Chemistry 2

Lecture 3

Particle on a ring approximation

THE UNIVERSITY OF SYDNEY

Learning outcomes from Lecture 2

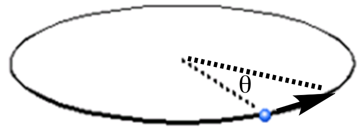
- Be able to explain why confining a particle to a box leads to quantization of its energy levels
- Be able to explain why the lowest energy of the particle in a box is not zero
- Be able to apply the particle in a box approximation as a model for the electronic structure of a conjugated molecule (given equation for E_n).

Assumed knowledge for today

Be able to predict the number of π electrons and the presence of conjugation in a ring containing carbon and/or heteroatoms such as nitrogen and oxygen.

Particle-on-a-ring

- Particle can be anywhere on ring



- Ground state is motionless

The de Broglie Approach

- The wavelength of the wave associated with a particle is related to its momentum:

$$p = mv = h / \lambda$$

- For a particle with only kinetic energy:

$$E = \tfrac{1}{2} mv^2 = p^2 / 2m = h^2 / 2m\lambda^2$$

The Schrödinger equation

- The total energy is extracted by the Hamiltonian operator.
- These are the "observable" energy levels of a quantum particle

$$\hat{H}\Psi(x) = \epsilon_i \Psi(x)$$

Hamiltonian operator

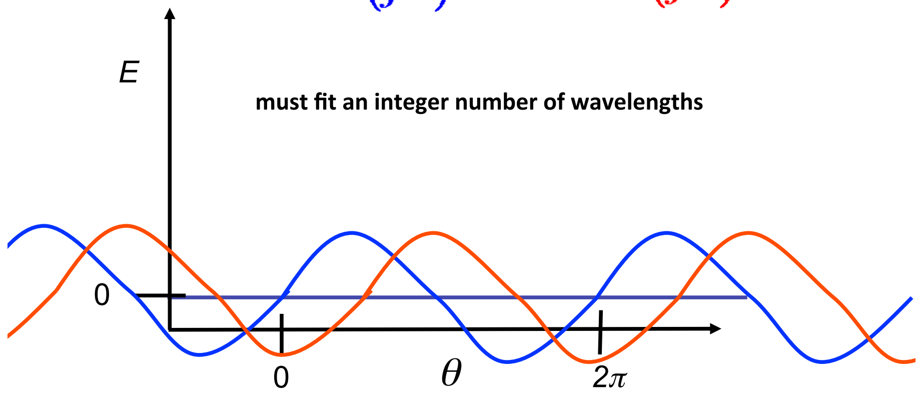
Energy eigenfunction

Energy eigenvalue

"The particle on a ring"

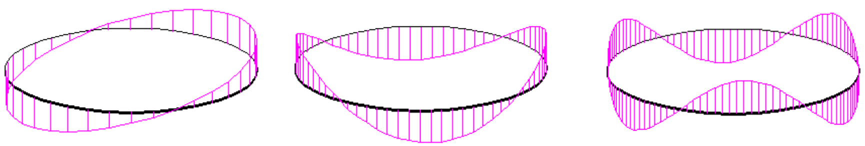
- *The ring is a cyclic 1d potential*

$$\Psi = \sin(j\theta) \quad \Psi = \cos(j\theta)$$



Particle-on-a-ring

- Ground state is motionless
- In higher levels, we must fit an integer number of waves around the ring



1 wave	2 waves	3 waves
$\lambda = 2\pi r$	$\lambda = 2\pi r/2$	$\lambda = 2\pi r/3$

The Schrödinger equation

- The Hamiltonian has parts corresponding to *Kinetic Energy* and *Potential Energy*. In terms of the angle θ:

$$\hat{H}\Psi = \left(-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\theta^2} + V(\theta) \right)\Psi$$

Hamiltonian operator

Kinetic Energy

Potential Energy

"The particle on a ring"

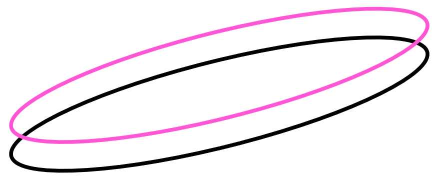
- On the ring, $V = 0$. Off the ring $V = \infty$.

$$\Psi = \sin(j\theta)$$

$$\hat{H}\Psi = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\theta^2}\sin(j\theta)$$
$$= \frac{\hbar^2 j^2}{2mr^2}\sin(j\theta) = \varepsilon_j \Psi \qquad j = 1, 2, 3\ldots.$$

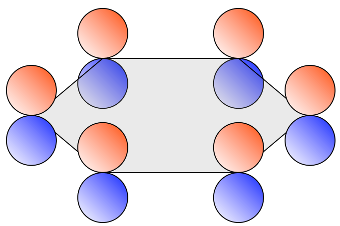
Particle-on-a-ring

- Ground state is motionless



Ψ = constant

"The particle on a ring"



