

Lecture 2

Application of Quantum mechanics

I- Translation motion

Particle-in-Box (PIB) Models

Quantum Mechanical Particle-in-Box

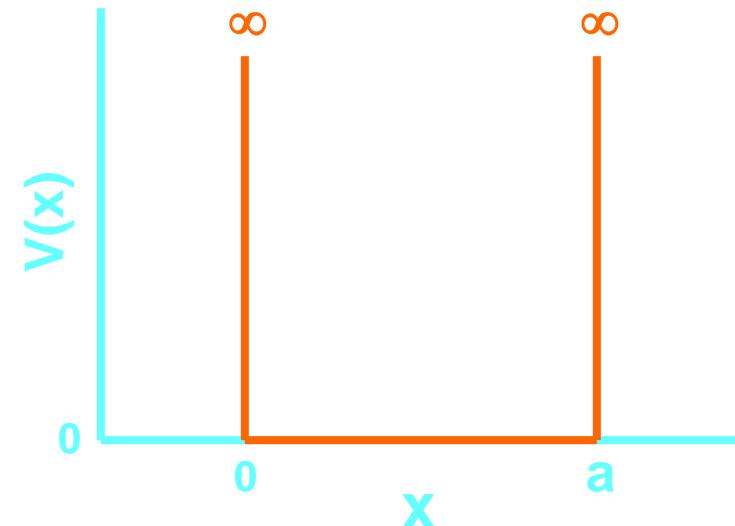
Schrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

Outside the box: $x < 0, x > a$

$$P(x) = \psi^*(x)\psi(x) = 0$$

$$\psi(x) = 0$$



$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) \rightarrow \infty \quad x < 0, x > a$$

Inside the box: $0 \leq x \leq a$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \text{or}$$

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

Solving the Equation

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

$$-\alpha^2\psi = -\frac{2mE}{\hbar^2}\psi$$

$$E = \frac{\alpha^2\hbar^2}{2m}$$

Assume

$$\psi = A\sin(\alpha x) + B\cos(\alpha x)$$

$$\frac{d\psi}{dx} = \alpha A\cos(\alpha x) - \alpha B\sin(\alpha x)$$

$$\frac{d^2\psi}{dx^2} = -\alpha^2 A\sin(\alpha x) - \alpha^2 B\cos(\alpha x)$$

$$\frac{d^2\psi}{dx^2} = -\alpha^2\psi$$

So far, there is no restriction on α and, hence none on the energy, E (other than that it cannot be negative)

Applying Boundary Conditions (BC's)

Because the wavefunction, ψ , is 0 outside the box, $x < 0$ and $x > a$, it must also be 0 inside the box at $x=0$ and $x=a$

$$\psi = A\sin(\alpha x) + B\cos(\alpha x)$$

BC-1: $\psi(0) = 0 = A\sin(0) + B\cos(0) = B$

Therefore, $\psi(x) = A\sin(\alpha x)$

BC-2: $\psi(a) = 0 = A\sin(\alpha a)$ $\sin(n\pi) = 0$

Therefore: $\alpha a = n\pi$ $n = 1, 2, 3, \dots$

or: $\alpha = \frac{n\pi}{a}$ $n = 1, 2, 3, \dots$

Why isn't $n = 0$ acceptable?

Wavefunctions and Energy Levels

$$\alpha = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots$$

$$\psi_n = A \sin(\alpha x) = A \sin\left(\frac{n\pi}{a} x\right) \quad n = 1, 2, 3, \dots$$

$$E = \frac{\alpha^2 \hbar^2}{2m} = \left(\frac{n\pi}{a}\right)^2 \frac{1}{2m} \left(\frac{\hbar}{2\pi}\right)^2 = \frac{n^2 \pi^2}{a^2} \cdot \frac{1}{2m} \cdot \frac{\hbar^2}{4\pi^2}$$

$$E_n = \frac{n^2 \hbar^2}{8ma^2}$$

$$n = 1, 2, 3, \dots$$

Note that

- (a) the allowed energies are quantized
- (b) $E = 0$ is **NOT** permissible (i.e. the particle can't stand still)

Energy Quantization results from application of the Boundary Conditions

$$E_n = \frac{n^2 h^2}{8ma^2}$$

$$E_1 = 1 \frac{h^2}{8ma^2}$$

$$E_2 = 4 \frac{h^2}{8ma^2}$$

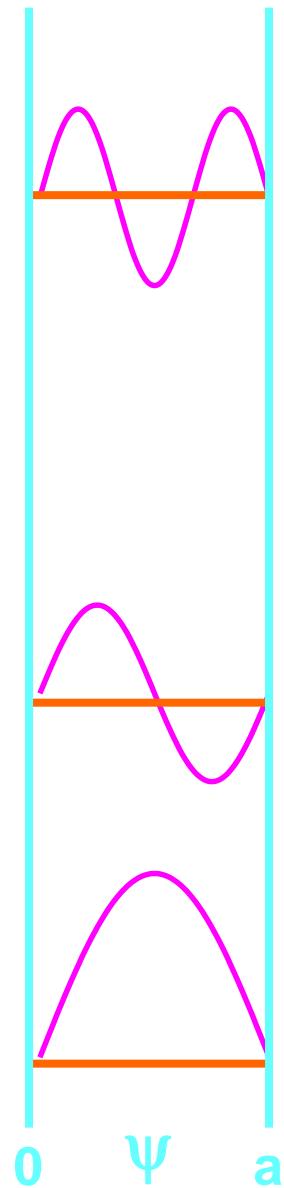
$$E_3 = 9 \frac{h^2}{8ma^2}$$

$$E_4 = 16 \frac{h^2}{8ma^2}$$

$$E_5 = 25 \frac{h^2}{8ma^2}$$

Wavefunctions

$$\psi_3 = A \cdot \sin\left(\frac{3\pi x}{a}\right)$$



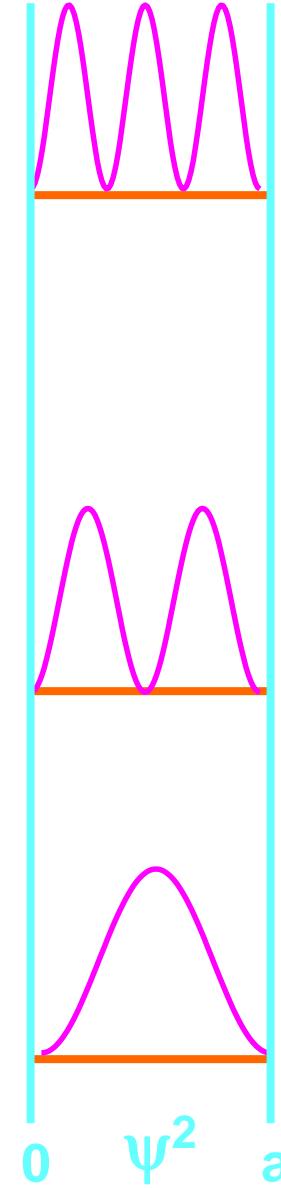
$$E_3 = \frac{9\hbar^2}{8ma^2}$$

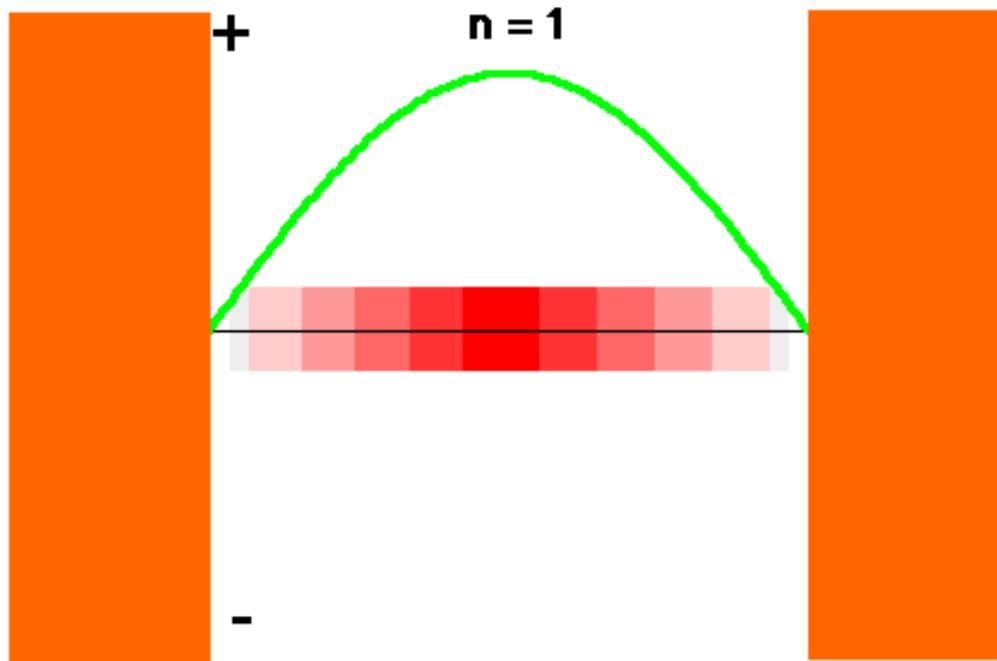
$$\psi_2 = A \cdot \sin\left(\frac{2\pi x}{a}\right)$$

$$E_2 = \frac{4\hbar^2}{8ma^2}$$

$$\psi_1 = A \cdot \sin\left(\frac{\pi x}{a}\right)$$

$$E_1 = \frac{1\hbar^2}{8ma^2}$$





Note that: The number of “nodes” increases with increasing quantum number.

The increasing number of nodes reflects the higher kinetic energy with higher quantum number.

