4.33: Modeling the Pi-electrons of Corannulene as Particles in a Ring

In this exercise the 20 π electrons of corannulene will be modeled as particles in a ring or circular corral. Corannulene is bowl-shaped not planar, so the model has some initial difficiencies.

Schrödinger's equation in plane polar coordinates and its energy eigenvalues are given below. R is the ring radius and C the ring circumference.

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

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.

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

The manifold of allowed energy levels up to the LUMO is shown below and is populated with 20 π electrons. Note that the states with L > 0 are doubly degenerate.

					$Z_{n,L}$	
LUMO	(1,4)	(1,−4)	___	___	7.588	
HOMO	(2,1)	(2,−1)	_xo_	_xo_	7.016	20
	(1,3)	(1,−3)	_xo_	_xo_	6.380	16
	(2,0)		_xo_		5.520	12
	(1,2)	(1,−2)	_xo_	_xo_	5.316	10
	(1,1)	(1,−1)	_xo_	_xo_	3.832	6
	(1,0)		_xo_		2.405	2

Corannulene has a strong electronic transition at 280 nm. This information will be used to calculate its circumference.

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

$$\lambda=280nm \qquad \frac{(Z_{2,\,1})^2h^2}{2m_eC^2}+\frac{hc}{\lambda}=\frac{(Z_{1,\,4})^2h^2}{2m_eC^2} \;\Bigg|\; \begin{array}{l}\text{float, 3}\\ \text{solve, C}\end{array}\rightarrow \left(\begin{array}{c} -\dfrac{0.0000533\sqrt{joule}\sqrt{nm}sec}{\sqrt{kg}\sqrt{m}} \\ \dfrac{0.0000533\sqrt{joule}\sqrt{nm}sec}{\sqrt{kg}\sqrt{m}}\end{array}\right)=\left(\begin{array}{c}-1.685\times10^3\\ 1.685\times10^3\end{array}\right)pm$$

The result is reasonable given that there are 15 c-c bonds on the circumference:

$$15(140)pm=2.1\times10^3 pm$$