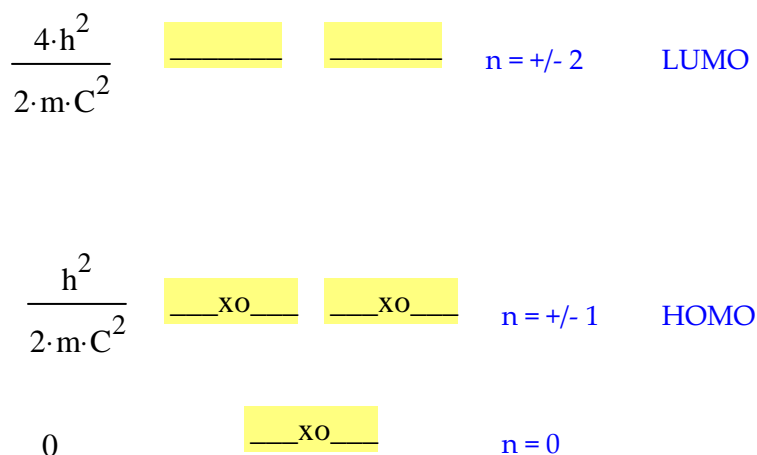


Modeling the π -Electrons of Benzene as Particles on a Ring

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



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} · m aJ := 10^{-18} · J

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

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

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

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

Calculate the photon energy and frequency.

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

Plot Wave Functions

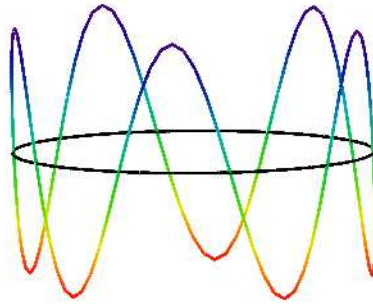
See Figure 7.6 (page 111) in *Quantum Chemistry and Spectroscopy*, by Engel.

The real part of the wave function is plotted below.

Quantum number: $n := 5$

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

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



$(x, y, \text{Re}(z)), (x, y, zz)$

The square of the absolute magnitude for all the wave functions (for all values of the quantum number n) is $1/2\pi$, 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 electron position must be uncertain. The result above confirms this; the electron density is distributed uniformly over the entire ring.