Modeling the π–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 π–electrons of benzene.

Energy Level Diagram for Benzene's π Electrons

$\frac{4 \cdot h^2}{2 \cdot m \cdot C^2}$ _____ _____ n = +/- 2 LUMO

$\frac{h^2}{2 \cdot m \cdot C^2}$ ___xo___ ___xo___ n = +/- 1 HOMO

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

$h := 6.6260755 \cdot 10^{-34} \cdot joule \cdot sec$ $c := 2.99792458 \cdot 10^8 \cdot \frac{m}{sec}$ $m_e := 9.1093897 \cdot 10^{-31} \cdot kg$

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

HOMO: $n_i := 1$ LUMO: $n_f := 2$ Benzene circumference: $C := 6 \cdot 140 \cdot pm$

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

Calculate the photon energy and frequency.

energy $\frac{h \cdot c}{\lambda} = 1.024\,aJ$ frequency $\frac{c}{\lambda} = 1.545 \times 10^{15}\,Hz$

Plot Wave Functions

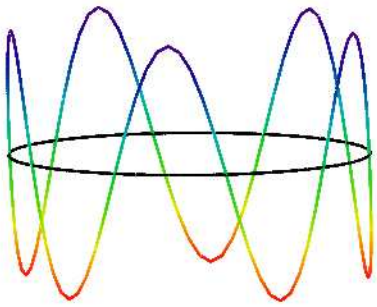
See Figure 7.6 (page 111) in *Quantum Chemistry and Spectroscopy*, by Engel.

The real part of the wave function is plotted below.

Quantum number: $n := 5$

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

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



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

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.

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

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.