, dx.$$

We can use the same integral as we did in the previous problem; in this case, we replace $\alpha$ by $\frac{2\pi}{L}$:

$$\langle x \rangle = \frac{2}{L} \left[ x^2 \cdot \frac{x}{2} - \frac{x}{2} \sin \left( \frac{4\pi x}{L} \right) \cdot \cos \left( \frac{4\pi x}{L} \right) \right]_0^L$$

Evaluating this expression at the limits gives the average value of the position for the first excited state,

$$\langle x \rangle = \frac{2}{L} \left[ \frac{L^2}{4} - \frac{L^2}{8\pi} \sin(4\pi) - \frac{L^2}{32\pi^2} \cos(4\pi) \right] - \frac{2}{L} \left[ 0 - 0 \cdot \sin(0) - \frac{L^2}{32\pi^2} \cos(0) \right]$$

$$= \frac{2}{L} \left[ \frac{L^2}{4} - 0 - \frac{L^2}{32\pi^2} \right] - \frac{2}{L} \left[ 0 - 0 - \frac{L^2}{32\pi^2} \right]$$

$$\langle x \rangle = \frac{L}{2}.$$

This is exactly the same result that we got for the ground state. This will not always happen – here we got the same result because of the symmetry of the potential energy and as a result the symmetry of the wavefunction about $x=L/2$.

From problem 4, we found that the most probable values for the first excited state occur at $x = \frac{L}{4}$ and $x = \frac{3L}{4}$.

Note that for the first excited state of the particle in a box, the average value and most probable values of $x$ are not the same.
10. Determine the average value of the momentum \( p_x \) for the ground state of the one-dimensional particle in a box.

The average value of the momentum is given by

\[
\langle p_x \rangle = \int_0^L \psi_1^*(x) \hat{p}_x \psi_1(x) \, dx = -i \hbar \int_0^L \psi_1^*(x) \frac{d}{dx} \psi_1(x) \, dx ,
\]

where the definition of the momentum operator, \( \hat{p}_x = -i \hbar \frac{d}{dx} \), has been used. In addition, the limits of the integral again are \( x=0 \) to \( x=L \) because the wavefunction vanishes outside this range.

The ground state wavefunction for the particle in a box is given by

\[
\psi_1(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) .
\]

Upon substitution, the expression for the average value of the momentum becomes

\[
\langle p_x \rangle = -i \hbar \int_0^L \psi_1^*(x) \frac{d}{dx} \psi_1(x) \, dx
\]

\[
= -i \hbar \int_0^L \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \frac{d}{dx} \left( \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \right) \, dx
\]

\[
= -\frac{2i \hbar}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \cdot \frac{d}{dx} \left( \sin \left( \frac{\pi x}{L} \right) \right) \, dx
\]

Next, the derivative must be evaluated,

\[
\frac{d}{dx} \left( \sin \left( \frac{\pi x}{L} \right) \right) = \frac{\pi}{L} \cos \left( \frac{\pi x}{L} \right) .
\]

Substituting, the average value of the momentum is

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

From the CRC Handbook (or handout of integrals),

\[
\int \sin bx \cos bx \, dx = \frac{\sin^2 bx}{2b} .
\]
Replacing $b$ by $\frac{\pi}{L}$, the average value of momentum becomes

$$\langle p_x \rangle = -\frac{2i\hbar \pi}{L^2} \left[ \frac{\sin^2 \left( \frac{2\pi x}{L} \right)}{2} \right]^L_0 .$$

Evaluating this expression at the limits gives the **average value of momentum** for the ground state,

$$\langle p_x \rangle = -\frac{2i\hbar \pi}{L^2} \left[ \frac{L}{2\pi} \sin^2(2\pi) \right] + \frac{2i\hbar \pi}{L^2} \left[ \frac{L}{2\pi} \sin^2(0) \right]$$

$$\langle p_x \rangle = -\frac{2i\hbar \pi}{L^2} \left[ 0 \right] + \frac{2i\hbar \pi}{L^2} \left[ 0 \right]$$

$$\langle p_x \rangle = 0 .$$

For the ground state of the particle in a box, the average value of momentum is 0. This is actually true for any state of the particle in a box, and reflects the idea that motion in the positive $x$-direction, corresponding to positive values of momentum, and motion in the negative $x$-direction, corresponding to negative values of momentum, are equally probable. Thus, the positive and negative values of momentum cancel, yielding an average value of 0.