Homework 12 Solution

1. Problem 2.2 in the book.

**Solution:** For the particle in a 1D box, \( E_n = \frac{n^2 \hbar^2}{8mL^2} \)

1 mole \((6.02 \times 10^{-23} \text{ molecules})\) weighs 28g = 0.028 kg.
So, 1 \( \text{N}_2 \) molecule weighs \( \frac{0.028}{(6.02 \times 10^{-23})} = 4.65 \times 10^{-26} \) kg.
So, the energy separation between \( n=1 \) and \( n=2 \) is,

\[
\Delta E = (2^2 - 1^2) \frac{\hbar^2}{8mL^2} = 3 \left( \frac{(6.626 \times 10^{-34})^2}{8 \times 4.65 \times 10^{-26} \times 10^{-4}} \right) = 3.54 \times 10^{-38} \text{ J}.
\]

The average thermal energy is \( \frac{1}{2} k_B T = \frac{1}{2} 1.38 \times 10^{-23} \times 300 = 2.07 \times 10^{-21} \text{ J} \)

\[
\Rightarrow 2.07 \times 10^{-21} = \frac{n^2 (6.626 \times 10^{-34})^2}{8 \times 4.65 \times 10^{-26} \times 10^{-4}}
\]

or, \( n = 4.19 \times 10^8 \)

When we move to very high energy states, quantum effects are no longer observed and classical behavior is recovered. The domain of quantum effects is generally the low temperature (~0 K) region, and at high temperatures statistical effects predominate.

**Turn in 2.** Calculate the probability of finding an electron in the one dimensional box, within \( L/3 \) and \( 2L/3 \), when its in a) the ground state \( (n=1) \) ; and b) 1st excited state \( (n=2) \).

What is the difference that you observe, and what can you infer about the shape of the wavefunction at the two different energy levels?

**Solution:** For the electron in a 1D box, the wavefunction is given by

\[
\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}
\]
So, probability density \( P(x) = |\psi(x)|^2 = \frac{2}{L} \sin^2\left(\frac{n \pi x}{L}\right) \)

a) \( n=1 \)

\[
P\left(\frac{L}{3} \to \frac{2L}{3}\right) = \frac{2}{L} \int_{L/3}^{2L/3} dx \sin^2\left(\frac{\pi x}{L}\right)
\]

Now, putting \( 2 \sin^2 x = 1 - \cos(2x) \) and integrating over the limits, we get

\[
P\left(\frac{L}{3} \to \frac{2L}{3}\right) = \frac{1}{3} - \frac{1}{2\pi} \left[ \sin \left(\frac{4\pi}{3}\right) - \sin \left(\frac{2\pi}{3}\right) \right]
\]

\[
= \frac{1}{3} + \frac{\sqrt{3}}{2\pi} \approx 0.61 \text{ or about 61%}
\]

b) \( n=2 \)

\[
P\left(\frac{L}{3} \to \frac{2L}{3}\right) = \frac{2}{L} \int_{L/3}^{2L/3} dx \sin^2\left(\frac{2\pi x}{L}\right)
\]

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

\[
= \frac{1}{3} - \frac{1}{4\pi} \left[ \sin \left(\frac{8\pi}{3}\right) - \sin \left(\frac{4\pi}{3}\right) \right]
\]

\[
= \frac{1}{3} - \frac{\sqrt{3}}{4\pi} \approx 0.19 \text{ or about 19%}
\]

You can see that the probability of finding the electron between \( L/3 \) and \( 2L/3 \) is higher in the ground state \( n=1 \) than the first excited state \( n=2 \).

This is a reflection of the corresponding wavefunctions, which has a maximum at \( L/2 \) for \( n=1 \), and has a node (zero probability) at \( L/2 \) for \( n=2 \).
3. Problem 2.4 in the book. This shows how ‘electron in a box’ wavefunctions can be applied to calculate energy levels of a conjugated molecule like carotene. We’ll talk about benzene and other such molecules later.

**Solution:**

a) For 22 C atoms, there are 22 energy levels. The first 11 are occupied, and the last 11 are unoccupied. So, the highest occupied level is n=11, and lowest unoccupied level is n=12. (You know about filling in 2 electrons per energy level due to spin; we’ll discuss this in detail soon in the lectures.)

\[
\therefore E_{12} - E_{11} = (12^2 - 11^2) \frac{h^2}{8mL^2}
\]

\[
= 23 \times \frac{(6.626 \times 10^{-34})^2}{8 \times (9.1 \times 10^{-31}) \times (3.17 \times 10^{-9})^2} \text{ J}
\]

\[
= 1.38 \times 10^{-19} \text{ J}
\]

b) \(\Delta E = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.38 \times 10^{-19}} = 1.44 \times 10^{-6} \text{ m}\)

b) To find the average number of electrons between \(C_{11}\) and \(C_{12}\), we proceed by taking the average value of probability density at the center of these C atoms, over ALL the occupied states (remember that occupancy in each state is 2).

Probability of finding one electron in this region is given by

\[
P = \frac{2}{L} \int_{C_{11}}^{C_{12}} dx \sin^2(n\pi x/L) \approx \frac{2}{L} \sin^2 \left(\frac{n\pi x}{L}\right) (C_{12} - C_{11})
\]

where we assumed the wavefunction to be constant in this small region, and \(C_{11}\) and \(C_{12}\) are the distances between the 12th and 11th carbon atoms.
Thus, to find the average number of electrons between \( C_{11} \) and \( C_{12} \), we sum from \( n=1 \) to \( n=12 \), with 2 electrons in each energy level (this IS the ground state!).

\[
N = 2 \times \frac{2}{L} \times \sum_{n=1}^{11} \sin^2 \left[ \frac{n\pi(C_{11} + C_{12})}{L} \right] \times (C_{12} - C_{11})
\]

Now, \( L = 3.17 \times 10^{-9} m \) (length of the box),

\[
C_{11} = 10.5 \times 144 \times 10^{-12} m, \quad \text{and} \quad C_{12} = 11.5 \times 144 \times 10^{-12} m
\]

Plugging in the values, we get \( N = 1.09 \). This is the average number of electrons between 11\(^{th}\) and 12\(^{th}\) carbon atoms in the ground state.

d) The bond order is basically a measure of the number of bonds. You also know that 2 paired electrons nominally make up one bond (we have yet to prove this formally – soon!). So, the number of Pi bonds afforded by 1.09 Pi electrons is, \( 1.09/2 = 0.545 \).

There is also one Sigma bond already present between the two carbon atoms, that we haven’t dealt with (we were just talking about Pi electrons). Thus, the total bond order between \( C_{11} \) and \( C_{12} \) is \( 1+0.545 = 1.545 \).