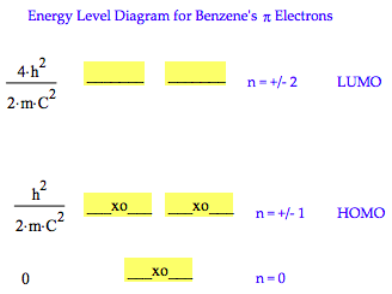
4.31: Calculating the Pi-electron HOMO-LUMO Electronic Transition for Benzene

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



Energy conservation requirements:

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

Fundamental constants and conversion factors:

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

$$h = 6.6260755(10^{-34}) \text{joule sec} \quad c = 2.99792458(10^8)\frac{m}{sec} \quad m_e = 9.1093897(10^{-31}) kg$$

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

$$\text{HOMO:} \quad n_i = 1 \quad \text{LUMO:} \quad n_f = 2 \quad \text{Benzene circumference:} \quad C = 6(140)pm$$

$$\lambda = \frac{n_i^2 h^2}{2m_e C^2} + \frac{hc}{\lambda} = \frac{n_f^2 h^2}{2m_e C^2} \quad \left| \begin{array}{l} \text{float, 3} \\ \text{solve, } \lambda \end{array} \right. \rightarrow .194e-6m^3 \frac{kg}{joule\ sec^2} \quad \lambda = 194nm$$

Calculate the photon energy and frequency.

$$\text{energy} \quad \frac{c}{\lambda} = 1.024aJ \quad \text{frequency} \quad \frac{c}{\lambda} = 1.545 \times 10^{15} Hz$$

Plot Wave Functions

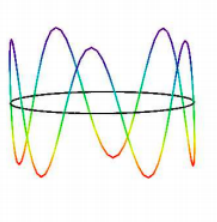
See Figure 7.6 (page 111) in *Quantum Chemistry and Spectroscopy*, by Engel.

The real part of the wave function is plotted below.

Quantum number: n = 5

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

$$x_{i,j} = \cos(\phi_i) \quad y_{i,j} = \sin(\phi_i) \quad z_{i,j} = \frac{1}{\sqrt{2\pi}} \exp(in\phi_i) \quad zz_{i,j} = 0$$



(x, y, Re(z)), (x, y, zz)

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

$$\left(\left|\frac{1}{\sqrt{2\pi}}\exp(in\phi)\right|\right)^2 \quad \text{simplifies to} \quad \frac{1}{2\pi}$$

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 elctron position must be uncertain. The result above confirms this; the electron density is distributed uniformly over the entire ring.
