1. The energy levels of the particle in a box are given by $\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$.

(a) Why does the lowest energy correspond to $n = 1$ rather than $n = 0$?

The wavefunction has the general form $\psi = \sin(n \pi x / L)$. If $n = 0$, $\psi = \sin(0 \times \pi x / L) = 0$. The wavefunction is zero everywhere and so is $\psi^2$. As the particle must be somewhere, this solution is not in accord with the Born interpretation and is not a useful or eigen solution.

(b) What is the separation between two adjacent levels? (Hint: $\Delta \varepsilon = \varepsilon_{n+1} - \varepsilon_n$)

The level with quantum number $n$ has energy $\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$.

The next level has quantum number $n + 1$ so has energy $\varepsilon_{n+1} = \hbar^2 (n+1)^2 \pi^2 / 2mL^2$.

The separation of the levels is therefore:

$$\Delta \varepsilon = \varepsilon_{n+1} - \varepsilon_n = \hbar^2 (n+1)^2 \pi^2 / 2mL^2 - \hbar^2 n^2 \pi^2 / 2mL^2$$

$$= \hbar^2 \pi^2 / 2mL^2 [(n+1)^2 - n^2]$$

$$= \hbar^2 \pi^2 / 2mL^2 [2n + 1]$$

(c) The $\pi$ chain in a hexatriene derivative has $L = 973$ pm and has 6 $\pi$ electrons. What is energy of the HOMO – LUMO gap?

With two electrons occupying each level, the highest occupied level with 6 electrons is $n = 3$. The HOMO – LUMO gap is:

$$\Delta \varepsilon = (2n+1)(\hbar^2\pi^2/2mL^2) = (2 \times 3 + 1)(\hbar^2\pi^2/2mL^2)$$

$$= 7\hbar^2\pi^2/2mL^2$$

Using $L = 973$ pm $= 973 \times 10^{-12}$ m:

$$\Delta \varepsilon = 7 \times (6.626 \times 10^{-34} / 2\pi)^2 \times \pi^2 / (2 \times 9.10953 \times 10^{-31} \times (973 \times 10^{-12})^2) \text{ J}$$

$$= 4.45 \times 10^{-19} \text{ J}$$

Using $\varepsilon = hc/\lambda$, this corresponds to a wavelength of light:

$$\lambda = hc/\varepsilon = (6.626 \times 10^{-34}(2.998 \times 10^8) / (4.45 \times 10^{-19}) = 4.46 \times 10^{-7} \text{ m} = 446 \text{ nm}$$

This wavelength corresponds to a wavenumber of 22400 cm$^{-1}$.

(d) What does the particle in a box model predicts happens to the HOMO – LUMO gap of polyenes as the chain length increases?

As the chain lengthens, both $n$ and $L$ increase. The HOMO – LUMO gap depends is given by $(2n+1)(\hbar^2\pi^2/2mL^2)$ and so decreases.