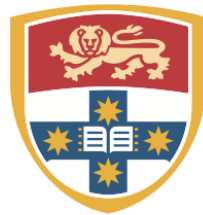


Chemistry 2

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:

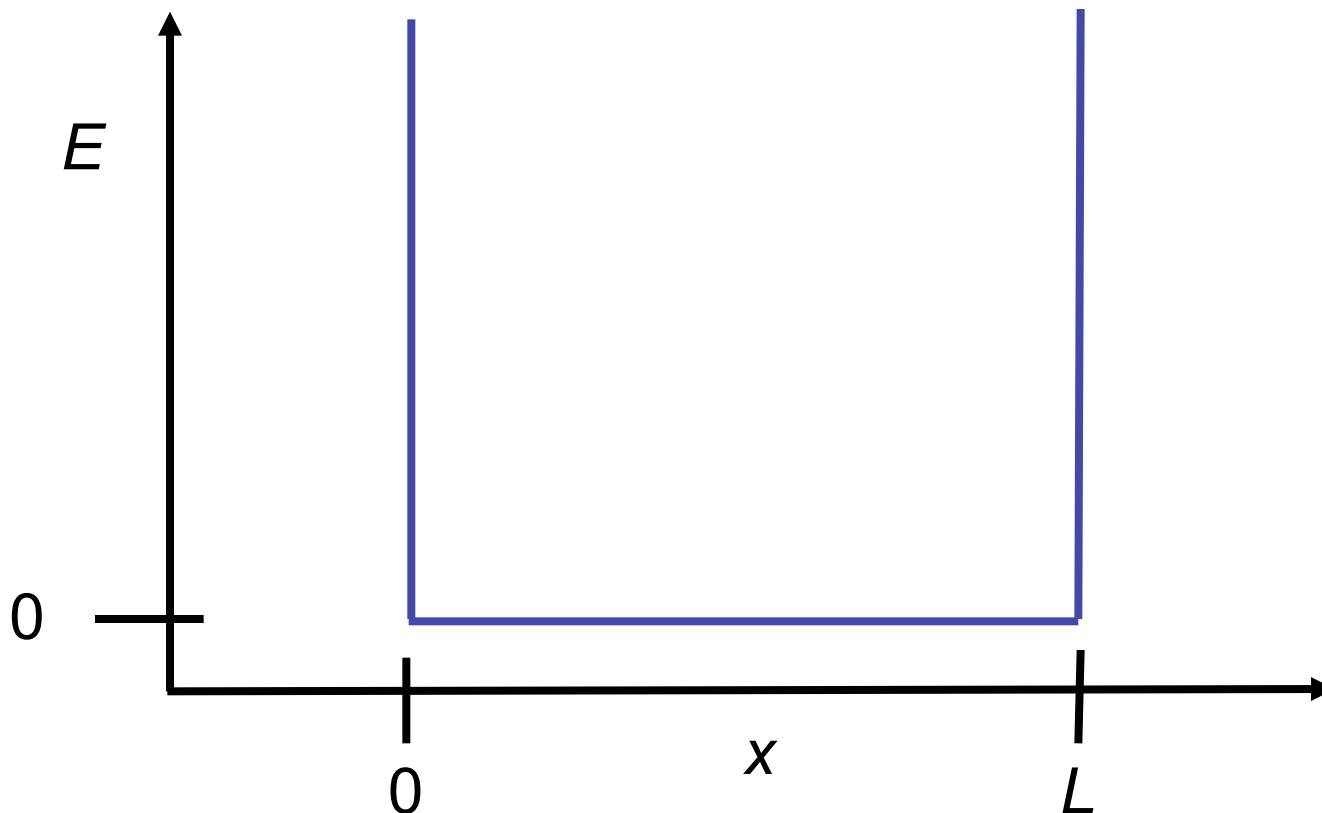
$$E = \frac{1}{2} mv^2 = p^2 / 2m = h^2 / 2m\lambda^2$$

- 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:

$$E_n = h^2 n^2 / 8mL^2$$

- 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

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

Hamiltonian operator

Energy eigenvalue

Energy eigenfunction

The diagram shows the Schrödinger equation $\hat{H}\Psi(x) = \epsilon_i\Psi(x)$ centered on the page. Three red arrows point from text labels to parts of the equation: one from 'Hamiltonian operator' to \hat{H} , one from 'Energy eigenvalue' to ϵ_i , and one from 'Energy eigenfunction' to $\Psi(x)$.

The Schrödinger equation

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

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

$\hbar = h / 2\pi$ ("h bar")

The diagram shows the Schrödinger equation with three red arrows pointing from labels to specific parts of the equation. One arrow points from the label 'Hamiltonian operator' to the $\hat{H}\Psi$ term on the left. Another arrow points from the label 'Kinetic Energy' to the $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ term inside the parentheses. A third arrow points from the label 'Potential Energy' to the $V(x)$ term inside the parentheses. Above the equation, the text ' $\hbar = h / 2\pi$ ("h bar")' is written with an arrow pointing to the \hbar symbol in the kinetic energy term.

