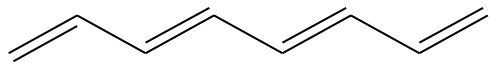
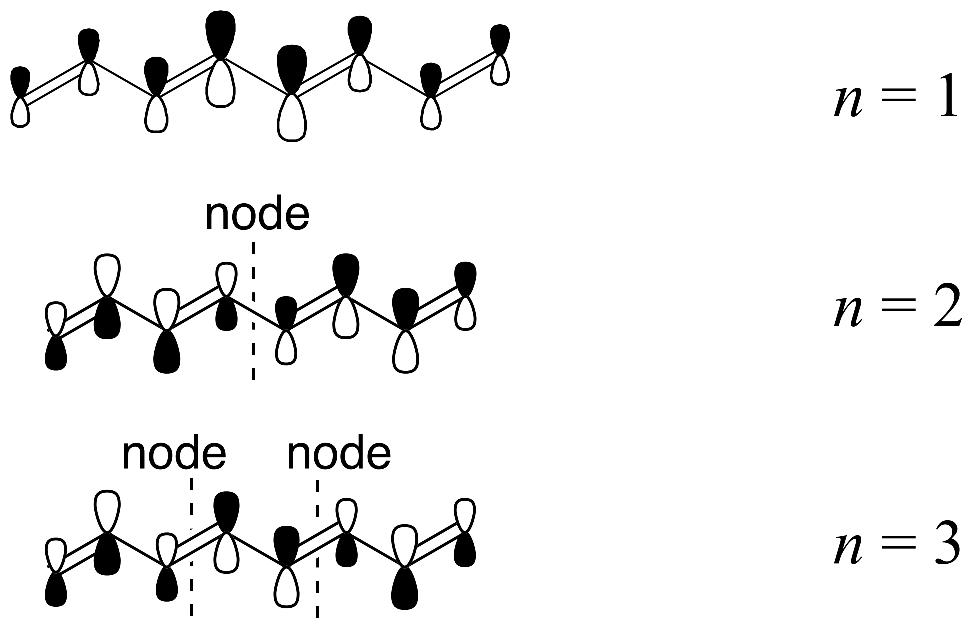
The energy levels of the π orbitals of a polyene such as octatetraene, pictured below, can be approximated to those of a particle in a one-dimensional box whose length is equal to the sum of the bonds in the conjugated system.



(a) Draw the second and third lowest-energy wavefunctions for octatetraene, showing the position of any nodes relative to the position of the carbon atoms in the molecule. The lowest energy wavefunction is drawn for you.



[3 marks **P**]

(b) What is the wavelength for $n = 2$ electrons, if the π-electrons are modelled as a particle inside a one-dimensional box of length L? [1 marks **P**]

1 wave spans the length of the molecule: wavelength = $\lambda = L$

(c) What is the wavelength for $n = 3$ electrons, if the π-electrons are modelled as a particle inside a one-dimensional box of length L? [1 marks **P**]

1½ waves span the length of the molecule: $\lambda = \frac{2}{3} L$

(d) What is the general formula for the wavelength of the electrons with quantum number n, if the π-electrons are modelled as a particle inside a one-dimensional box of length L?

[1 marks **P**]

For $n = 1$, wavelength = $2L$. For $n = 2$, wavelength = L. For $n = 3$, $\lambda = 3L/2$.
In general:

$$\lambda = 2L/n$$

(e) How many π-electrons are there in octatetraene, and therefore, what is the quantum number, n_{HOMO}, of the highest occupied molecular orbital, if the π-electrons are modelled as a particle inside a one-dimensional box? is this text needed? [2 marks **P**]

Each carbon atom contributes 1 electron to the π system. Octatetraene therefore has 8 π electrons.

As 2 electrons can occupy each level and the levels are non-degenerate for a particle in a box, these 8 electrons doubly occupy n = 1, 2, 3 and 4. n_{HOMO} = 4.

(f) If each C-C bond is 0.139 nm in length, what is the length of the box for octatetraene? [1 marks **P**]

The molecule is contains 7 C-C bonds: the length of the molecule is:

$L = 7 \times 0.139 \text{ nm} = 0.973 \text{ nm}$

(g) Noting that $E = p^2/2m$, for a particle with no potential energy, use de Broglie's equation, $p = mv = h/\lambda$, to show that the separation between adjacent energy levels (n, n+1) for a particle inside a one-dimensional box of length L and infinitely high sides is given by:

$$\Delta E = \frac{h^2(2n+1)}{8mL^2}$$

As $E = p^2 / 2m$ and $p = h / \lambda$,

$$E = (h/\lambda)^2 / 2m = h^2 / 2m\lambda^2$$

From (d), $\lambda = 2L/m$,

$$E = h^2 / 2m(2L/n)^2 = h^2 n^2/8mL^2$$

The energy difference between adjacent levels E_n and E_{n+1} is therefore,

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= [h^2 (n+1)^2/8mL^2] - [h^2 n^2/8mL^2] \\ &= (h^2/8mL^2) \times (n^2 + 2n + 1 - n^2) \\ &= (h^2 n^2/8mL^2) \times (2n + 1) \\ &= h^2 (2n+1)/8mL^2\end{aligned}$$

[3 marks **CR**]

(h) To what does the m in the above equation refer? What is its value in kg? [1 mark **P**]

The expression is for the energy levels of an electron: m refers to the mass of an electron:

$$m = 9.11 \times 10^{-31} \text{ kg}$$

(i) Calculate the energy of a photon emitted when an electron relaxes from the n_{HOMO}+1 level to the n_{HOMO} level.

[2 marks **CR**]

With n_{HOMO} = 4 and L = 0.973 nm:

$$\Delta E = h^2(2n+1)/8mL^2$$

$$= \frac{(6.626\times10^{-34})^2(2\times4+1)}{8\times(9.11\times10^{-31})\times(0.973\times10^{-9})^2} = 5.73\times10^{-19}\,\mathrm{J}$$

(j) Predict what will happen to the energy of the equivalent transition as the length of the polyene increases. Explain your answer.

[2 marks **D**]

As the polyene lengths, *both* n_{HOMO} and L will increase as the polyene will contain more electrons and will grow in length.

As ΔE is proportional to 2n+1)/L^2, the effect of the increase in L is greater than the effect of the increase in n. The HOMO – LUMO gap will *decrease*.

(i) Taking the limit of infinite (~N_A carbons) chain length, within the particle-in-a-box model, do you expect the resulting material to be a conductor, insulator, or semiconductor. Explain your answer with reference to terminology used for the electronic structure of network solids such as silicon.

[3 marks **HD**]

$\Delta E \rightarrow 0$ as $L \rightarrow \infty$. There is no gap between the top of the valence band and the conduction band. Electrons are easily excited into the conduction band and are then mobile charge carriers. The infinite polyene is thus predicted to be a conductor by this model.