2.7: The Free Electron Model

Consider a long molecule that is a conjugated polyene. Kuhn (Kuhn, 1949) has suggested a model for the electrons involved in this π-bond system in which an electron is said to have a finite potential energy when it is "on" the molecule and an infinite potential energy when it is "off" the molecule. The model (known as the free electron model) is very much analogous to the particle in a box problem as we have presented it in class.

Let’s consider a conjugated polyene molecule in which there are twelve atoms in the conjugated polyene chain. Each atom contributes one π electron and each bond contributes $0.139\ \mathrm{nm}$ (the $\mathrm{C=C}$ bond length in benzene.) We can consider each energy level in the system as one orbital. As in all other cases involving electrons, each orbital can contain two electrons. Using the model, we can predict the wavelength of light the molecule will absorb to excite one electron from the HOMO to the LUMO (highest occupied molecular orbital to the lowest unoccupied molecular orbital.)

First, there are 11 bonds in the chain. Since each bond contributes $0.139\ \mathrm{nm}$, the "box" is $1.529\ \mathrm{nm}$ long. The energy levels of the molecular orbitals are then given by:

$$E_n = \frac{n^2 h^2}{8ma^2}$$

where $n = 1, 2, 3 \ldots$, h is Plank’s constant $\left(h = 6.63 \times 10^{-34}\mathrm{Js}\right)$, m is the mass of an electron $\left(m_\mathrm{e} = 9.11 \times 10^{-31}\ \mathrm{kg}\right)$ and a is the length of the box $\left(a = 1.529 \times 10^{-9}\ \mathrm{m}\right)$.

The energy levels will be filled with the 12π electrons packing two electrons per orbital. Thus, the HOMO will be the state with $n = 6$. The LUMO will be the state with $n = 7$ - the next state up in energy. The difference in energy is what we want in order to predict the wavelength of light the molecule will absorb.

$$\begin{aligned} E_6 &= \frac{6^2\left(6.63 \times 10^{-34}\mathrm{Js}\right)^2}{8\left(9.11 \times 10^{-31}\ \mathrm{kg}\right)\left(1.529 \times 10^{-9}\ \mathrm{m}\right)^2} = 9.288 \times 10^{-19}\ \mathrm{J} \\ E_7 &= \frac{7^2\left(6.63 \times 10^{-34}\mathrm{Js}\right)^2}{8\left(9.11 \times 10^{-31}\ \mathrm{kg}\right)\left(1.529 \times 10^{-9}\ \mathrm{m}\right)^2} = 1.2642 \times 10^{-18}\ \mathrm{J} \end{aligned}$$

So the energy of excitation will be $3.354 \times 10^{-19}\ \mathrm{J}$. This corresponds to an absorption wavelength of $593\ \mathrm{nm}$ (which is in the visible region of the spectrum.) How would the absorption wavelength change for more or fewer atoms in the conjugated polyene chain? The solution is left as an exercise.