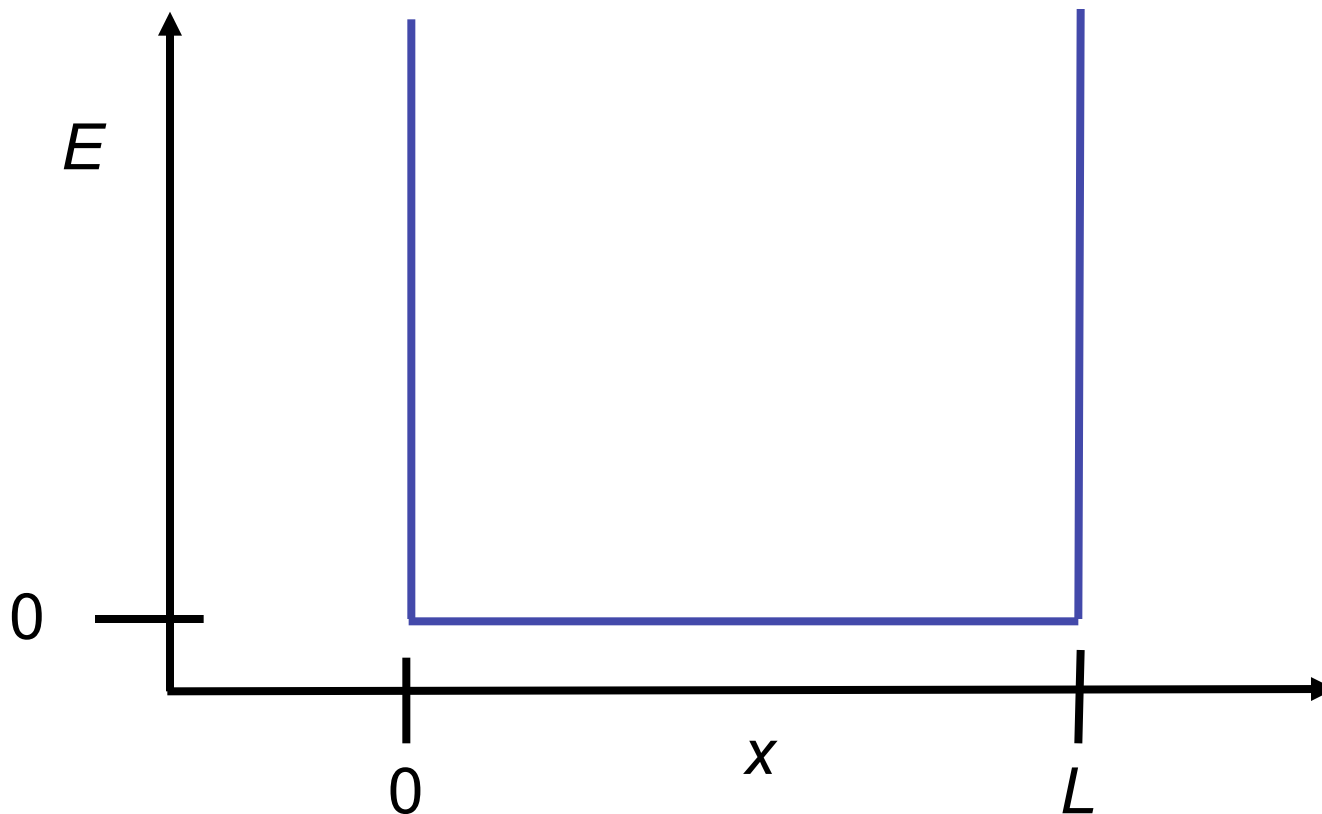
Hamiltonian operator

Kinetic Energy

Potential Energy

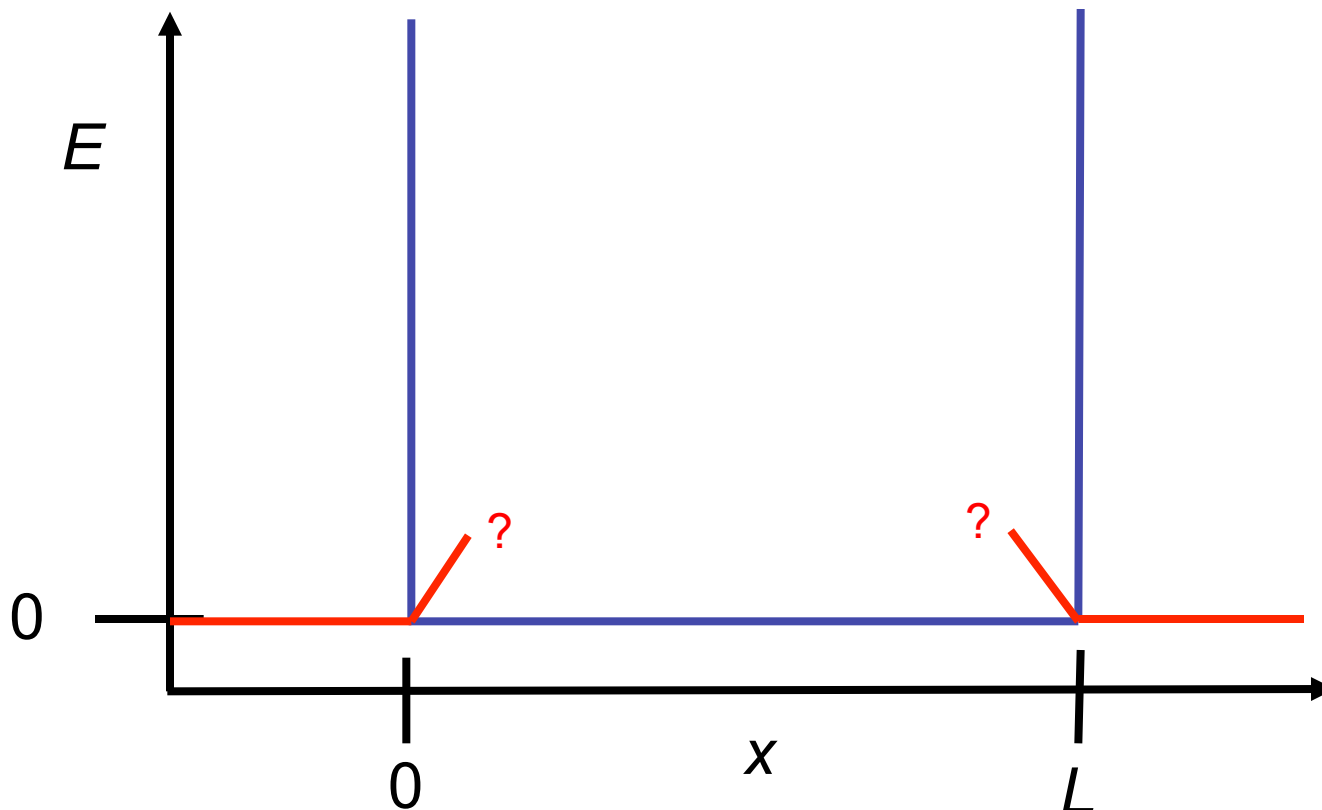
“The particle in a box”

