4.29: Modeling the Pi-electrons of Benzene as Particles on a Ring

From previous work we know that the momentum eigenfunction in coordinate space is given by

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi}}\exp\left(\frac{ipx}{\hbar}\right)$$

Quantum mechanical wave functions must be single-valued, which in this application (electron on a ring) requires a cyclical boundary condition: the wave function must match at points separated by one circumference, C = 2πR.

$$\langle x+C|p\rangle = \langle x|p\rangle$$
$$\exp\left(\frac{pi(x+C)}{\hbar}\right) = \exp\left(\frac{ipx}{\hbar}\right)$$
$$\exp\left(\cdot\right)\exp\left(\frac{pix}{\hbar}\right) = \exp\left(\frac{ipC}{\hbar}\right)$$
$$\exp\left(\frac{ipC}{\hbar}\right) = 1$$

This equation is satisfied if $\frac{pC}{\hbar} = 2\pi m$ where $m = 0, \pm 1, \pm 2...$ You can easily verify this with Mathcad. Thus the quantum number is required in order to satisfy the cyclic boundary condition. Next we calculate the kinetic energy and express it in terms of the circumference of the ring.

$$T_m = \frac{p^2}{2m_e} = \frac{m^2h^2}{2m_eC^2} \ \ \text{where } m = 0, \pm 1, \pm 2 \ldots$$

Substitution of $\frac{2\pi m\hbar}{C}$ for p and recognizing that $\phi = \frac{2\pi x}{C}$ allow one to transform the first equation to,

$$\langle \phi|m\rangle = \frac{1}{\sqrt{2\pi}}\exp(im\backslash\mathrm{hi})$$

1. Sketch an energy level diagram for a particle on a ring.
2. Use the aufbau principle and the Pauli exclusion principle to place the π-electrons of benzene in the allowed energy levels.
3. Calculate the wavelength of the lowest allowed electronic transition (HOMO ÷ LUMO). The average c - c bond length in benzene is 140 pm.