Some Useful Integrals

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)}$$

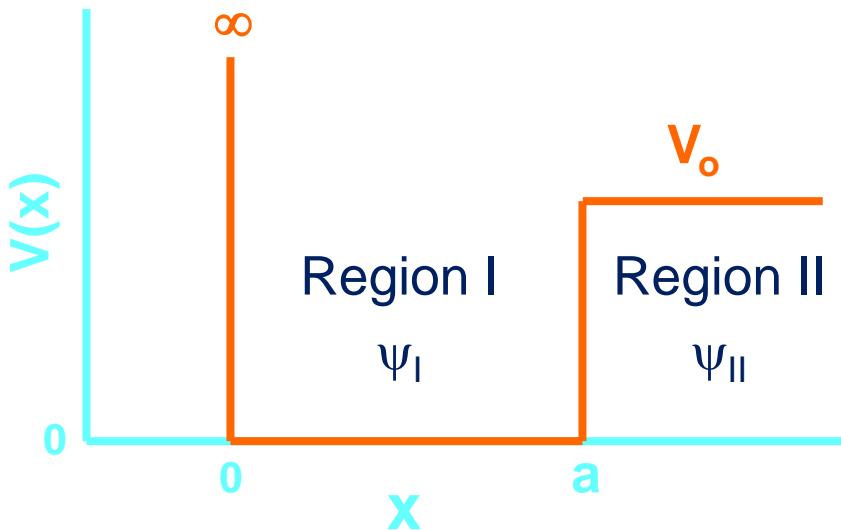
$$\int \sin(\alpha x) \cos(\alpha x) dx = \frac{1}{2\alpha} \sin^2(\alpha x)$$

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

Other PIB Models

1. PIB with one non-infinite wall



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

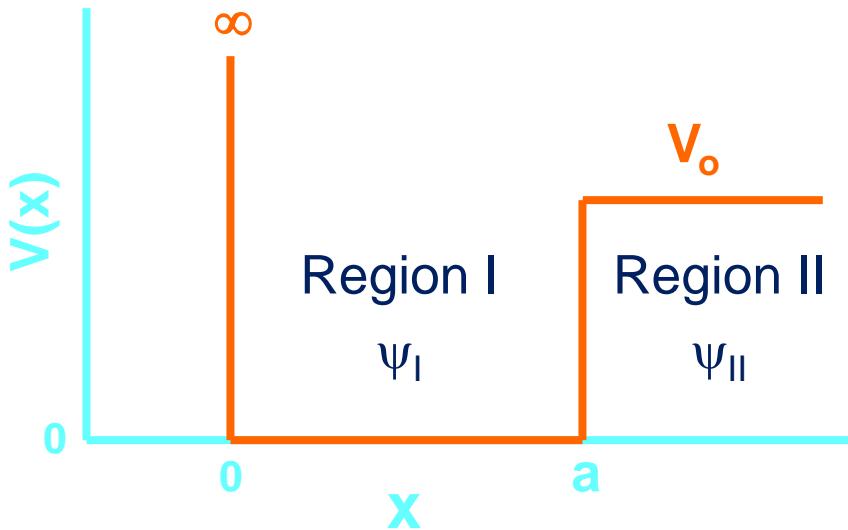
$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Boundary Conditions

The wavefunction must satisfy two conditions at the boundaries ($x=0$, $x=a$, $x \rightarrow \infty$)

- 1) ψ must be continuous at all boundaries.
- 2) $d\psi/dx$ must be continuous at the boundaries **unless** $V \rightarrow \infty$ at the boundary.



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Region I

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} + 0 = E\psi_I$$

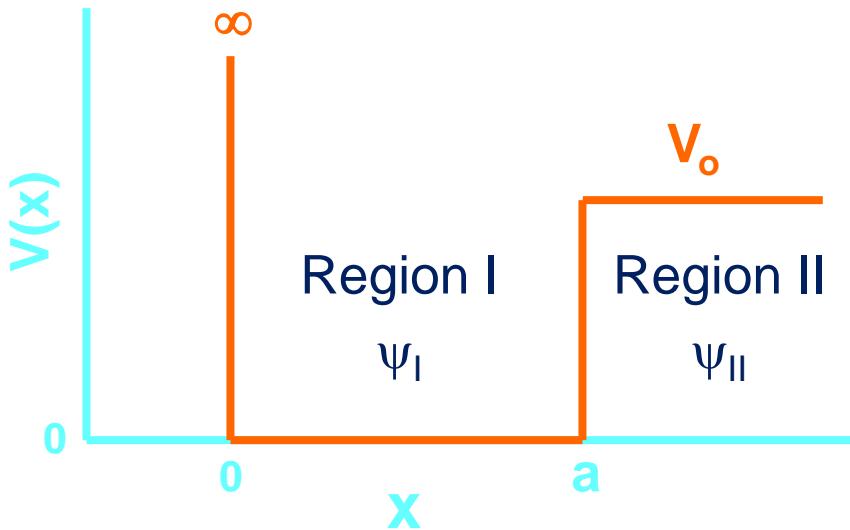
$$\frac{d\psi_I}{dx} = A\alpha \cos(\alpha x) - B\alpha \sin(\alpha x)$$

$$\frac{d^2\psi_I}{dx^2} = -A\alpha^2 \sin(\alpha x) - B\alpha^2 \cos(\alpha x)$$

$$\frac{d^2\psi_I}{dx^2} = -\alpha^2 \psi_I$$

$$\psi_I = A\sin(\alpha x) + B\cos(\alpha x)$$

can
assume



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Region I

Relation between α and E

$$\frac{d^2\psi_I}{dx^2} = -\frac{2mE}{\hbar^2}\psi_I$$



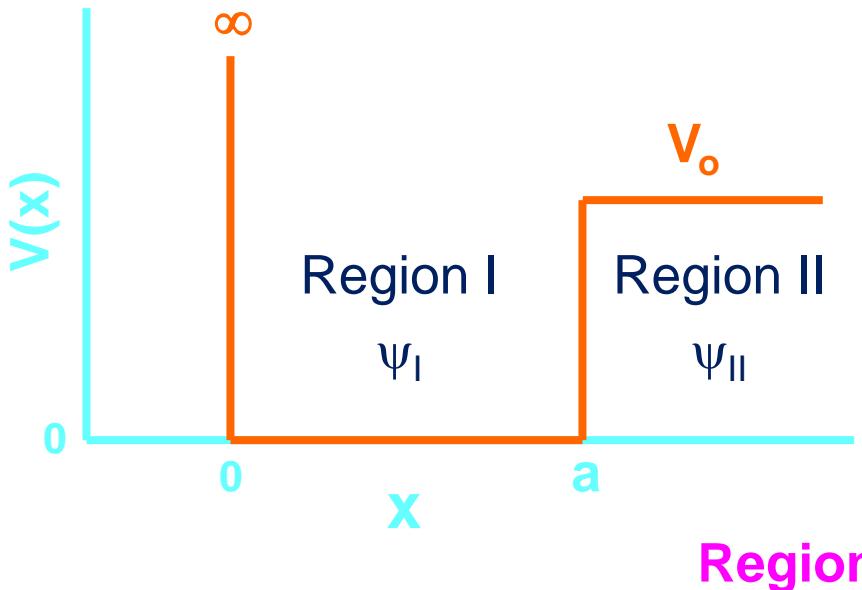
$$-\alpha^2\psi_I = -\frac{2mE}{\hbar^2}\psi_I$$

$$\psi_I = A\sin(\alpha x) + B\cos(\alpha x)$$

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} = -\alpha^2\psi_I$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}}$$



$$-\frac{\hbar^2}{2m} \frac{d^2\psi_{II}}{dx^2} + V_0\psi_{II} = E\psi_{II}$$

$$\frac{d^2\psi_{II}}{dx^2} = -\frac{2m}{\hbar^2}(E - V_0)\psi_{II}$$

$$\frac{d^2\psi_{II}}{dx^2} = +\frac{2m}{\hbar^2}(V_0 - E)\psi_{II} = +\text{const} \cdot \psi_{II}$$

↓
can
assume

$$\psi_{II} = Ce^{\beta x} + De^{-\beta x}$$

$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

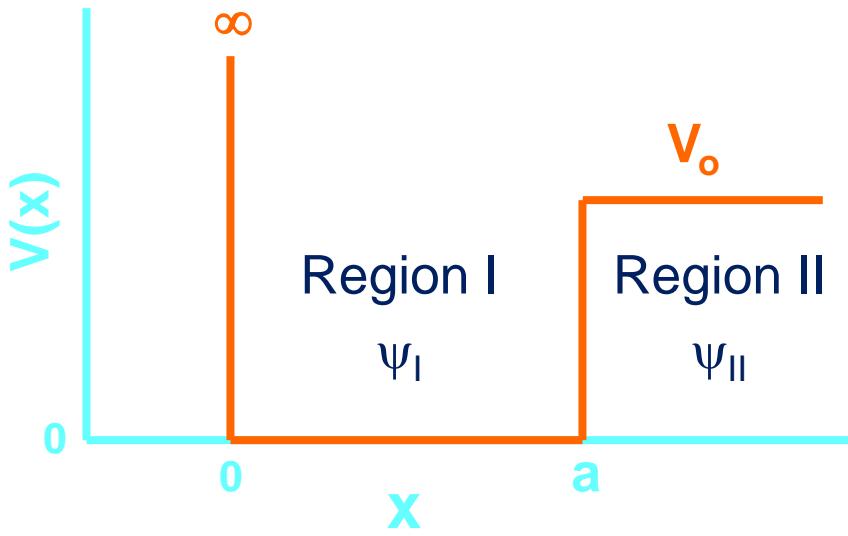
$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