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



“The particle in a box”

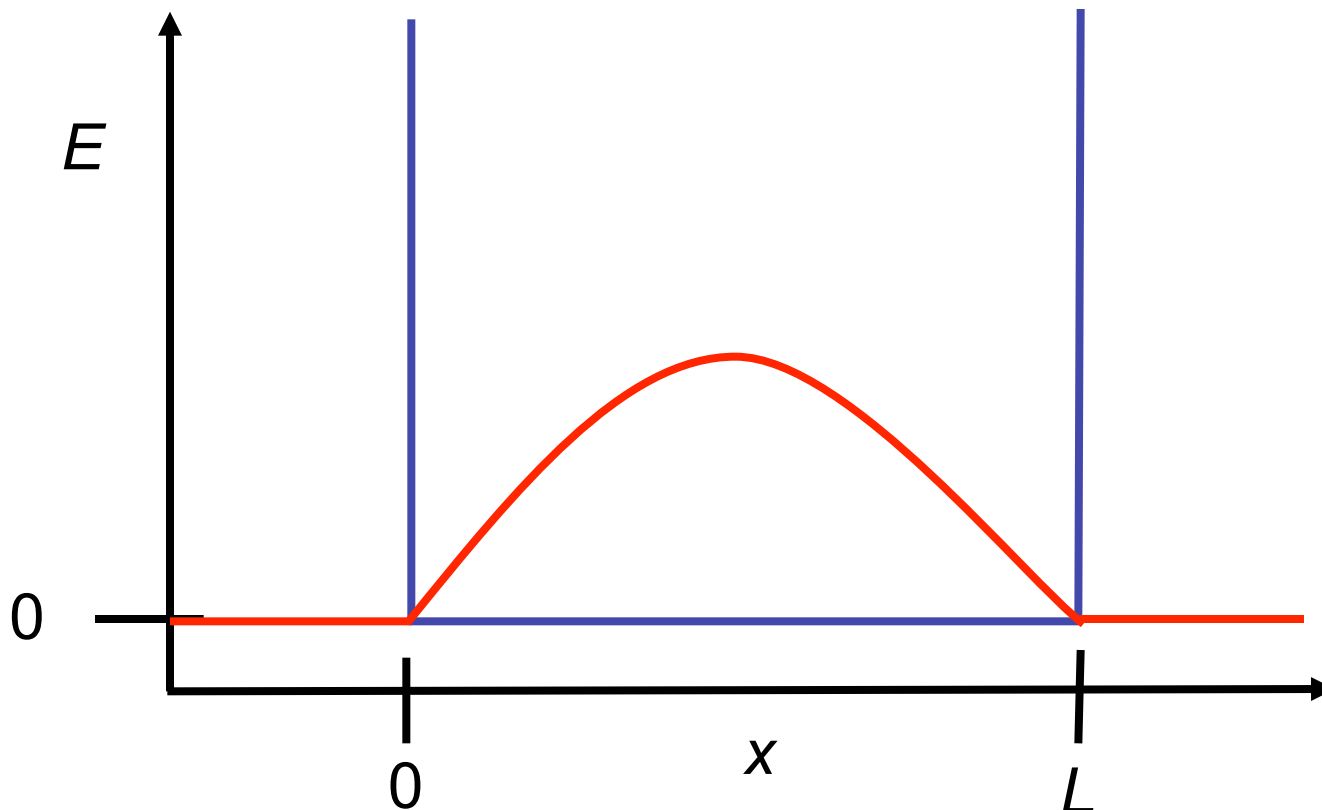
- The particle cannot exist outside the box...
 $\Psi = 0$ $\{x < 0; x > L$ (boundary conditions)*



“The particle in a box”

