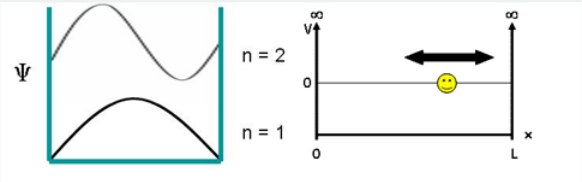
2.17: Conjugation Length

Delocalization Length

Delocalized electrons are electrons that are not associated with a single atom or a covalent bond. Term delocalization is general and can have slightly different meanings in different fields. In organic chemistry, this refers to resonance in conjugated systems and aromatic compounds. In solid-state physics, this refers to free electrons that facilitate electrical conduction. In quantum chemistry, this refers to molecular orbital electrons that have extended over several adjacent atoms. Standard ab initio quantum chemistry methods lead to delocalized orbitals that, in general, extend over an entire molecule and have the symmetry of the molecule as discussed previously.

The Particle in a Box Model to decribe Delocalization Effects

In general, Molecular Orbitals may be delocalized over the entire length of the molecule. The Particle-in-a-box quantum model is useful in describing the impact of delocalization length on the electronic transition of the molecule.



These PIB energies for an electron trapped in a box of length L goes as

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{2.17.1}$$

The observed frequency for a transition is calculated from the change in energy using the following equalities,

$$\begin{aligned} \Delta E &= E_f - E_i \\ &= h\nu \end{aligned}$$

Then, for the specific case of the particle-in-a-box (via Equation 2.17.1):

$$\begin{aligned} \Delta E &= E_f - E_i \\ &= \frac{(n_f^2 - n_i^2)h^2}{8mL^2} \end{aligned} \tag{2.17.2}$$

where n_f is the quantum number associated with the final state and n_i is the quantum number for the initial state.

Equation 2.17.2 argues that the larger the box (i.e., the number of atoms the electron is delocalized over), the smaller the energy differences between quantum levels.

This is a simplistic model for bonding, compared to the molecular orbital approaches discussed so far, but guides general intuition around delocalization effects in comparing molecules with different sizes.

Molecular Orbitals from One double bond

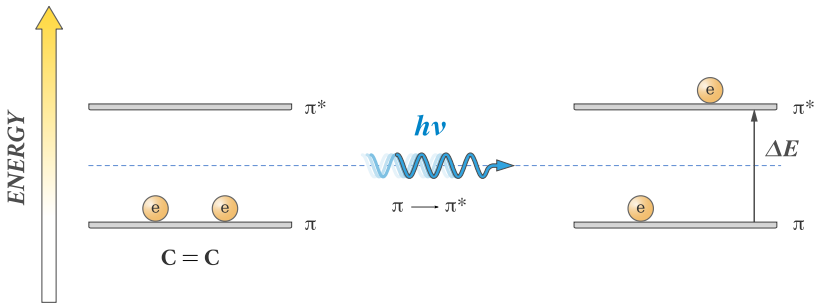


Figure 2.17.2: Scheme of electronic transition due to delocalization of molecular orbitals over two atoms (one double bond in a simple local bonding perspective). (CC BY-NC; Ümit Kaya via Libretexts)

Molecular Orbitals from Two double bonds

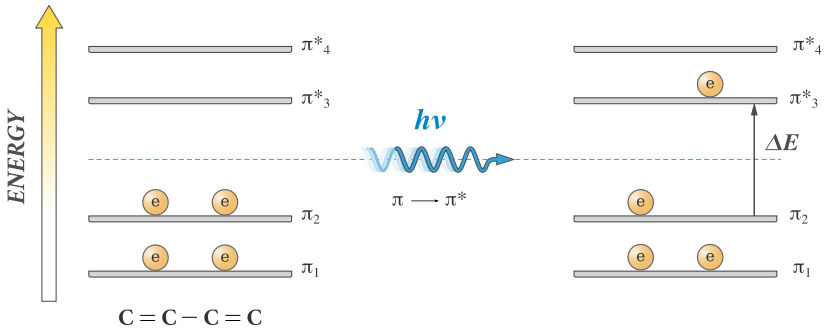


Figure 2.17.3: Scheme of electronic transition due to delocalization of molecular orbitals over found four atoms (two double bonds and one single bond in a simple local bonding perspective). (CC BY-NC; Ümit Kaya via Libretexts)