π-system of benzene is like a bunch of electrons on a ring

"The particle on a ring"

- On the ring, $V = 0$. Off the ring $V = \infty$.

$$\Psi = \cos(j\theta)$$

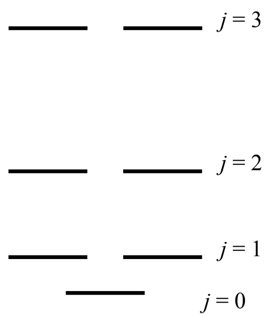
$$\hat{H}\Psi = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\theta^2}\cos(j\theta)$$
$$= \frac{\hbar^2 j^2}{2mr^2}\cos(j\theta) = \varepsilon_j \Psi \qquad j = 0, 1, 2, 3\ldots.$$

"The particle on a ring"

$$\varepsilon_j = \frac{\hbar^2 j^2}{2mr^2} = \frac{2\pi^2\hbar^2 j^2}{mL^2} \qquad j = 0, 1, 2, 3\ldots$$

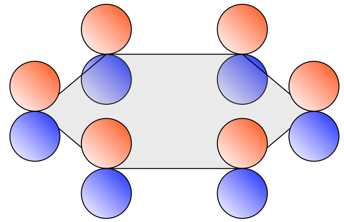
radius of ring

length of circumference



Application: benzene

Question: how many π-electrons in benzene?

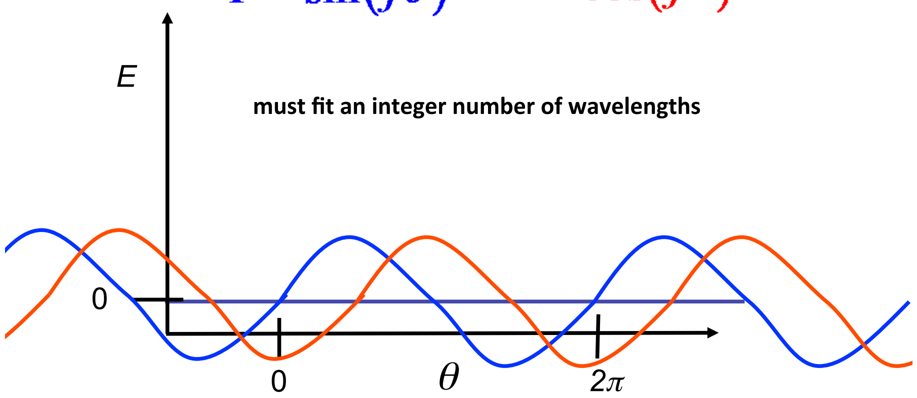


Answer: Looking at the structure, there are 6 carbon atoms which each contribute one electron each. Therefore, there are 6 electrons.

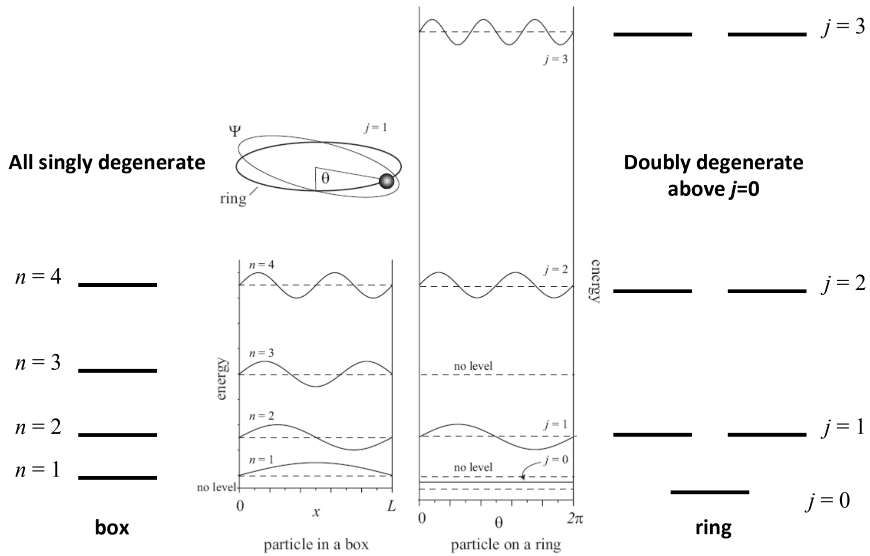
"The particle on a ring"

- *The ring is a cyclic 1d potential*

$$\Psi = \sin(j\theta) \qquad \Psi = \cos(j\theta)$$



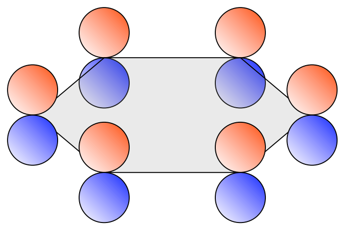
"The particle on a ring"



benzene

Question: what is the length over which the π-electrons are delocalized, if the average bond length is 1.40 Å?