- *Let's try some test solutions*

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



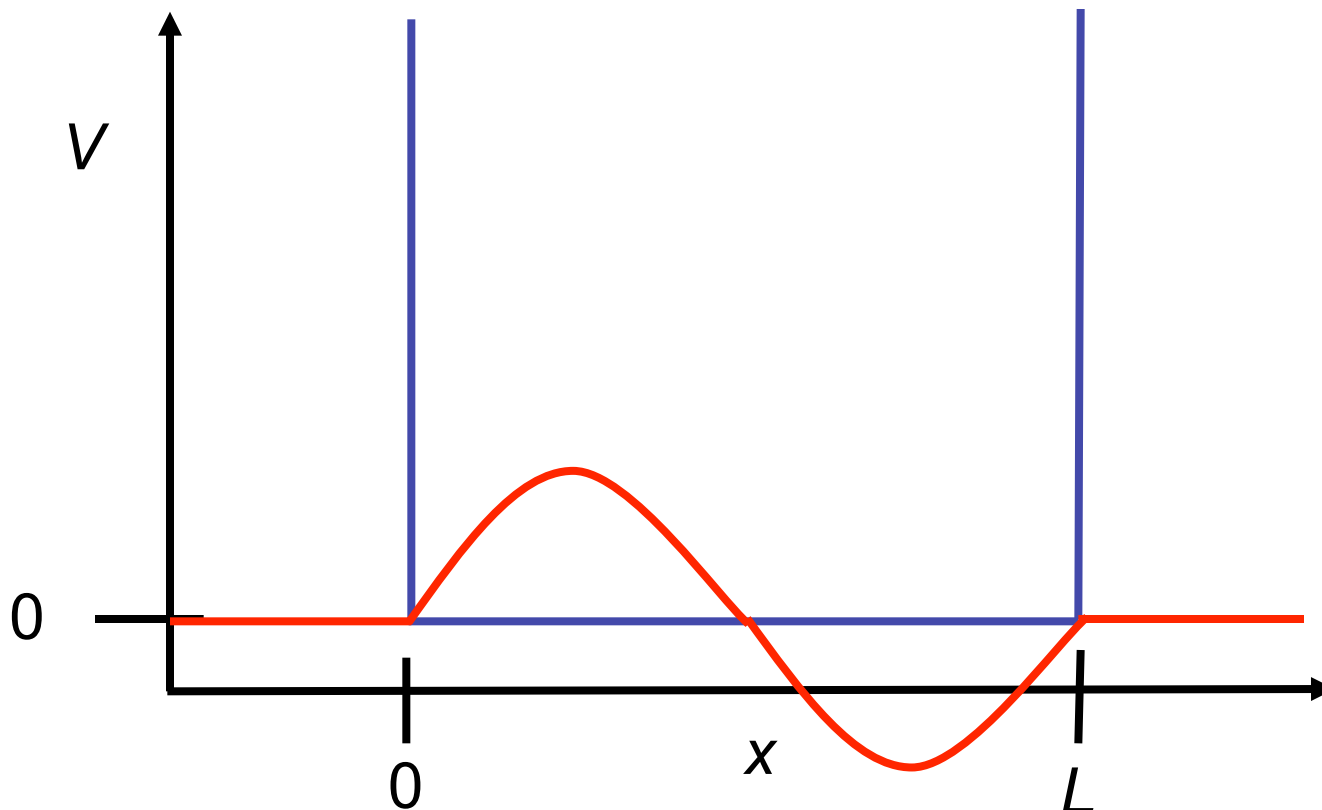
“The particle in a box”

$$\begin{aligned} \hat{H}\Psi &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi + V(x)\Psi && \text{Zero potential inside box} \\ &= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} \Psi \right) + 0\Psi \\ &= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} \sin(\pi x/L) \right) \\ &= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} (\pi/L \cos(\pi x/L)) \\ &= -\frac{\hbar^2}{2m} \left(-\pi^2/L^2 \sin(\pi x/L) \right) \\ &= \frac{\hbar^2 \pi^2}{2mL^2} \sin(\pi x/L) = \frac{\hbar^2 \pi^2}{2mL^2} \Psi = \epsilon \Psi !!! \end{aligned}$$

“The particle in a box”

