Chemistry 2

Lecture 2

Particle in a box approximation

THE UNIVERSITY OF SYDNEY

Learning outcomes from Lecture 1

- Use the principle that the mixing between orbitals depends on the energy difference, and the resonance integral, β.
- Apply the separation of σ and π bonding to describe electronic structure in simple organic molecules.
- Rationalize differences in orbital energy levels of diatomic molecules in terms of s-p mixing.

Assumed knowledge for today

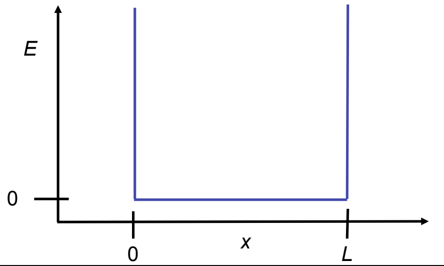
Be able to predict the geometry of a hydrocarbon from its structure and account for each valence electron. Predict the hybridization of atomic orbitals on carbon atoms.

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:
  $E = \frac{1}{2} mv^2 = p^2 / 2m = h^2 / 2m\lambda^2$
- For a free particle, λ, can have any value:
  E for a free particle is *not* quantized

"The particle in a box"

- *The box is a 1d well, with sides of infinite potential, where the particle cannot be…*



see worksheet

"The particle in a box"

- Energy is quantized:
  $E_n = h^2n^2 / 8mL^2$
- Lowest energy (*zero point*) is not zero:
  $E_{n=1} = h^2 / 8mL^2$
- Allowed levels are separated by:
  $\Delta E = E_{n+1} - E_n = h^2(2n+1) / 8mL^2$

The Schrödinger Equation Approach

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

Energy eigenfunction

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

Hamiltonian operator

Energy eigenvalue

The Schrödinger equation

- The Hamiltonian has parts corresponding to *Kinetic Energy* and *Potential Energy. In one dimension, x:*

ħ = *h* / 2π (“*h* bar”)

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

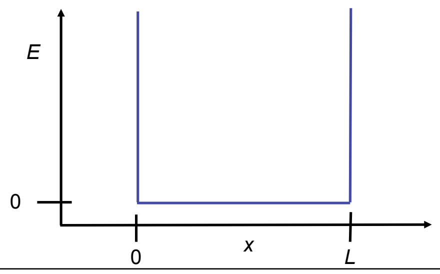
Hamiltonian operator

Kinetic Energy

Potential Energy

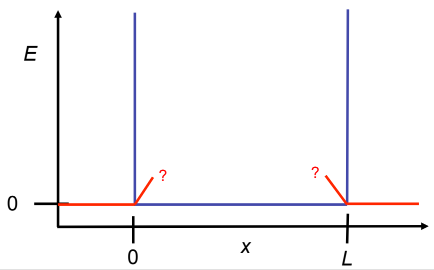
“The particle in a box”

- *The box is a 1d well, with sides of infinite potential, where the electron cannot be…*



“The particle in a box”

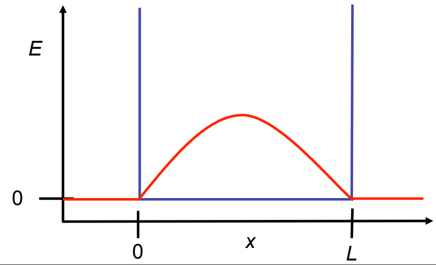
- *The particle cannot exist outside the box… $\Psi = 0$ {x<0;x>L} (boundary conditions)*



"The particle in a box"

- *Let's try some test solutions*

  Ψ = sin(πx/L) {x>0;x<L



"The particle in a box"

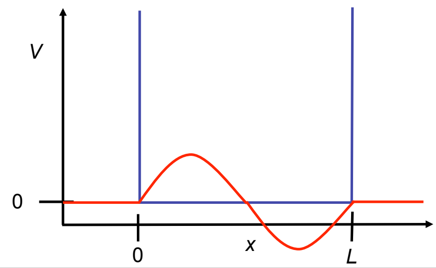
$$
\begin{aligned}
\hat{H}\Psi &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V(x)\Psi \\
&= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\Psi\right) + 0\Psi \\
&= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\sin(\pi x/L)\right) \\
&= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}(\pi/L\cos(\pi x/L)) \\
&= -\frac{\hbar^2}{2m}\left(-\pi^2/L^2\sin(\pi x/L)\right) \\
&= \frac{\hbar^2\pi^2}{2mL^2}\sin(\pi x/L) = \frac{\hbar^2\pi^2}{2mL^2}\Psi \;\mathbf{=\varepsilon\Psi\ !!!}
\end{aligned}
$$

Zero potential inside box

"The particle in a box"

- *Other solutions?*

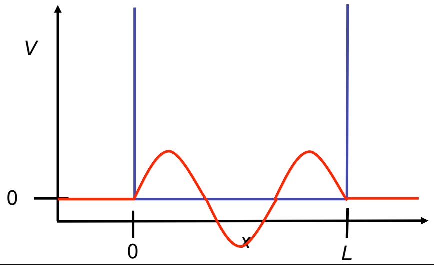
  Ψ = sin(2πx/L) {x>0;x<L



"The particle in a box"

