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 ψ^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:

$$\begin{aligned}\Delta\varepsilon = \varepsilon_{n+1} - \varepsilon_n &= \hbar^2(n+1)^2\pi^2/2mL^2 - \hbar^2 n^2\pi^2/2mL^2 \\ &= (\hbar^2\pi^2/2mL^2)[(n+1)^2 - n^2] \\ &= (\hbar^2\pi^2/2mL^2)[n^2+2n + 1 - n^2] \\ &= (\hbar^2\pi^2/2mL^2)[2n + 1] \\ &= (2n+1)(\hbar^2\pi^2/2mL^2)\end{aligned}$$

(c) The π chain in a hexatriene derivative has L = 973 pm and has 6 π 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:

$$\begin{aligned}\Delta\varepsilon &= (2n+1)(\hbar^2\pi^2/2mL^2) = (2 \times 3 + 1)(\hbar^2\pi^2/2mL^2) \\ &= 7\hbar^2\pi^2/2mL^2\end{aligned}$$

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

$$\begin{aligned}\Delta\varepsilon &= 7 \times (6.626 \times 10^{-34} / 2\pi)^2 \times \pi^2 / (2 \times 9.10953 \times 10^{-31} \times (973 \times 10^{-12})^2)\ \text{J} \\ &= 4.45 \times 10^{-19}\ \text{J}\end{aligned}$$

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.