- *Other solutions?*

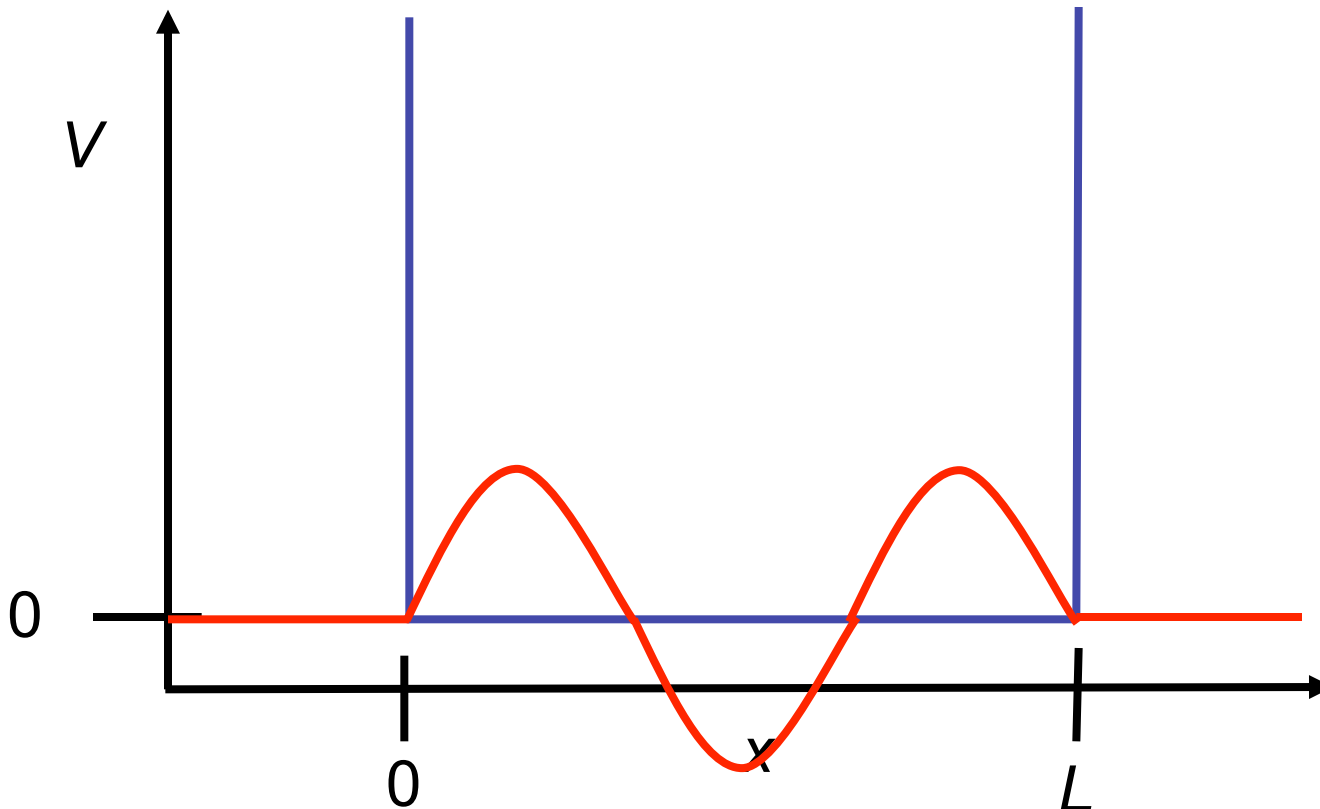
$$\Psi = \sin(2\pi x/L) \quad \{x>0; x<L$$



“The particle in a box”

- *Other solutions?*

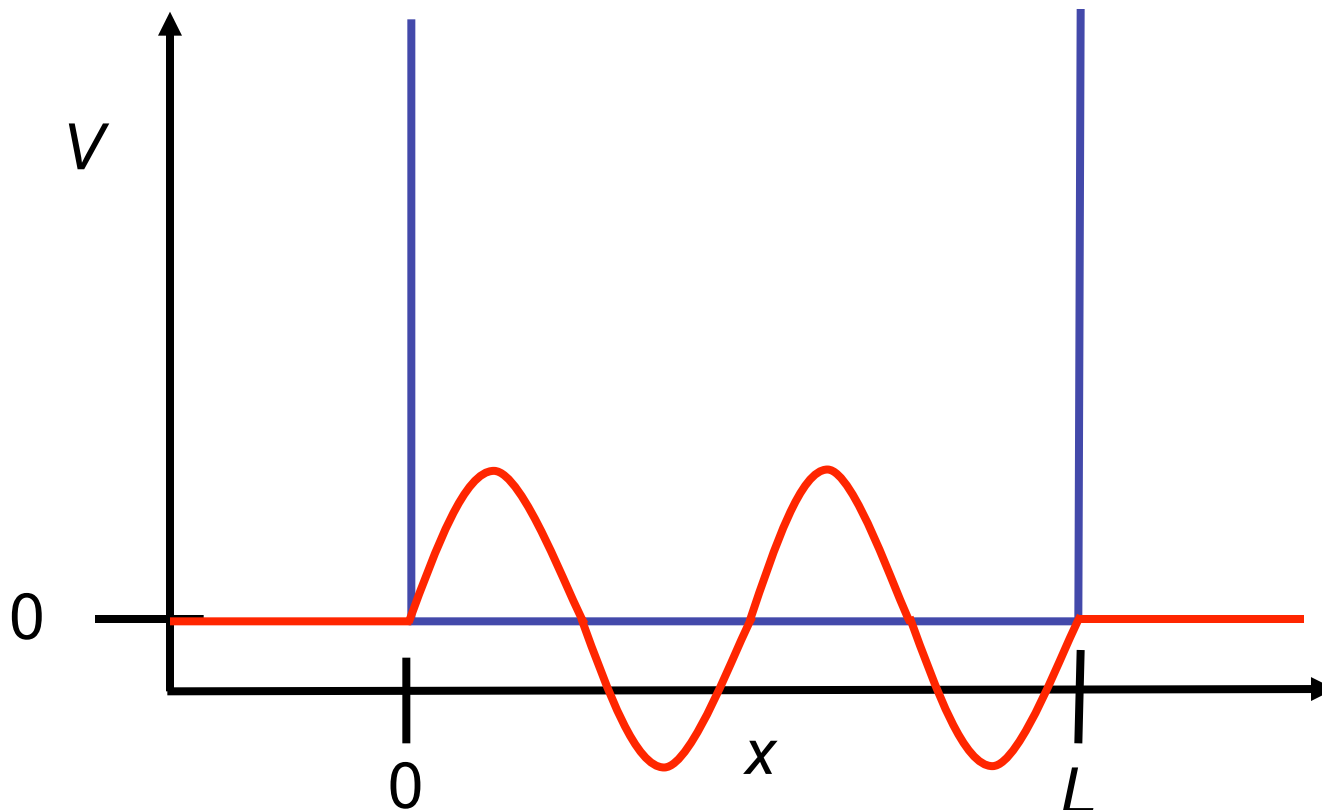
$$\Psi = \sin(3\pi x/L) \quad \{x>0; x<L$$