$$\frac{d\psi_{II}}{dx} = C\beta e^{\beta x} - D\beta e^{-\beta x}$$

$$\frac{d^2\psi_{II}}{dx^2} = C\beta^2 e^{\beta x} + D\beta^2 e^{-\beta x}$$

$$\frac{d^2\psi_{II}}{dx^2} = \beta^2 \psi_{II}$$



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Region II

Relation between β and E

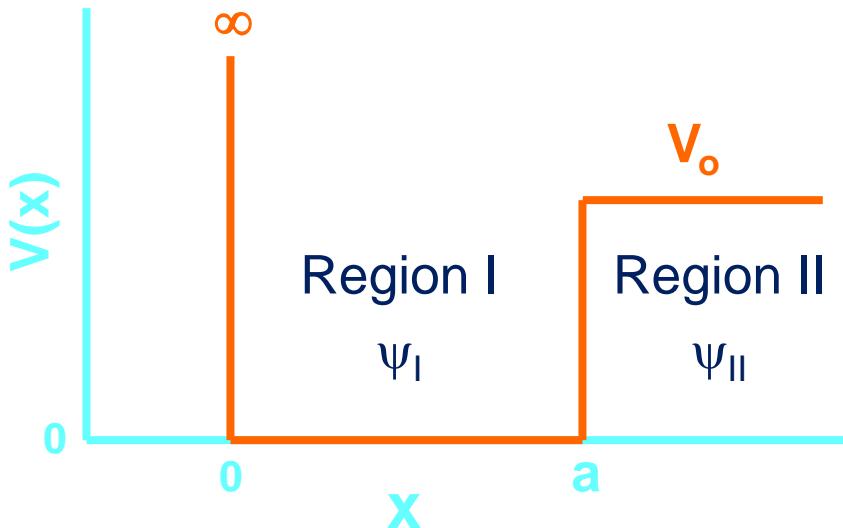
$$\frac{d^2\psi_{II}}{dx^2} = +\frac{2m}{\hbar^2}(V_0 - E)\psi_{II} \longrightarrow \beta^2\psi_{II} = +\frac{2m}{\hbar^2}(V_0 - E)\psi_{II}$$

$$\psi_{II} = Ce^{\beta x} + De^{-\beta x}$$

$$\beta^2 = +\frac{2m}{\hbar^2}(V_0 - E)$$

$$\frac{d^2\psi_{II}}{dx^2} = \beta^2\psi_{II}$$

$$\boxed{\beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}}$$



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

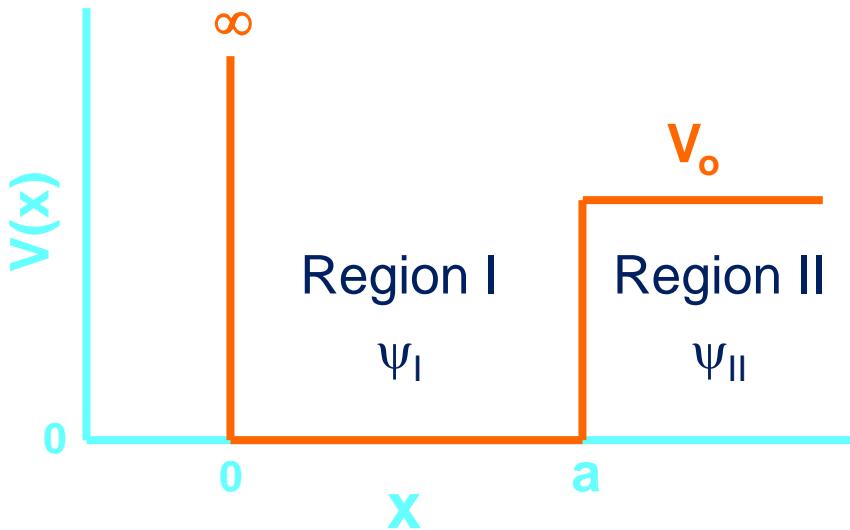
Boundary Conditions

BC: $x = 0$

$$\psi_I = A\sin(\alpha x) + B\cos(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_I(0) = 0 = A\sin(0) + B\cos(0) = B \quad \longrightarrow \quad B = 0$$

Therefore: $\boxed{\psi_I = A\sin(\alpha x)}$



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

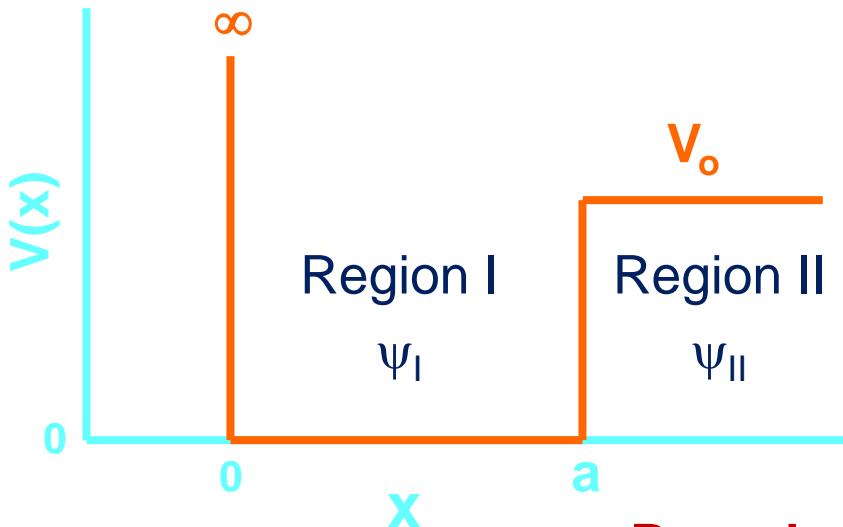
Boundary Conditions

BC: $x = \infty$

$$\psi_{II} = Ce^{\beta x} + De^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

$$\psi_{II}(\infty) = 0 = Ce^{\infty} + De^{-\infty} = Ce^{\infty} \quad \rightarrow \quad C = 0$$

Therefore: $\boxed{\psi_{II} = De^{-\beta x}}$



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Boundary Conditions

BC's: $x = a$

$$\psi_I = A \sin(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_{II} = D e^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

$$\frac{d\psi_I}{dx} = A\alpha \cos(\alpha x)$$

$$\frac{d\psi_{II}}{dx} = -D\beta e^{-\beta x}$$

$$\psi_I(a) = \psi_{II}(a)$$

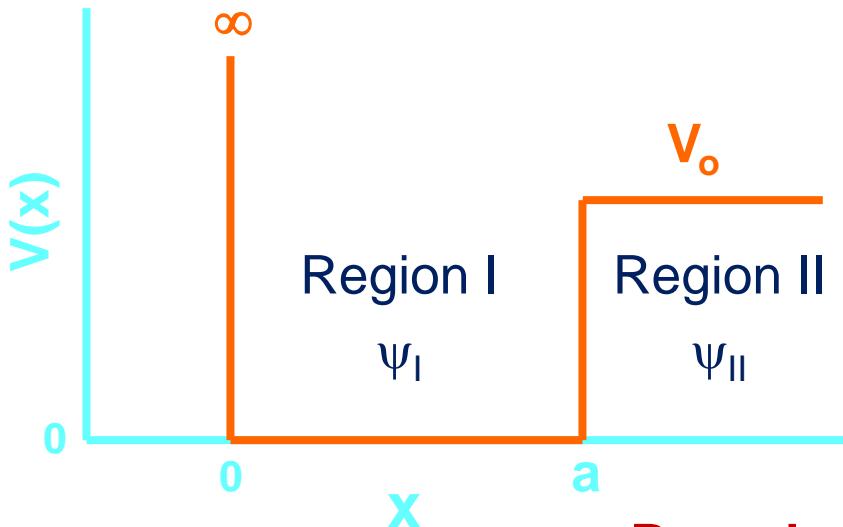
$$\left(\frac{d\psi_I}{dx} \right)_a = \left(\frac{d\psi_{II}}{dx} \right)_a$$

or

or

$$A \sin(\alpha a) = D e^{-\beta a}$$

$$A\alpha \cos(\alpha a) = -D\beta e^{-\beta a}$$



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Boundary Conditions

BC's: $x = a$

$$\psi_I = A \sin(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}} \quad \psi_{II} = D e^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

$$A \sin(\alpha a) = D e^{-\beta a}$$

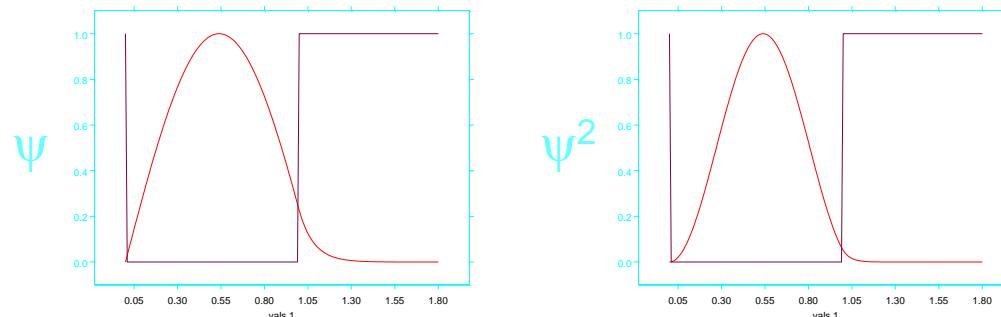
$$A \alpha \cos(\alpha a) = -D \beta e^{-\beta a}$$

These equations can be solved analytically to obtain the allowed values of the energy, E . However, it's fairly messy.

