

Treating the Pi-electrons of Benzene as Particles on a Ring

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Wave-particle duality for massive objects as expressed by the de Broglie equation ($\lambda = h/mv = h/p$) is a foundational concept of quantum theory. Classical potential energy carries over to quantum mechanics unchanged, but classical kinetic energy is, as shown below, transformed into a quantum mechanical confinement energy by the de Broglie relation. Confined objects with wave properties are subject to interference which restricts the allowed values of λ , which in turn leads to energy quantization.

$$T = \frac{p^2}{2m} \xrightarrow{p=h/\lambda} \frac{h^2}{2m\lambda^2}$$

A general one-dimensional function, $\Psi(x) = \frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{x}{\lambda}\right)$, is used to represent the wave character of a particle on a ring (POR) where in order to avoid self-interference the head and tail of the wave function must match after one revolution.

$$\Psi(x) = \Psi(x + C) \quad C = 2\cdot\pi\cdot R$$

This requirement restricts the allowed values of the wavelength and leads to a manifold of quantized energies as is now demonstrated. The structure of the manifold of allowed energies depends on the nature of the confinement, each problem gives a characteristic energy manifold. For the particle on a ring we find,

$$\frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{x}{\lambda}\right) = \frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{x+C}{\lambda}\right) = \frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{x}{\lambda}\right) \cdot \frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{C}{\lambda}\right)$$

It follows that $\frac{1}{\sqrt{2\cdot\pi}} \cdot \exp\left(i\cdot 2\cdot\pi\cdot\frac{C}{\lambda}\right) = 1$ which requires $\lambda = \frac{C}{n}$ where $n = 0, +/-1, +/-2, \dots$

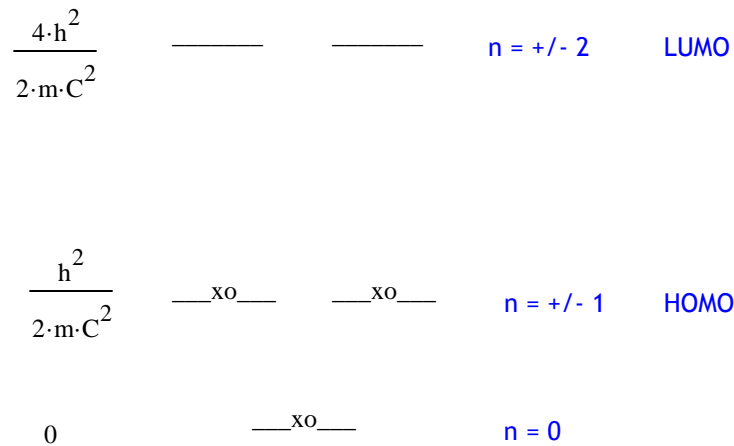
Substitution of this restriction for λ into the quantum expression for kinetic energy yields an equation for the allowed energy states in terms of Planck's constant, the particle mass, the ring circumference and the quantum number, n .

$$T = \frac{h^2}{2\cdot m\cdot\lambda^2} \text{ substitute, } \lambda = \frac{C}{n} \rightarrow T = \frac{h^2\cdot n^2}{2\cdot C^2\cdot m}$$

An obvious POR application is to treat the π -electrons of benzene as particles on a ring. The energy level diagram is constructed using the above energy expression and the allowed values for the quantum number, n . Then the energy level diagram is populated with six π -electrons using the aufbau principle and the Pauli exclusion principle.

The validity of the model is tested by calculating the wavelength of the photon required for the HOMO-LUMO transition. The average c-c bond length in benzene is 140 pm, so the ring circumference is approximated as 6x140 pm. As shown below the photon wavelength required for the HOMO-LUMO transition is 194 nm, a value that might be described as "in the ball park."

Energy Level Diagram for Benzene's π Electrons



Energy conservation for the HOMO-LUMO transition 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: $\text{pm} := 10^{-12} \cdot \text{m}$ $\text{aJ} := 10^{-18} \cdot \text{J}$

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

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

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

$$\lambda := \frac{n_i^2 \cdot h^2}{2 \cdot m_e \cdot C^2} + \frac{h \cdot c}{\lambda} = \frac{n_f^2 \cdot h^2}{2 \cdot m_e \cdot C^2} \left| \begin{array}{l} \text{solve, } \lambda \\ \text{float, 3} \end{array} \right. \rightarrow \frac{1.94\text{e-}7 \cdot \text{kg} \cdot \text{m}^3}{\text{joule} \cdot \text{sec}^2} \quad \lambda = 194 \cdot \text{nm}$$