“The particle in a box”

- *Other solutions?*

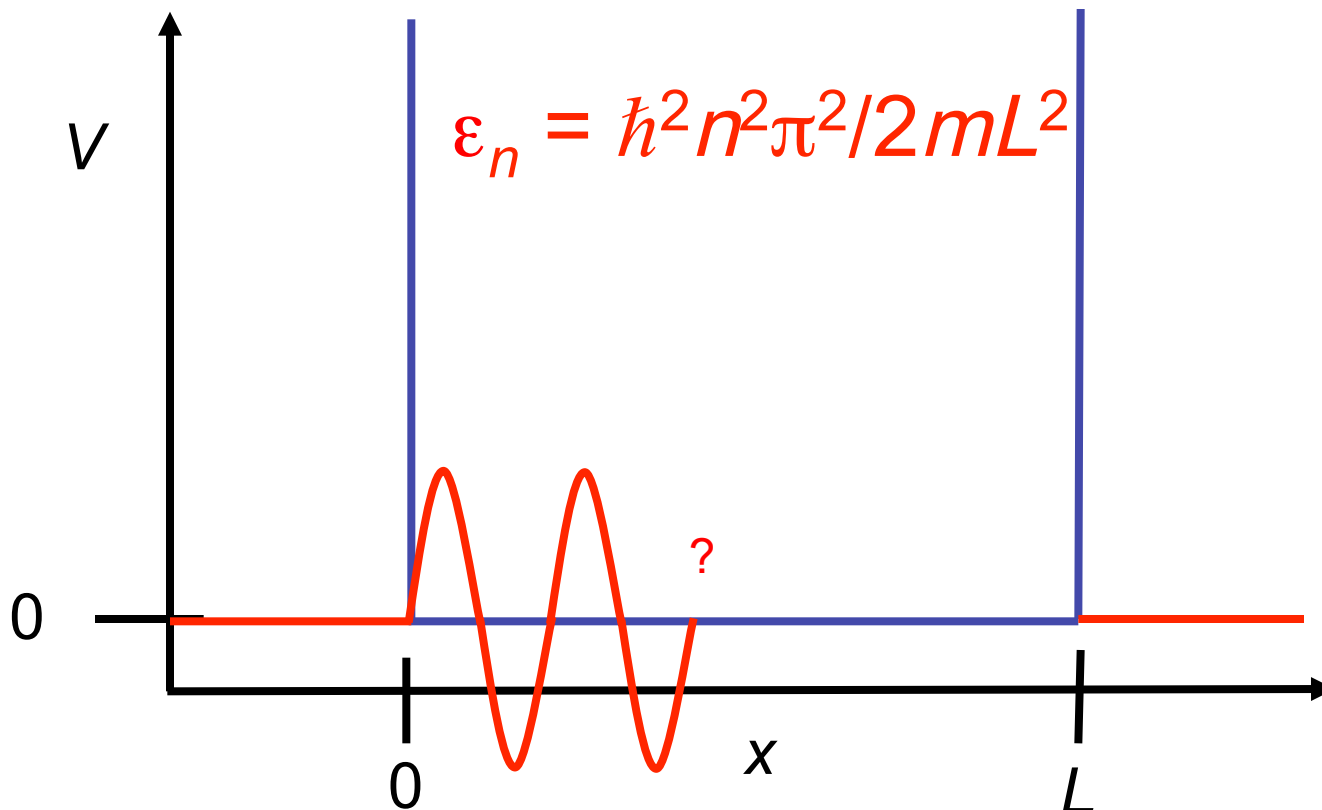
$$\Psi = \sin(4\pi x/L) \quad \{x>0; x<L\}$$



“The particle in a box”

- *Other solutions?*

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



“The particle in a box”