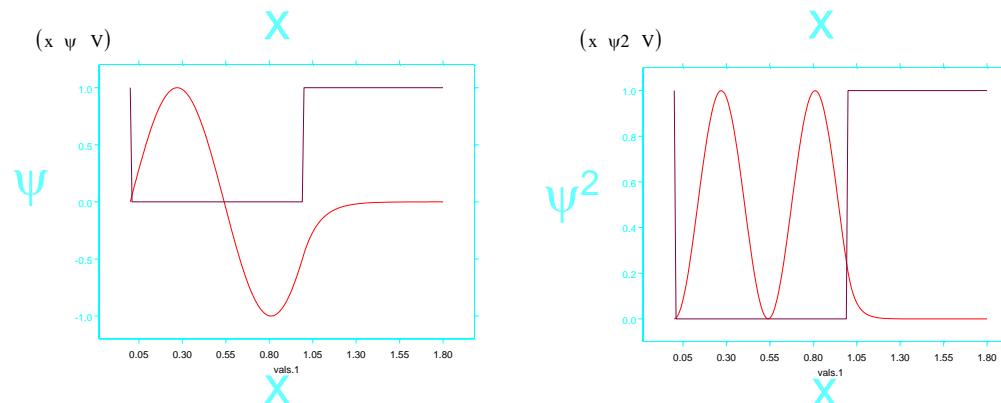
I'll just show you some results obtained by numerical solution of the Schrödinger Equation.

$$V_0 = 30 \frac{h^2}{8ma^2} \text{ This is an arbitrary value of } V_0$$

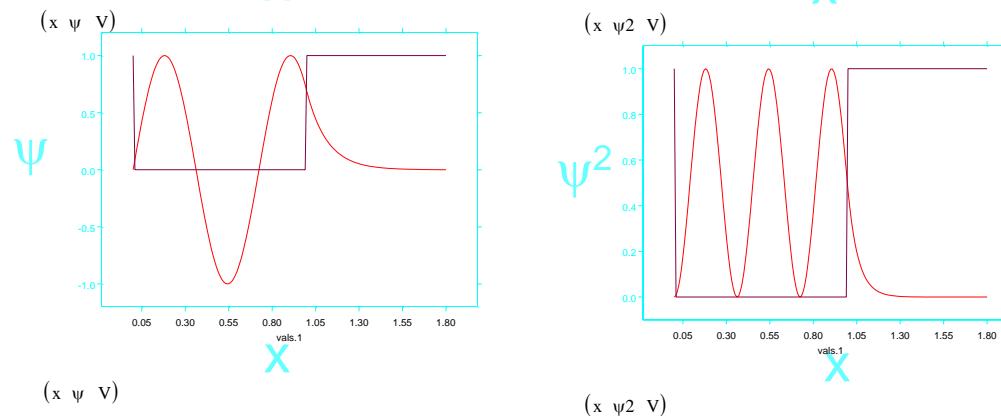
$$E_1 = 0.9 \frac{h^2}{8ma^2}$$



$$E_2 = 3.4 \frac{h^2}{8ma^2}$$

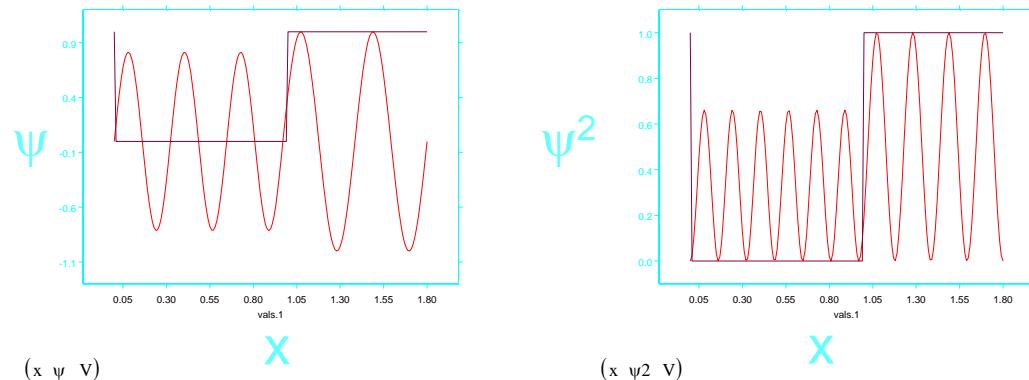


$$E_3 = 7.6 \frac{h^2}{8ma^2}$$



$$V_0 = 30 \frac{h^2}{8ma^2}$$

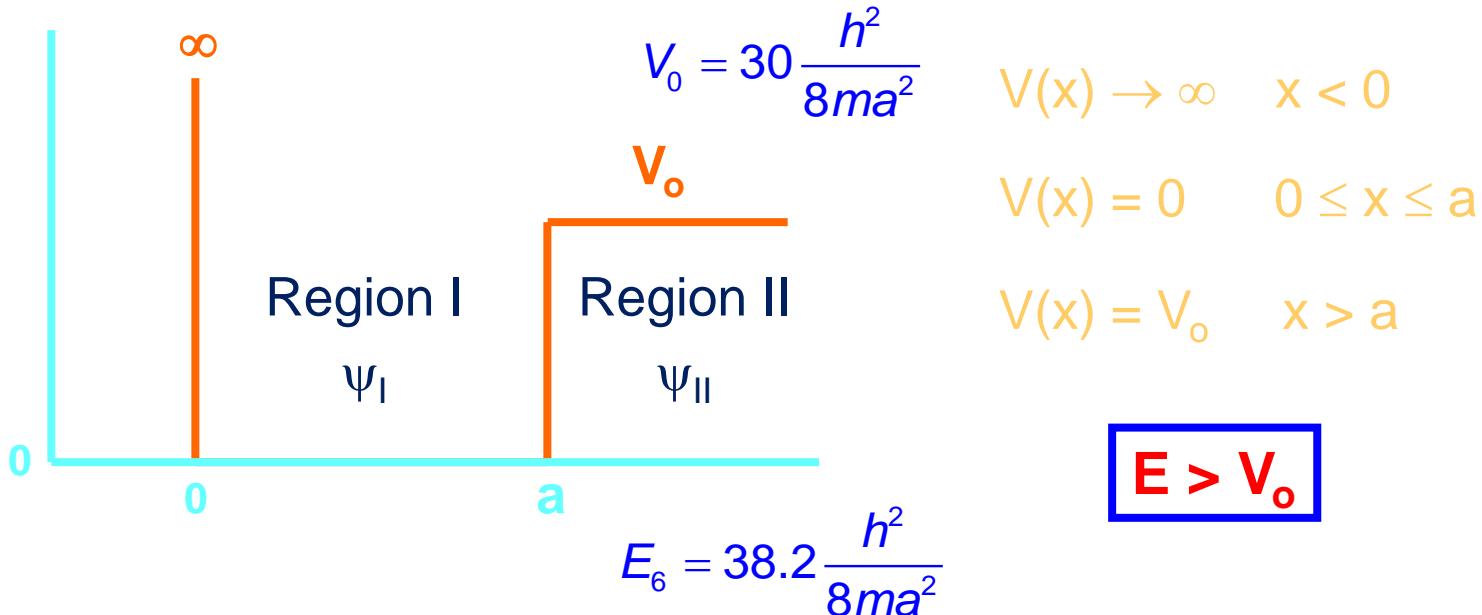
$$E_6 = 38.2 \frac{h^2}{8ma^2}$$



What happened??

Why is the wavefunction so different?

The condition for the earlier solution, $E < V_0$, is no longer valid.



Region I

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} + 0 = E\psi_I$$

$$\frac{d^2\psi_I}{dx^2} = -\frac{2mE}{\hbar^2} \psi_I = -const \cdot \psi_I$$



$$\psi_I = A\sin(\alpha x) + B\cos(\alpha x)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_{II}}{dx^2} + V_0\psi_{II} = E\psi_{II}$$

~~$$\frac{d^2\psi_{II}}{dx^2} = -\frac{2m}{\hbar^2} (E - V_0) \psi_{II} = +const \cdot \psi_{II}$$~~