- *Other solutions?*

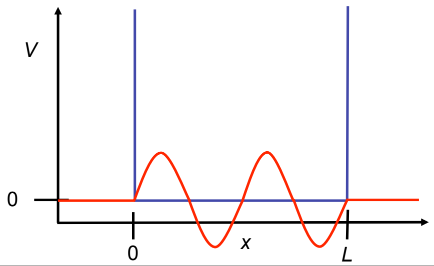
  $\Psi = \sin(3\pi x/L)$ {x>0;x<L



"The particle in a box"

- *Other solutions?*

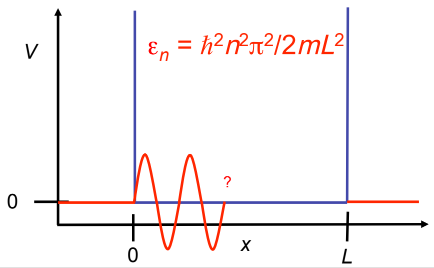
  $\Psi = \sin(4\pi x/L)$ {x>0;x<L



"The particle in a box"

- *Other solutions?*

  $\Psi = \sin(n\pi x/L)$ {x>0;x<L



"The particle in a box"

$\Psi = \sin(n\pi x/L)\ \{x>0; x<L; n>0\}$

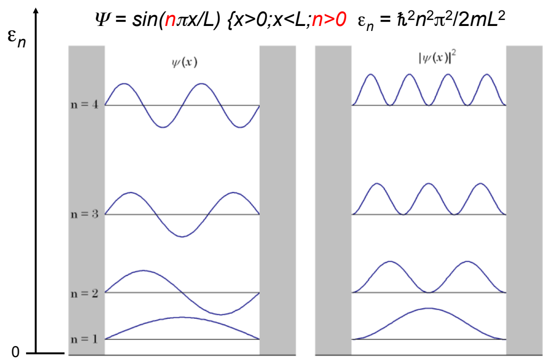
$\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$

Philosophical question: why is $n = 0$ not an appropriate solution?

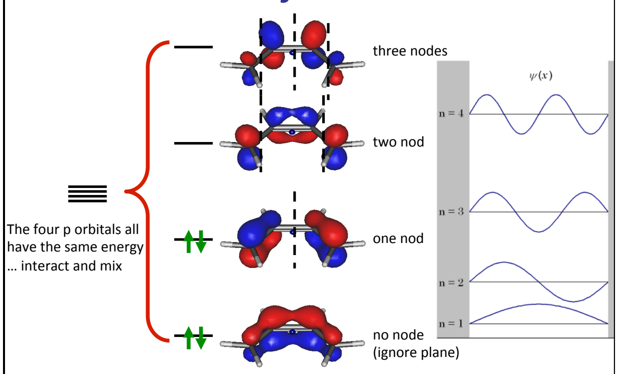
Hint: what's the probability of observing the particle?

"The particle in a box"

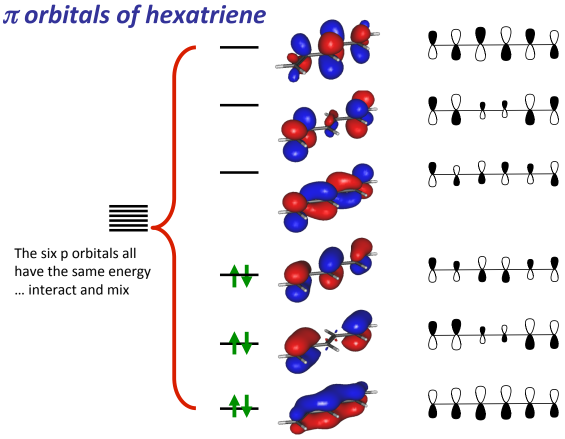
$\Psi = \sin(n\pi x/L)\ \{x>0; x<L; n>0\}$ $\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$



π orbitals of cis-butadiene

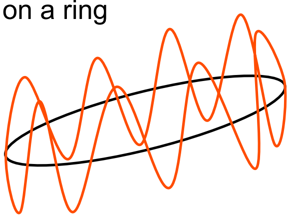


π orbitals of hexatriene



Something to think about

- Particle on a ring



Must fit even wavelengths into whole cycle

Next lecture

- Particle-on-a-ring model

Week 10 tutorials

- Schrödinger equation and molecular orbitals for diatomic molecules

Learning outcomes

- 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).

Practice Questions

1. The energy levels of the particle in a box are given by $\varepsilon_n = \hbar^2 n^2 p^2/2mL^2$.

   (a) Why does the lowest energy correspond to n = 1 rather than n = 0?

   (b) What is the *separation* between two adjacent levels? (*Hint: $\Delta\varepsilon = \varepsilon_{n+1} - \varepsilon_n$*)

   (c) The π chain in a hexatriene derivative has L = 973 pm and has 6 π electrons. What is energy of the HOMO – LUMO gap? (Hint: remember that 2 electrons are allowed in each level.)

   (d) What does the particle in a box model predicts happens to the HOMO – LUMO gap of polyenes as the chain length increases?