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

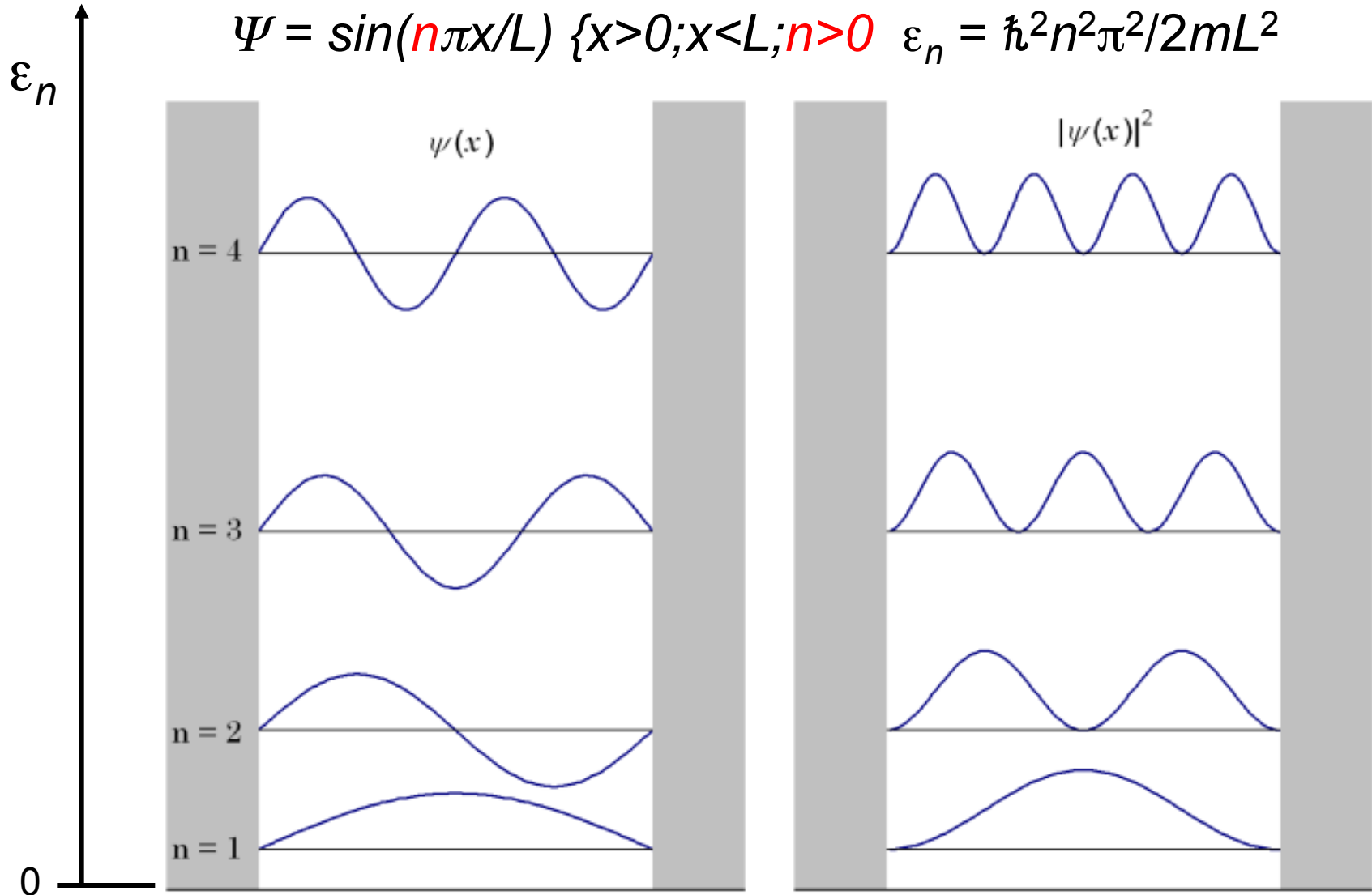
$$\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$$

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

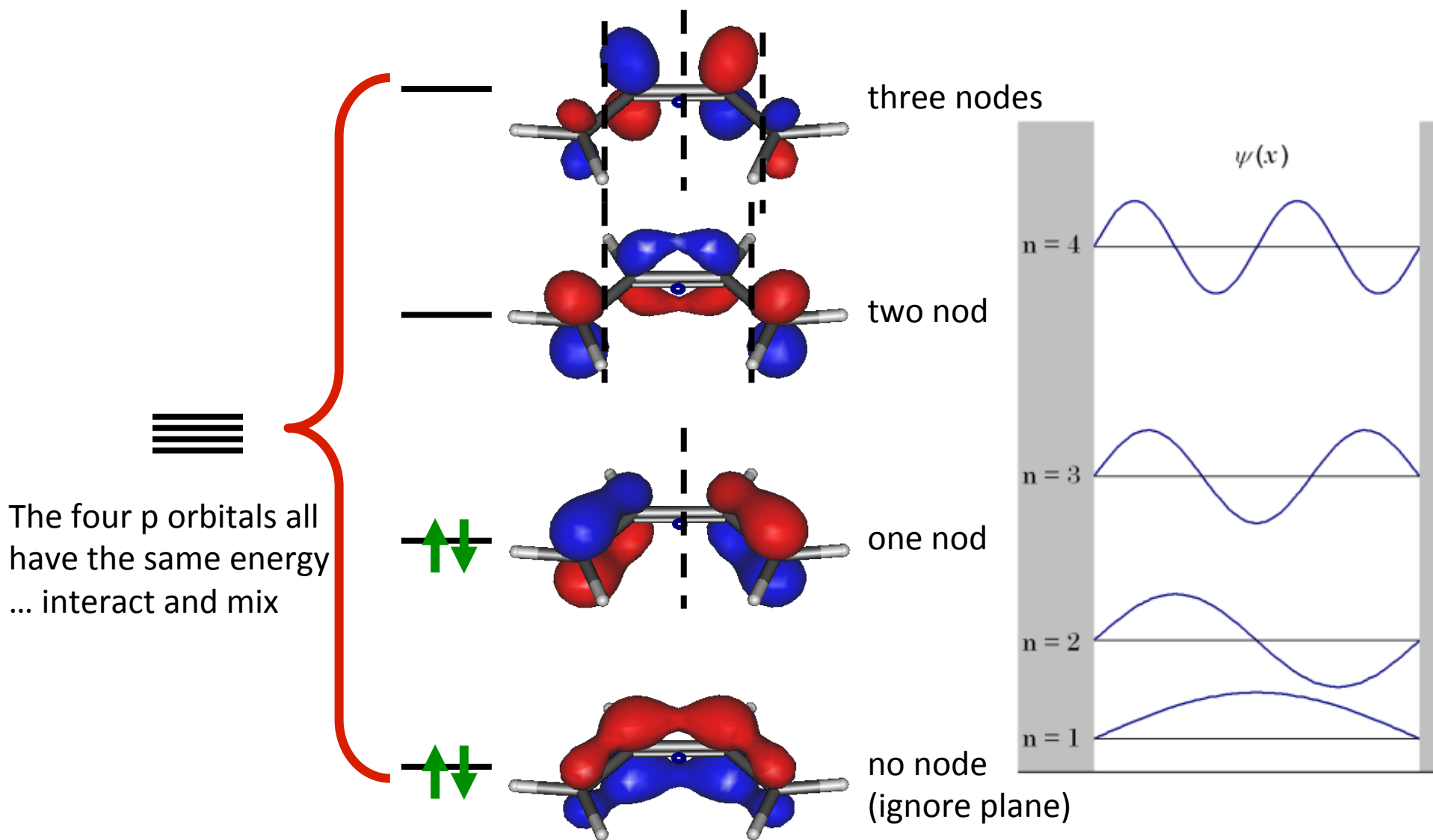
Hint: what's the probability of observing the particle?