$$\psi_{II} = C\sin(\beta x) + D\cos(\beta x)$$

PIB with central barrier: Tunneling

Preliminary: Potential Energy Barriers in Classical Mechanics

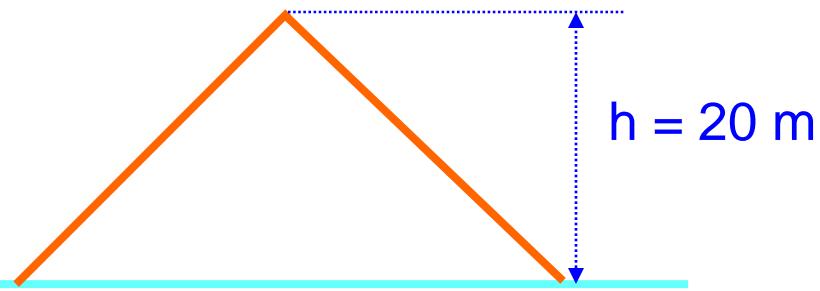
Bowling Ball

$$m = 16 \text{ lb} = 7.3 \text{ kg}$$

$$v = 30 \text{ mph} = 13.4 \text{ m/s}$$

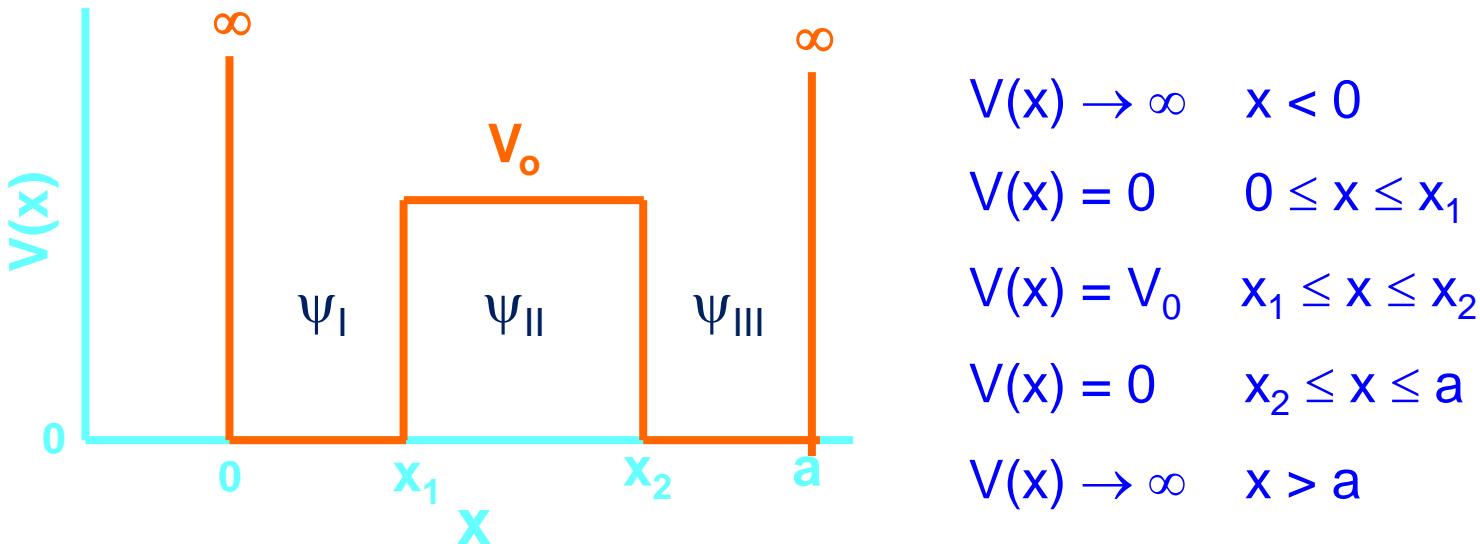
$$V_0 = mgh = 1430 \text{ J}$$

$$KE = \frac{1}{2}mv^2 = 650 \text{ J}$$



Will the bowling ball make it over the hill? Of course not!!

In classical mechanics, a particle cannot get to a position in which the potential energy is greater than the particle's total energy.



I'll just show the Boundary Conditions and graphs of the results.

BC: $x=0$

$$\psi_I(0) = 0$$

BC's: $x=x_1$

$$\psi_I(x_1) = \psi_{II}(x_1)$$

BC's: $x=x_2$

$$\psi_{II}(x_2) = \psi_{III}(x_2)$$

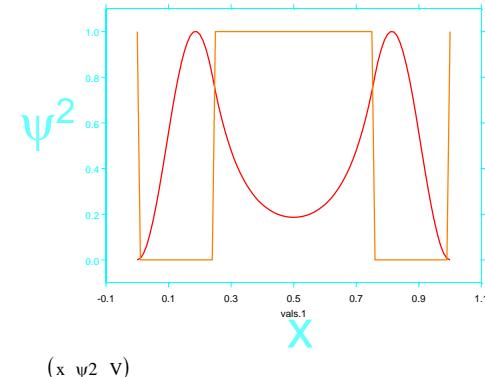
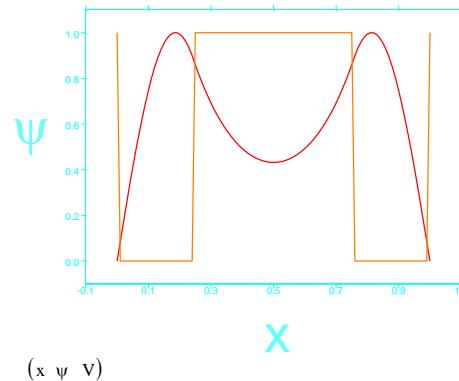
BC: $x=a$

$$\psi_{III}(a) = 0$$

$$\left(\frac{d\psi_I}{dx} \right)_{x_1} = \left(\frac{d\psi_{II}}{dx} \right)_{x_1} \quad \left(\frac{d\psi_{II}}{dx} \right)_{x_2} = \left(\frac{d\psi_{III}}{dx} \right)_{x_2}$$

$$V_0 = 20 \frac{h^2}{8ma^2}$$

$$E_1 = 7.2 \frac{h^2}{8ma^2}$$



Note that there is a significant probability of finding the particle inside the barrier, even though $V_0 > E$.

This means that the particle can get from one side of the barrier to the other by **tunneling** through the barrier.

We have just demonstrated the quantum mechanical phenomenon called **tunneling**, in which a particle can be in a region of space where the potential energy is higher than the total energy of the particle.

This is not simply an abstract phenomenon, but is known to occur in many areas of Chemistry and Physics, including:

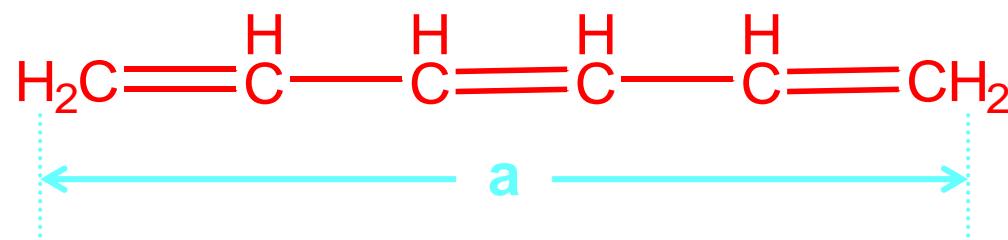
- Ammonia inversion (the ammonia clock)
- Kinetic rate constants
- Charge carriers in semiconductor devices
- Nuclear radioactive decay
- Scanning Tunneling Microscopy (STM)

Application of PIB model

Free Electron Molecular Orbital (FEMO) Model

What is the main application of “particle in a box” model???

To a good approximation, the π electrons in conjugated polyalkenes are free to move within the confines of the π orbital system.

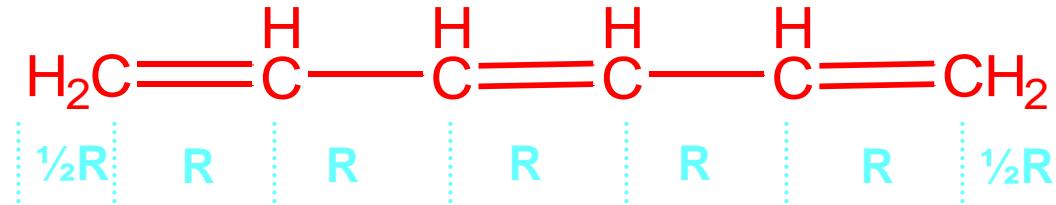


Notes: Estimation of the box length, a , will be discussed later.

Each carbon in this conjugated system contributes 1 π electron. Thus, there are 6 electrons in the π -system of 1,3,5-hexatriene (above)

The Box Length

Hexatriene

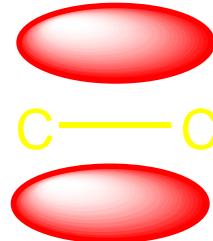
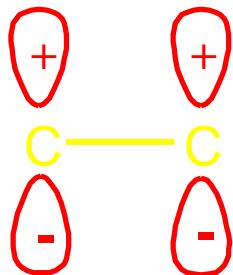


$$a = 5 \cdot R + 2 \cdot (\frac{1}{2}R) = 6 \cdot R$$

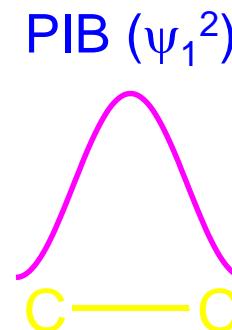
General: $a = nb \cdot R + 2 \cdot (\frac{1}{2}R) = (nb+1) \cdot R$ $R = 1.40 \text{ \AA} = 0.14 \text{ nm}$

π Bonding in Ethylene

Bonding (π) Orbital

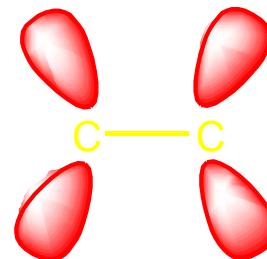
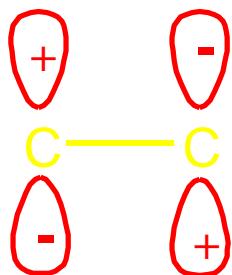


Maximum electron density between C's

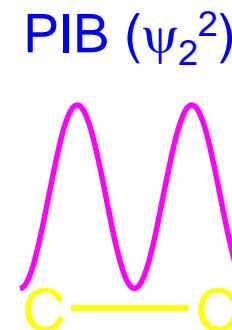


Maximum electron density between C's

Anti-bonding (π^*) Orbital

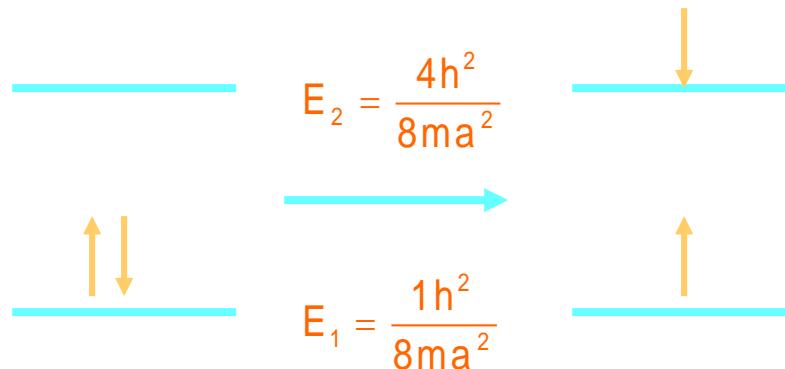


Electron density node between C's



Electron density node between C's

$\pi \rightarrow \pi^*$ Transition in Ethylene using FEMO

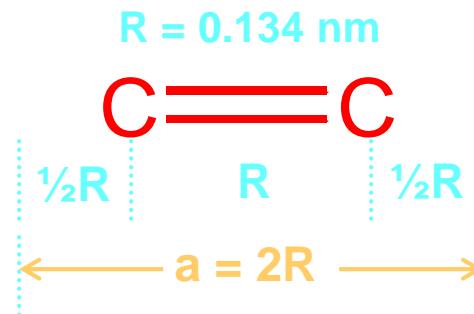


$$\Delta E = E_2 - E_1 = \frac{4h^2}{8ma^2} - \frac{1h^2}{8ma^2} = \frac{3h^2}{8ma^2}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$a = ??? = 0.268 \text{ nm}$$