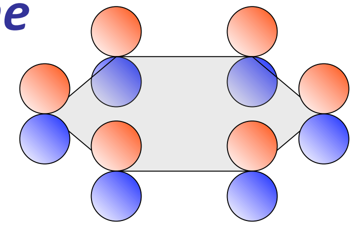
Answer: There are six bonds, which equates to 6 × 1.40 Å = 8.40 Å

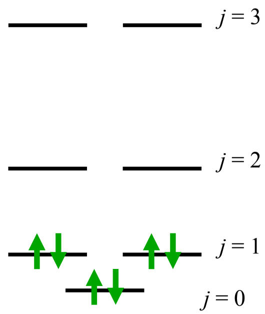


benzene

Question: if the energy levels of the electrons are given by $\varepsilon_n = 2\hbar^2 j^2\pi^2/mL^2$, what is the energy of the HOMO in eV?

Answer: since there are 6 π-electrons, and therefore the HOMO must have j=1. We know that L = 6 × 1.40 Å = 8.4 0Å. From these numbers, we get $\varepsilon_j = 3.41\times10^{-19} j^2$ in Joules. The energy of the HOMO is thus $\varepsilon_1 = 3.41\times10^{-19}$J = 2.13 eV.

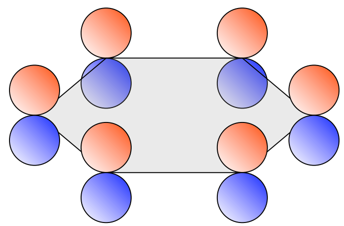


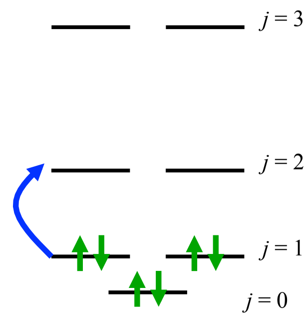


benzene

Question: what is the energy of the LUMO, and thus the HOMO-LUMO transition?

Answer: $\varepsilon_j = 3.41\times10^{-19} j^2$ in Joules. The energy of the LUMO is thus $\varepsilon_2 = 1.365\times10^{-18}$J = 8.52 eV. The energy of the HOMO-LUMO transition is thus 6.39 eV.



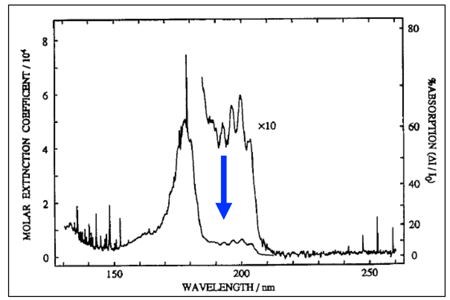


benzene

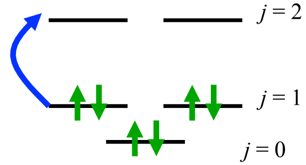
Question: how does the calculated value of the HOMO-LUMO transition compare to experiment?

Answer: The calculated energy of the HOMO-LUMO transition is 6.39 eV. This corresponds to photons of wavelength

$\lambda = hc/(6.39\times 1.602\times10^{-19}) \sim 194$ nm, which is not so far from the experimental value (around 200 nm).



Hiraya and Shobatake, J. Chem. Phys. 94, 7700 (1991)



Next lecture

- Quantitative molecular orbital theory for beginners

Week 10 tutorials

- Schrödinger equation and molecular orbitals for diatomic molecules

Learning Outcomes

- Be able to explain why confining a particle on a ring leads to quantization of its energy levels
- Be able to explain why the lowest energy of the particle on a ring is zero
- Be able to apply the particle on a ring approximation as a model for the electronic structure of a cyclic conjugated molecule (given equation for E_n).

Practice Questions

1. The particle on a ring has an infinite number of energy levels (since j = 0, 1,2, 3, 4, 5 …) whereas for a ring C_nH_n has only n p-orbitals and so n energy levels.

   C_6H_6, for example, only has levels with j = 3 (one level), j = 1 (two levels), j = 2 (two levels) and j = 3 (one level)

   (a) Using the analogy between the particle on a ring waves and the π-orbitals on slide 17, draw the four π molecular orbitals for C_4H_4 and the six π molecular orbitals for C_6H_6

   (b) Using *qualitative* arguments (based on the number of nodes and/or the number of in-phase or out-of-phase interactions between neighbours) construct energy level diagrams and label the orbitals as bonding, non-bonding or antibonding

   (c) Based on your answer to (b), why is C_6H_6 aromatic and C_4H_4 antiaromatic?