# 4.32: Modeling the Pi-electrons of Benzene as Particles in a Ring

In this exercise benzene's six π electrons will be modeled as particles in a ring or circular corral. Schrödinger's equation in plane polar coordinates and its energy eigenvalues are given below. R is the ring radius and C the ring circumference.

$$\frac{-h^2}{8\pi^2 m_e}\left(\frac{d^2}{dr^2}\Psi(r)+\frac{1}{r}\frac{d}{dr}\Psi(r)-\frac{L^2}{r^2}\Psi(r)\right)=E\Psi(r) \qquad E_{n,\,L}=\frac{(Z_{n,\,L})^2 h^2}{8\pi^2 m_e R^2}=\frac{(Z_{n,\,L})^2 n^2}{2m_e C^2}$$

$J_L$ is the $L^{th}$ order Bessel function, L is the angular momentum quantum number, n is the principle quantum number, $Z_{n,L}$ is the $n^{th}$ root of $J_L$. Dirac notation is used to describe the electronic states, |n,L>. The roots of the Bessel function are given below in terms of the n and L quantum numbers.

$$\begin{array}{l} \text{L quantum number} \\ Z=\left(\begin{array}{cccccccc|c} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & "n" \\ \hline 2.405 & 3.832 & 5.316 & 6.380 & 7.588 & 8.771 & 9.936 & 11.086 & 1 \\ 8.654 & 10.173 & 11.620 & 13.015 & 14.373 & 15.700 & 17.004 & 18.288 & 3 \\ 11.792 & 13.324 & 14.796 & 16.223 & 17.616 & 18.980 & 20.321 & 21.642 & 4 \\ 14.931 & 16.471 & 17.960 & 19.409 & 20.827 & 22.218 & 23.586 & 24.935 & 5 \end{array}\right) \quad \text{n quantum number} \end{array}$$

The manifold of allowed energy levels up to the LUMO is shown below and is populated with 6 π electrons. Note that the states with L > 0 are doubly degenerate.

| | | | | | $Z_{n,L}$ | |
|---|---|---|---|---|---|---|
| LUMO | (1,2) | (1,−2) | ___ | ___ | 5.316 | |
| HOMO | (1,1) | (1,−1) | _xo_ | _xo_ | 3.832 | 6 |
| | (1,0) | | _xo_ | | 2.405 | 2 |

The photon wavelength required for the first electronic transition involving the π electrons is now calculated. The ring circumference is approximated as six benzene carbon-carbon bond lengths.

$$h=6.6260755(10^{-34})\text{joule sec} \quad c=2.99792458(10^8)\frac{m}{sec} \quad m_e=9.1093897(10^{-31})kg \quad pm=10^{-12}m$$

$$C=6(140)pm \qquad \frac{(Z_{1,\,1})^2 h^2}{2m_e C^2}+\frac{hc}{\lambda}=\frac{(Z_{1,\,2})^2 h^2}{2m_e C^2}\ \Bigg|\ \begin{array}{l}\text{float, 3}\\ \text{solve, }\lambda\end{array} \rightarrow \frac{4.28e{-}8kg\,m^3}{joule\ sec^2}=42.8nm$$

Benzene has a strong electronic transition at about 200 nm.