“The particle in a box”

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

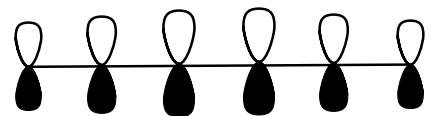
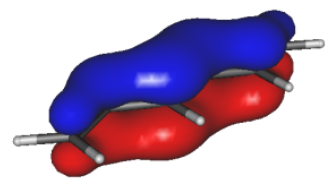
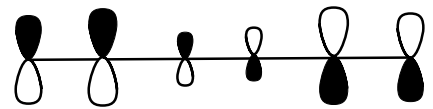
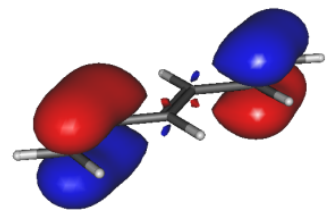
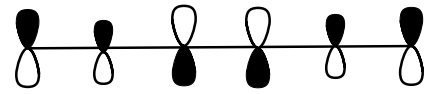
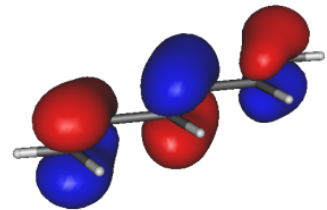
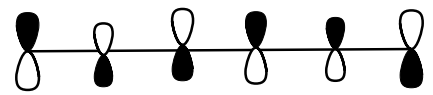
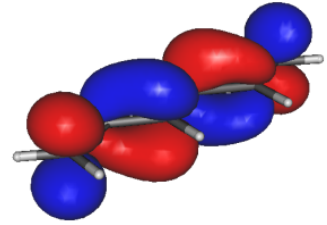
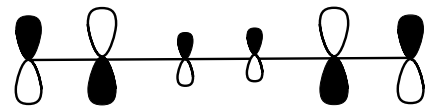
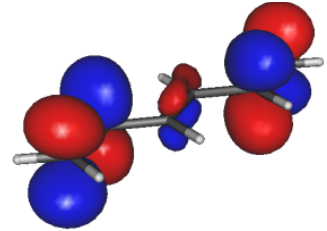
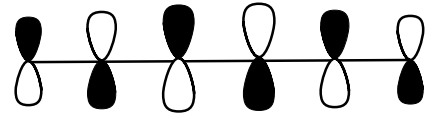
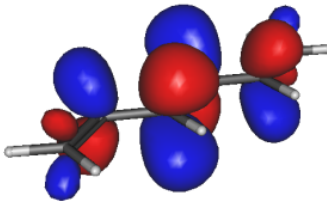
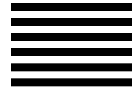


π orbitals of cis-butadiene



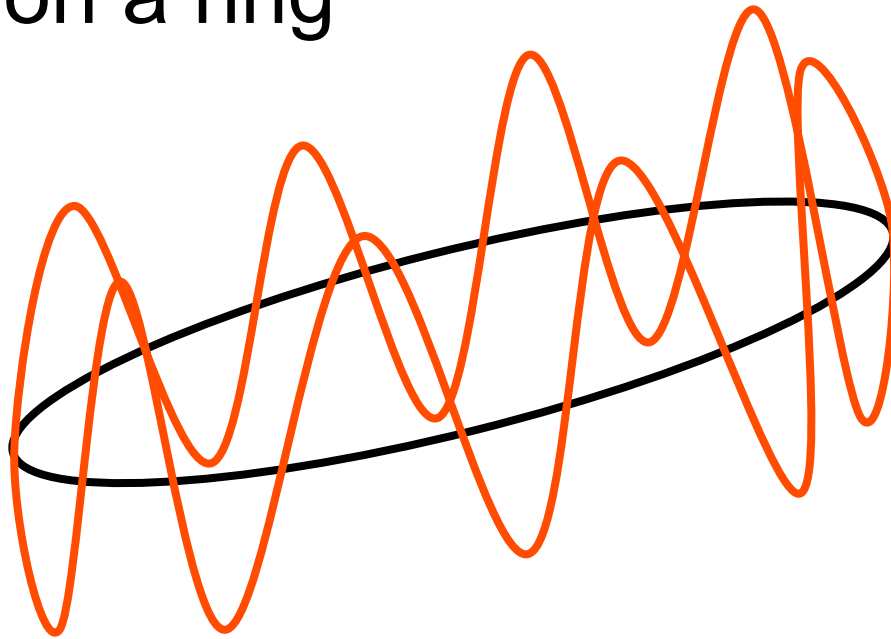
π orbitals of hexatriene

The six p orbitals all have the same energy ... interact and mix



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?