It is common (although not universal) to assume that the π electrons are free to move approximately $\frac{1}{2}$ bond length beyond each outermost carbon.

$$\Delta E = \frac{3h^2}{8ma^2} = \frac{3(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.11 \times 10^{-31} \text{ kg})(0.268 \times 10^{-9} \text{ m})^2} = 2.52 \times 10^{-18} \text{ J}$$

Units: $\frac{\text{J}^2 \cdot \text{s}^2}{\text{kg} \cdot \text{m}^2} = \frac{\text{J} \cdot \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \cdot \text{s}^2}{\text{kg} \cdot \text{m}^2} = \text{J}$

Calculation of λ_{\max}

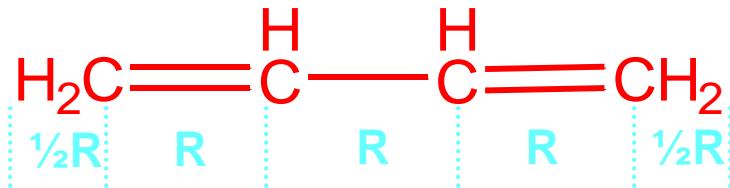
$$\Delta E = E_{\text{phot}} = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.52 \times 10^{-18} \text{ J}}$$

$$\lambda = 7.9 \times 10^{-8} \text{ m} \approx 80 \text{ nm}$$

$$\lambda(\text{exp}) = 190 \text{ nm}$$

The difficulty with applying FEMO to ethylene is that the result is extremely sensitive to the assumed box length, a .

Application of FEMO to 1,3-Butadiene



It is common to use $\text{R} = 0.14 \text{ nm}$ (the C-C bond length in benzene, where the bond order is 1.5) as the average bond length in conjugated polyenes.

$$E_3 = \frac{9h^2}{8ma^2}$$

$$L = 3 \cdot \text{R} + 2 \cdot (\frac{1}{2}\text{R}) = 4 \cdot \text{R}$$

$$L = 4 \cdot 0.14 \text{ nm} = 0.56 \text{ nm}$$

$$E_1 = \frac{1h^2}{8ma^2}$$
$$E_2 = \frac{4h^2}{8ma^2}$$
$$E_3 = \frac{9h^2}{8ma^2}$$

$$\Delta E = E_3 - E_2 = \frac{9h^2}{8ma^2} - \frac{4h^2}{8ma^2} = \frac{5h^2}{8ma^2}$$

$$\Delta E = \frac{5h^2}{8ma^2} = \frac{5(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.11 \times 10^{-31} \text{ kg})(0.56 \times 10^{-9} \text{ m})^2} = 9.62 \times 10^{-19} \text{ J}$$

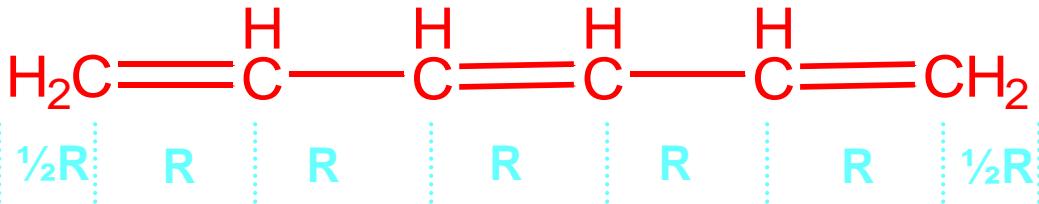
Calculation of λ_{\max}

$$\Delta E = E_{\text{phot}} = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{9.62 \times 10^{-19} \text{ J}}$$

$$\lambda = 2.07 \times 10^{-7} \text{ m} \approx 207 \text{ nm}$$

$$\lambda(\text{exp}) = 217 \text{ nm}$$

Application of FEMO to 1,3,5-Hexatriene



$E_4 = \frac{16h^2}{8ma^2}$

A horizontal teal line represents the energy level E_4 . Two orange arrows, one pointing up and one pointing down, represent two electrons in a p-orbital with opposite spins.

$$a = 5 \cdot R + 2 \cdot (\frac{1}{2}R) = 6 \cdot R$$

$$a = 6 \cdot 0.14 \text{ nm} = 0.84 \text{ nm}$$

$$\Delta E = E_4 - E_3 = \frac{16h^2}{8ma^2} - \frac{9h^2}{8ma^2} = \frac{7h^2}{8ma^2}$$

$$\Delta E = 5.98 \times 10^{-19} \text{ J}$$

$$\lambda(\text{exp}) = 258 \text{ nm}$$

$E_3 = \frac{9h^2}{8ma^2}$

A horizontal teal line represents the energy level E_3 . One orange arrow pointing up represents one electron in a p-orbital with spin up.

$E_2 = \frac{4h^2}{8ma^2}$

A horizontal teal line represents the energy level E_2 . Two orange arrows, one pointing up and one pointing down, represent two electrons in a p-orbital with opposite spins.

$E_1 = \frac{1h^2}{8ma^2}$

A horizontal teal line represents the energy level E_1 . Two orange arrows, one pointing up and one pointing down, represent two electrons in a p-orbital with opposite spins.

$\boxed{\lambda = 332 \text{ nm}}$

PIB and the Color of Vegetables

Introduction

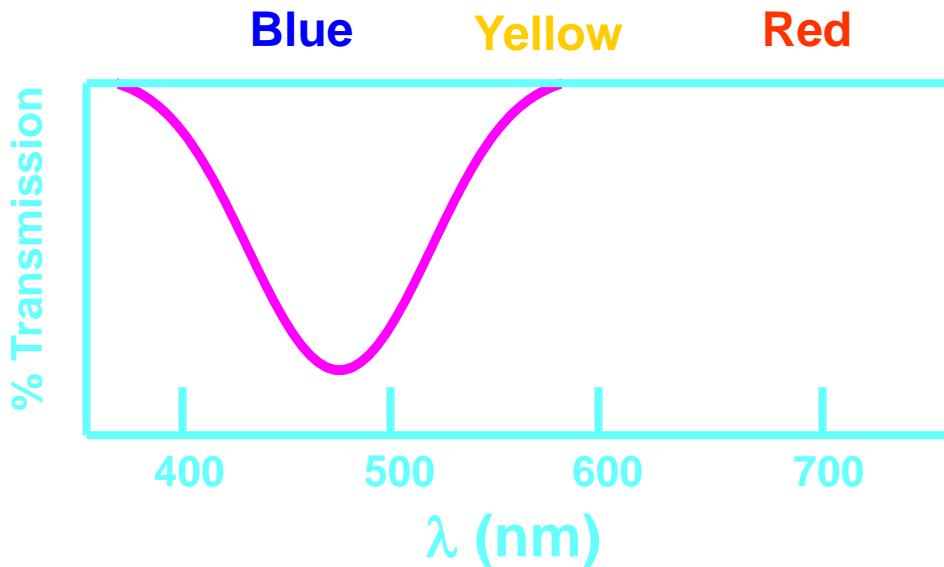
The FEMO model predicts that the $\pi \rightarrow \pi^*$ absorption wavelength, λ , increases with the number of double bonds, #DB

Compound	#DB	λ (FEMO)
Ethylene	1	80 nm
Butadiene	2	207
Hexatriene	3	333

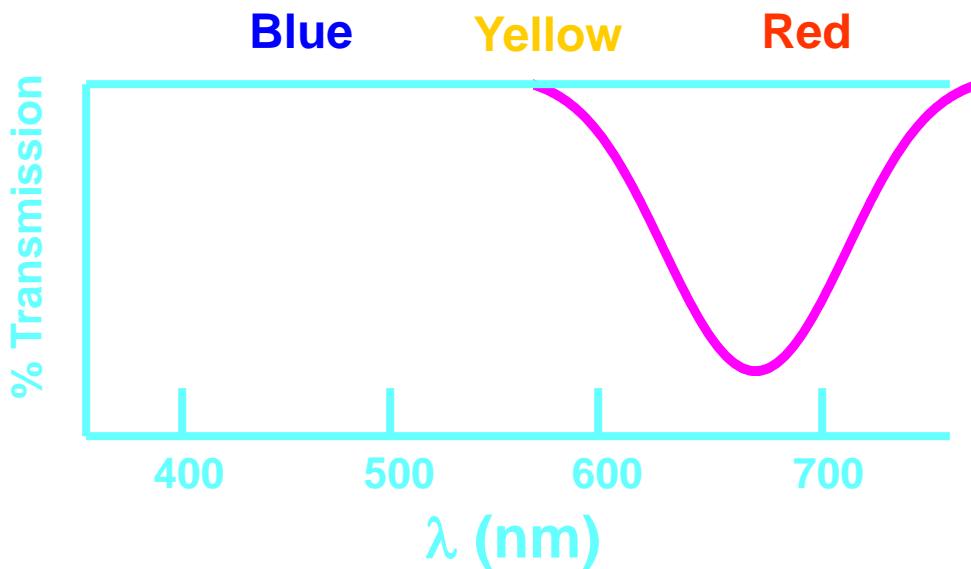
This is because: $\Delta E \propto \frac{(N+1)^2 - N^2}{a^2} \stackrel{\text{roughly}}{\propto} \frac{nb}{(nb)^2} \propto \frac{1}{nb}$ $N = \# \text{ of electron pairs}$

and: $\lambda \propto \frac{1}{\Delta E} \propto nb$

Light Absorption and Color

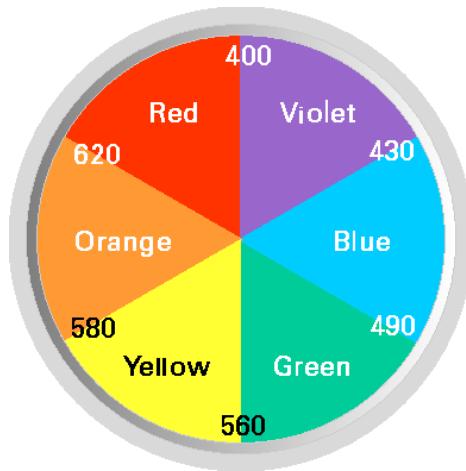


If a substance absorbs light in the blue region of the visible spectrum, the color of the transmitted (or reflected) light will be red.



