

QUANTUM MECHANICS A (SPA 5319)

Electrons in Conjugated Polymers

There are many practical examples of quantum well structures that provide good experimental tests of the simple quantum mechanical problems met in this module. In the laboratory experiment described here you will be shown how infrared spectra are measured for a group of long chain polymers, the so-called conjugated polymers. As a rather unusual application of our simple quantum mechanical well problems you will be asked to investigate whether or not these spectra can be understood by modelling the chain as an escape-proof box to which the electrons are confined. These are the electrons involved in producing the observed ultra violet (UV) spectral lines.

The polymers in question consist of N sub-units joined together in a linear chain. Each subunit has a linear size

$$a \simeq 0.12 \text{ nm} \quad (1)$$

so that the total length of the molecule is

$$L = Na \quad (2)$$

For example, in the weekly problems you will have met the Hexatriene molecule illustrated in the following figures.

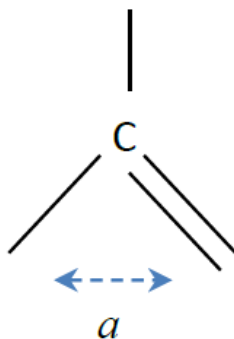


Figure 1: *Basic building block of the Hexatriene molecule.*

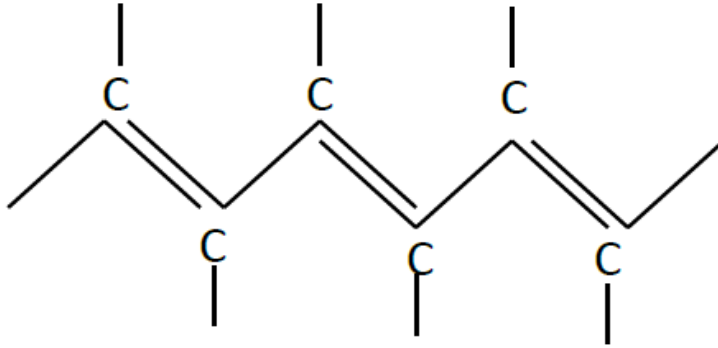


Figure 2: *The Hexatriene molecule.*

Typically, each link in the chain contributes one mobile electron that can travel along the backbone of the polymer – these are known as delocalised electrons, although they are still confined to the polymer chain. Consider a long chain polymer that contains N electrons free to move along the chain. Take N = even. The Pauli exclusion principle allows only one electron per quantum state, i.e. 1 electron per energy level. Because its spin also provides an electron with its own internal quantum state with two possibilities – spin “up” or spin “down” – therefore are at most two electrons that can occupy each energy level, one with spin up and the other with spin down. We can therefore depict the ground state (state of lowest energy) of the N electrons confined to the polymer.

If the polymer is placed in a beam of radiation with wavelength comparable to the energy level spacing, then an electron can be excited into a higher energy level by absorbing a photon. However the electrons in lower energy levels cannot be excited into neighbouring levels because these are already completely filled with their complement of 2 electrons. The lowest energy photon that can be absorbed would result in one of the electrons in the highest filled level jumping up to the lowest empty level; this is the first excited state of the polymer. We now use our knowledge of the quantised energy levels of the escape-proof box:

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \quad (3)$$

where m is the electron mass. We see that the energy gap between the highest occupied level and the lowest unoccupied level is

$$\Delta E = E_{n_{\max}+1} - E_{n_{\max}} = E_{\frac{N}{2}+1} - E_{\frac{N}{2}} \quad (4)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} [(N/2 + 1)^2 - (N/2)^2] \quad (5)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} [(N/2)^2 + 2(N/2) + 1 + (N/2)^2] \quad (6)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} (N + 1) \quad (7)$$

Finally we use $L = Na$, equation (2), to obtain

$$\Delta E = \frac{\hbar^2 \pi^2}{2ma^2} \frac{(N+1)}{N^2} \quad (8)$$

Thus, when illuminated with a beam of electromagnetic radiation the lowest energy photons such a polymer would absorb have a frequency ν given by

$$h\nu = \Delta E = \frac{\hbar^2 \pi^2}{2ma^2} \frac{(N+1)}{N^2} \quad i.e. \quad \nu = \frac{h}{8ma^2} \frac{(N+1)}{N^2} \quad (9)$$

On absorbing the photon the energy levels would be occupied in a new configuration, and the radiation passing through the material would show an absorption line at this frequency.