Modeling the $\pi$-Electrons of Benzene as Particles on a Ring

Calculate the wavelength of the photon required for the first allowed (HOMO-LUMO) electronic transition involving the $\pi$-electrons of benzene.

Energy Level Diagram for Benzene's $\pi$ Electrons

$$\frac{4\cdot h^2}{2\cdot m\cdot C^2}$$  

\[ n = +/- 2 \quad \text{LUMO} \]

$$\frac{h^2}{2\cdot m\cdot C^2}$$  

\[ n = +/- 1 \quad \text{HOMO} \]

\[ n = 0 \]

Energy conservation requires:

$$\frac{n_i^2\cdot h^2}{2\cdot m_e\cdot C^2} + \frac{h\cdot c}{\lambda} = \frac{n_f^2\cdot h^2}{2\cdot m_e\cdot C^2}$$

Fundamental constants and conversion factors:

$$\text{pm} := 10^{-12} \cdot \text{m} \quad \text{aJ} := 10^{-18} \cdot \text{J}$$

$$h := 6.6260755\cdot 10^{-34}\cdot \text{Joule} \cdot \text{sec} \quad c := 2.99792458\cdot 10^8\cdot \text{m} \cdot \text{sec}^{-1} \quad m_e := 9.1093897\cdot 10^{-31}\cdot \text{kg}$$

Calculate the photon wavelength for the HOMO-LUMO electronic transition.

$$\lambda := \frac{n_i^2\cdot h^2}{2\cdot m_e\cdot C^2} + \frac{h\cdot c}{\lambda} = \frac{n_f^2\cdot h^2}{2\cdot m_e\cdot C^2}$$

\[ \text{solve}, \lambda, \text{float}, 3 \rightarrow 194\cdot 10^{-15}\cdot \text{m} \cdot \text{kg} \cdot \text{sec}^{-2} \quad \lambda = 194\text{nm} \]

Calculate the photon energy and frequency.

$$\text{energy} \quad \frac{h\cdot c}{\lambda} = 1.024\text{ aJ}$$

$$\text{frequency} \quad \frac{c}{\lambda} = 1.545 \times 10^{15}\text{ Hz}$$
Plot Wave Functions

See Figure 7.6 (page 111) in *Quantum Chemistry and Spectroscopy*, by Engel.

The real part of the wave function is plotted below.

Quantum number: \( n := 5 \)

\[
\text{numpts} := 100 \quad i := 0..\text{numpts} \quad j := 0..\text{numpts} \quad \phi_i := \frac{2\pi i}{\text{numpts}}
\]

\[
x_{i,j} := \cos(\phi_i) \quad y_{i,j} := \sin(\phi_i) \quad z_{i,j} := \frac{1}{\sqrt{2\pi}} \exp(i \cdot n \cdot \phi_i) \quad zz_{i,j} := 0
\]

The square of the absolute magnitude for all the wave functions (for all values of the quantum number \( n \)) is \( 1/2\pi \), as shown below.

\[
\left( \frac{1}{\sqrt{2\pi}} \cdot \exp(i \cdot n \cdot \phi) \right)^2 \quad \text{simplifies to} \quad \frac{1}{2\pi}
\]

The wave functions for the electron on a ring are eigenstates of the momentum operator. In other words the momentum is precisely known: \( p = nh/C \), where \( n \) is the quantum number and \( C \) is the ring circumference. According to the uncertainty principle, the electron position must be uncertain. The result above confirms this; the electron density is distributed uniformly over the entire ring.