If a substance absorbs light in the red region of the visible spectrum, the color of the transmitted (or reflected) light will be blue.

Conjugated π Systems and the Color of Substances



White light contains all wavelengths of visible radiation ($\lambda = 400 - 700$ nm)

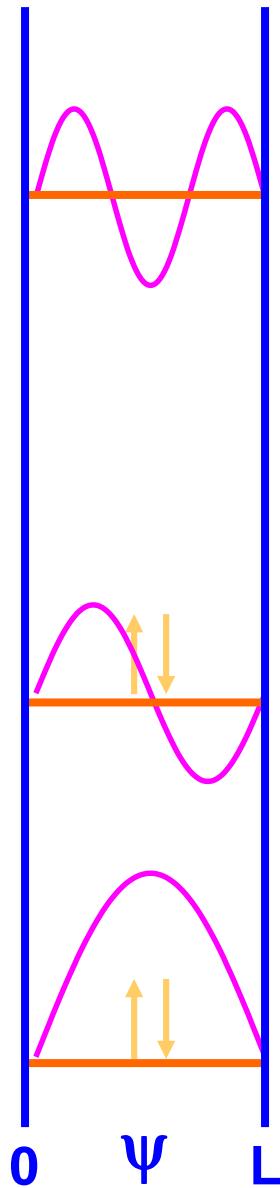
If a substance absorbs certain wavelengths, then the remaining light is reflected, giving the appearance of the complementary color.

e.g. a substance absorbing violet light appears to be yellow in color.

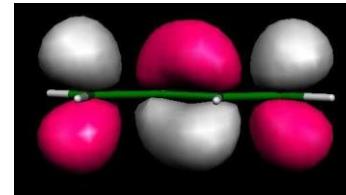
Molecule	No. of Conj. Doub. Bonds	λ_{\max}	Region	
Ethylene	1	190 nm	UV	
1,3-Butadiene	2	217	UV	
1,3,5-Hexatriene	3	258	UV	
β -Carotene	11	~450	Vis.	Carrots
Lycopene	13	~500	Vis.	Tomatoes

Comparison of FEMO and QM Wavefunctions

$$\psi_3 = A \cdot \sin\left(\frac{3\pi x}{a}\right)$$

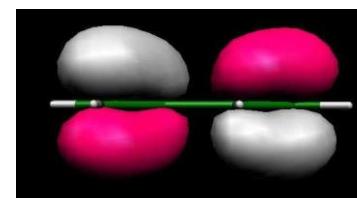


LUMO



$$\psi_2 = A \cdot \sin\left(\frac{2\pi x}{a}\right)$$

HOMO



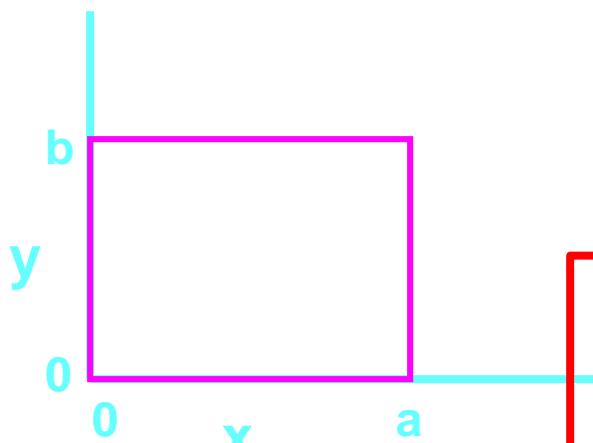
$$\psi_1 = A \cdot \sin\left(\frac{\pi x}{a}\right)$$

Part II. The 2D PIB

The 2D Hamiltonian: $H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y)$

The 2D Schr. Eqn.: $-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x, y) + V(x, y)\psi(x, y) = E\psi(x, y)$

The Potential Energy



$$V(x, y) = 0 \quad 0 \leq x \leq a \quad \text{and} \quad 0 \leq y \leq b$$

$$V(x, y) \rightarrow \infty \quad x < 0 \text{ or } x > a \text{ or } y < 0 \text{ or } y > b$$

Outside of the box

i.e. $x < 0$ or $x > a$ or $y < 0$ or $y > b$

$$\psi(x, y) = 0$$

Solution: Separation of Variables

The 2D Schr. Eqn.: $-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x, y) + V(x, y)\psi(x, y) = E\psi(x, y)$

Inside the box: $V(x, y) = 0 \quad 0 \leq x \leq a \quad \text{and} \quad 0 \leq y \leq b$

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$$

Note: This two dimensional differential equation can be solved by the method of **Separation of Variables**.

Inside the box: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$

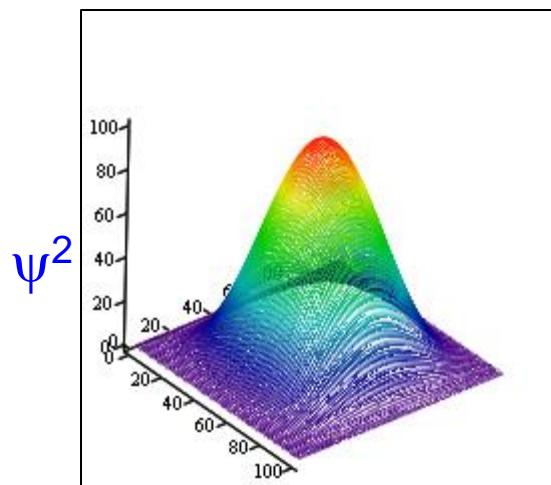
$$\psi(x, y) = X(x)Y(y) \quad E = E_x + E_y$$

The Wavefunctions

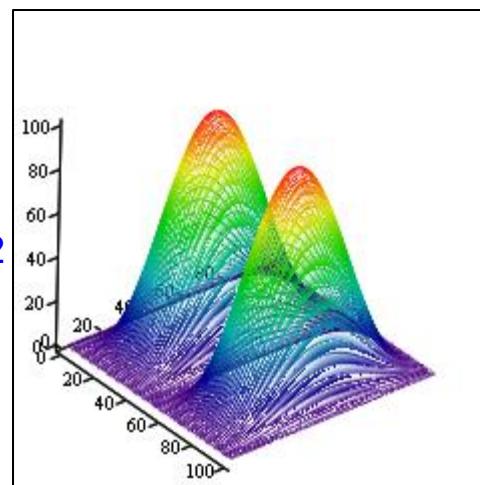
$$\psi(x,y) = X(x) \cdot Y(y) = \left[A_x \sin\left(\frac{n_x \pi x}{a}\right) \right] \cdot \left[A_y \sin\left(\frac{n_y \pi y}{b}\right) \right] \quad A_x = \sqrt{\frac{2}{a}} \quad A_y = \sqrt{\frac{2}{b}}$$

$$\psi(x,y) = \sqrt{\frac{4}{ab}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \quad n_x = 1, 2, 3, \dots \quad n_y = 1, 2, 3, \dots$$

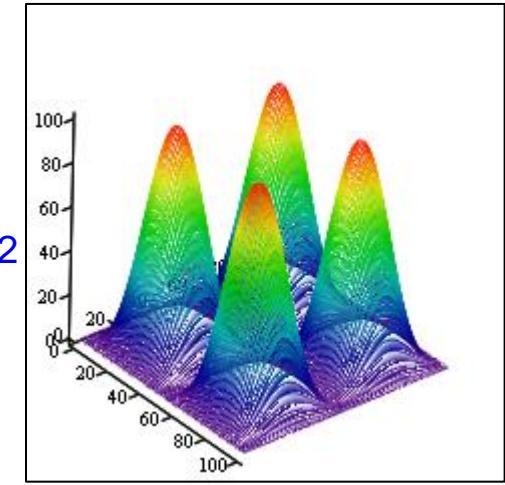
Range
 $0 \leq x \leq a$
 $0 \leq y \leq b$



$$\psi^2 \quad n_x = 1 \quad n_y = 1$$



$$\psi^2 \quad n_x = 2 \quad n_y = 1$$



$$\psi^2 \quad n_x = 2 \quad n_y = 2$$

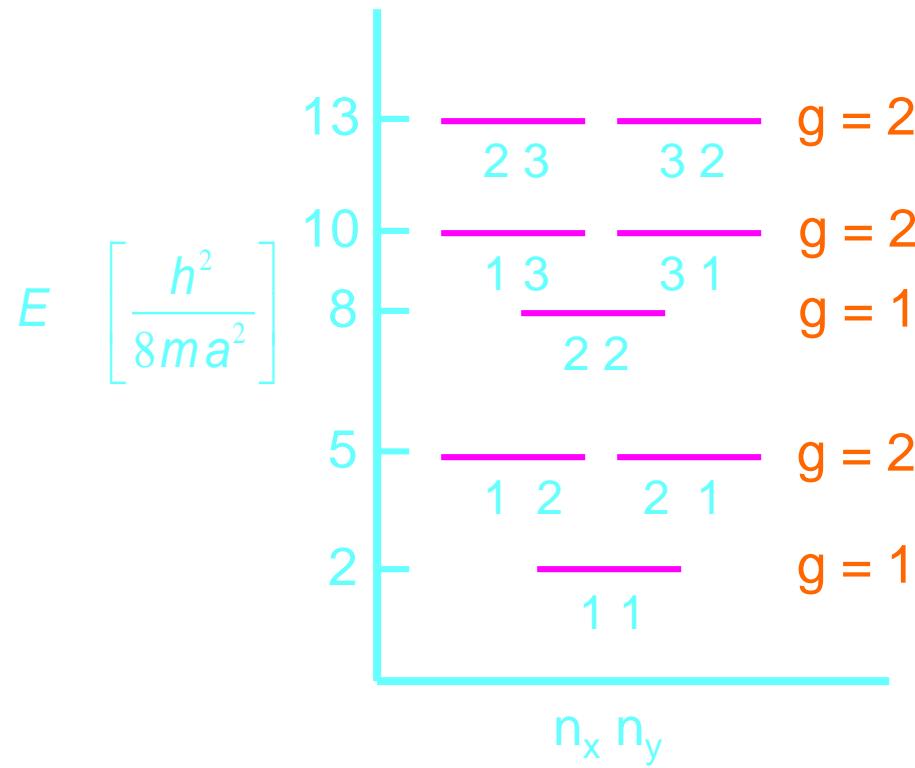
The Energies: Wavefunction Degeneracy

$$E = E_x + E_y = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right)$$
$$n_x = 1, 2, 3, \dots$$
$$n_y = 1, 2, 3, \dots$$