Molecular Orbitals from Three double bonds

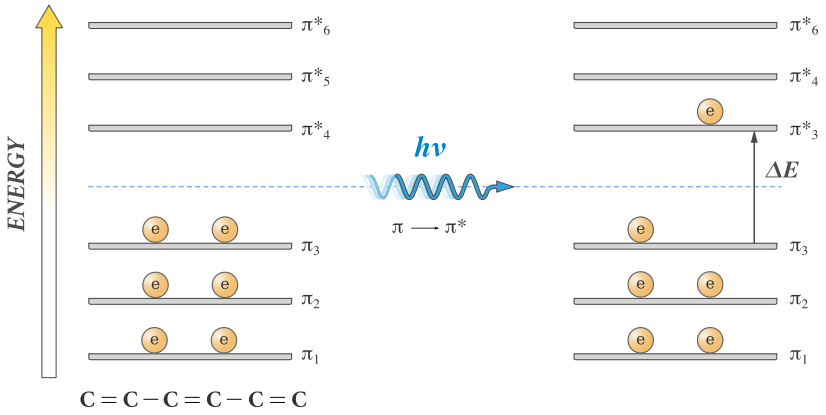


Figure 2.17.4: Scheme of electronic transition due to delocalization of molecular orbitals over found six atoms (three double bonds and two single bonds in a simple local bonding perspective). (CC BY-NC; Ümit Kaya via Libretexts)

For a more detailed overview of the the effect of delocalization on the ground state energies check Section 10.5 and Section 10.6 of the physical chemistry textbook.

The added conjugation in naphthalene (pink), anthracene (green) and tetracene (blue) causes bathochromic (red-shifts) shifts of these absorption bands, as displayed in the chart on the left below. All the absorptions do not shift by the same amount, so for anthracene (green shaded box) and tetracene (blue shaded box) the weak absorption is obscured by stronger bands that have

experienced a greater red shift. As might be expected from their spectra, naphthalene and anthracene are colorless, but tetracene is orange. *What break's conjugation lengths? Aliphatic bonding does.*

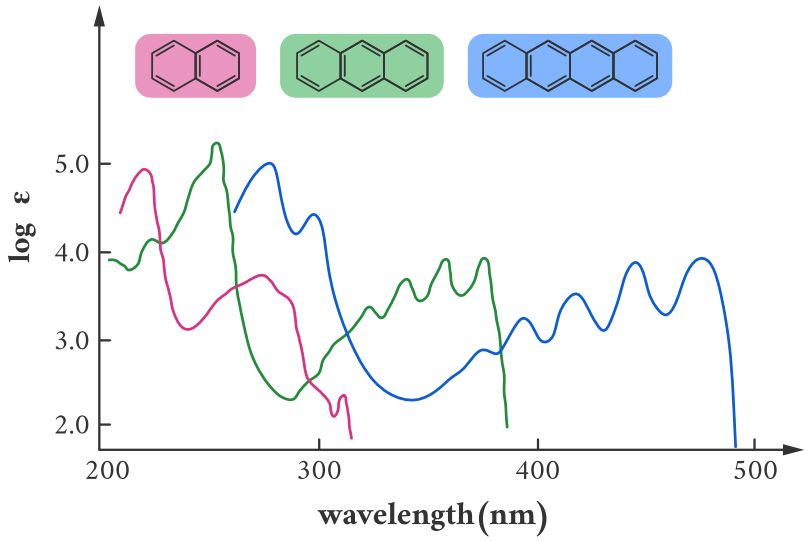
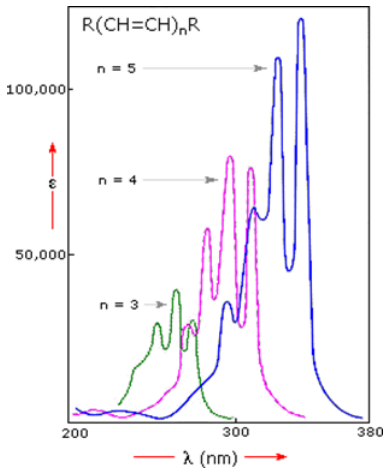


Figure 2.17.1: Conjugation effects for fused ring systems. As the molecular orbitals extend over more atoms, the electronic transitions shift red-shift (CC BY-NC; Ümit Kaya via Libretexts)

What about Oscillator Strength?

The greater the conjugation strength, the greater the molar The greater the conjugation strength, the greater the molar absortivity.



That is the end of Electronic Absorption Spectroscopy. We did not cover may interesting and powerful tweaks to this field, including ORD, CD, or MCD.