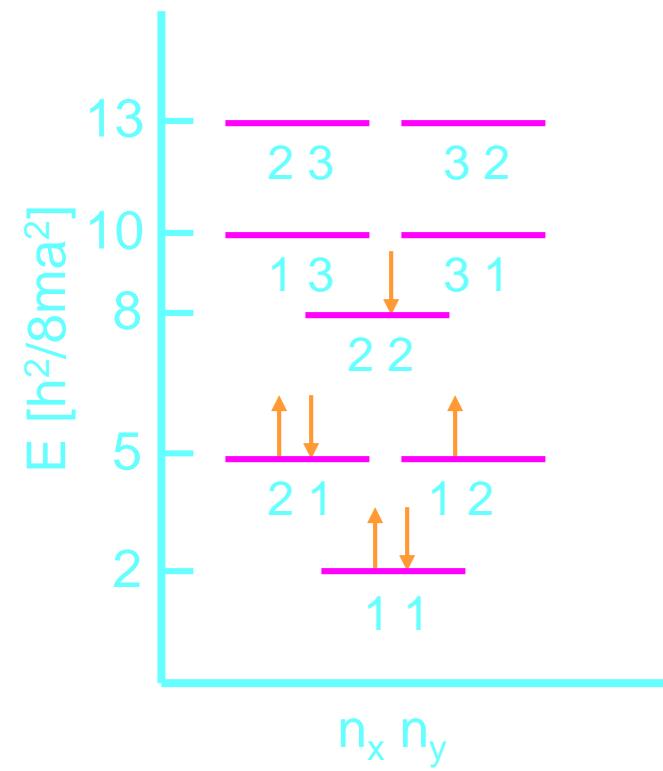
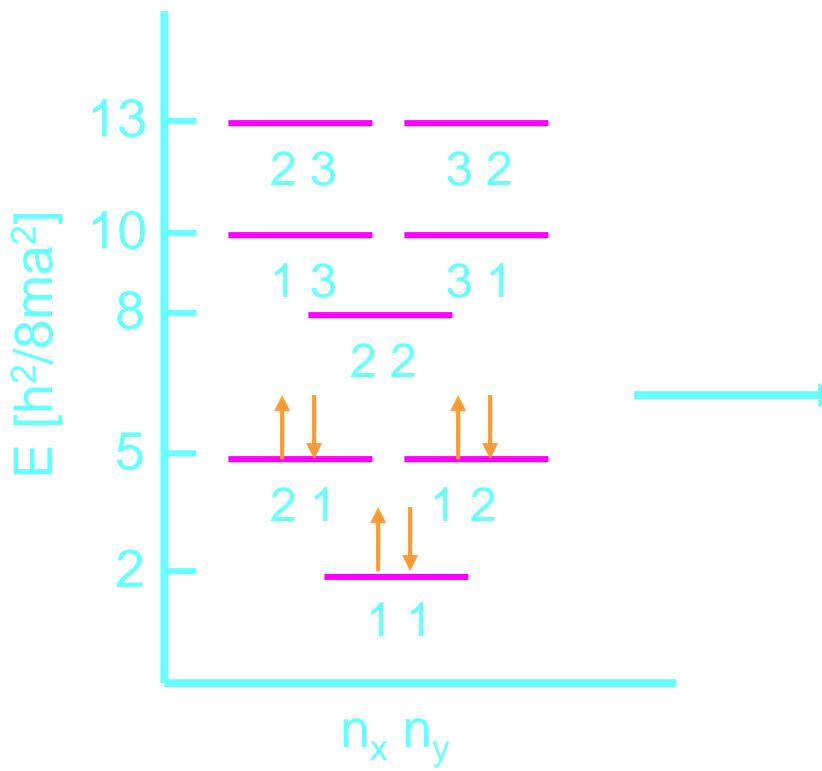
Square Box

$$a = b$$

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2)$$



Application: $\pi \rightarrow \pi^*$ Absorption in Benzene

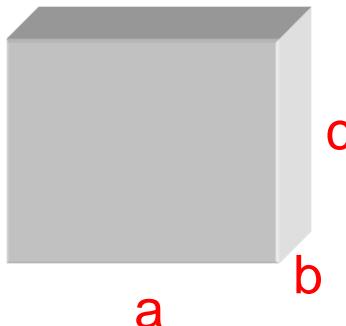


The six π electrons in benzene can be approximated as particles in a square box.

One can estimate the wavelength of the lowest energy $\pi \rightarrow \pi^*$ from the 2D-PIB model

Three Dimensional PIB

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + V(x, y, z) \psi(x, y, z) = E \psi(x, y, z)$$



$$V(x, y, z) = 0 \quad 0 \leq x \leq a$$

$$0 \leq y \leq b$$

$$0 \leq z \leq c$$

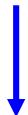
$$V(x, y, z) \rightarrow \infty \quad \text{Outside the box}$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E \psi(x, y, z)$$

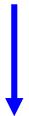
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = (H_x + H_y + H_z) \psi = E \psi$$

Assume: $\psi(x, y, z) = X(x) \cdot Y(y) \cdot Z(z)$

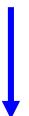
$$-\frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} = E_x X$$



$$-\frac{\hbar^2}{2m} \frac{\partial^2 Y}{\partial y^2} = E_y Y$$



$$-\frac{\hbar^2}{2m} \frac{\partial^2 Z}{\partial z^2} = E_z Z$$



$$E_x = \frac{n_x^2 \hbar^2}{8ma^2} \quad n_x = 1, 2, 3, \dots$$

$$X(x) = A_x \sin\left(\frac{n_x \pi x}{a}\right)$$

$$A_x = \sqrt{\frac{2}{a}}$$

$$E_y = \frac{n_y^2 \hbar^2}{8mb^2} \quad n_y = 1, 2, 3, \dots$$

$$Y(y) = A_y \sin\left(\frac{n_y \pi y}{b}\right)$$

$$A_y = \sqrt{\frac{2}{b}}$$

$$E_z = \frac{n_z^2 \hbar^2}{8mc^2} \quad n_z = 1, 2, 3, \dots$$

$$Z(z) = A_z \sin\left(\frac{n_z \pi z}{c}\right)$$

$$A_z = \sqrt{\frac{2}{c}}$$

$$\psi(x,y,z) = X(x) \cdot Y(y) \cdot Z(z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$n_x = 1, 2, 3, \dots$$

$$n_y = 1, 2, 3, \dots$$

$$n_z = 1, 2, 3, \dots$$

$$E = E_x + E_y + E_z = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Cubical Box $a = b = c$

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

Note: You should be able to determine the energy levels and degeneracies for a cubical box and for various ratios of a:b:c

Question: construct the energy Diagram for a PIB in 3 D

- a) For cubical box
- b) For a box with $a = 2b$ and $c = 2a$

Thanks

Examples and Answers

Particle in a Box

For a particle in a box with Wavefunctions and Energy:

$$\psi_n = A \sin\left(\frac{n\pi}{a}x\right) \quad E_n = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, \dots$$

1. Show that the wavefunction is an eigenfunction of the Hamiltonian operator.
2. Normalize the wavefunction and find A
3. Calculate the following quantities:

$\langle x \rangle$ $\langle x^2 \rangle$ $\langle p \rangle$ $\langle p^2 \rangle$ σ_x^2 σ_p^2 $\sigma_x \sigma_p$ $\langle KE \rangle$ $\langle PE \rangle$ $\Delta x \Delta P$

- 4 Find the number and position of nodes for $n= 1, 2, 3, 4$
5. Find the probability of finding the particle in

- $I. \quad 0.24L \leq x \leq 0.26L$
- $II. \quad 0. \leq x \leq 0.25L$

The Correspondence Principle

The predictions of Quantum Mechanics cannot violate the results of classical mechanics on macroscopically sized systems.

Consider an electron in a 1 Angstrom box.

Calculate (a) the Zero Point Energy (i.e. minimum energy)

(b) the minimum speed of the electron

$$m_e = 9.1 \times 10^{-31} \text{ kg}$$
$$a = 1 \times 10^{-10} \text{ m}$$
$$h = 6.63 \times 10^{-34} \text{ J-s}$$

$$E_1 = \frac{h^2}{8ma^2} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.1 \times 10^{-31} \text{ kg})(1 \times 10^{-10} \text{ m})^2} = 6.04 \times 10^{-18} \text{ J}$$

$$E_1 = \frac{mv_1^2}{2} \rightarrow v_1 = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2(6.04 \times 10^{-18} \text{ kg} \cdot \text{m}^2 / \text{s}^2)}{9.1 \times 10^{-31} \text{ kg}}}$$

$$v_1 = 3.6 \times 10^6 \text{ m/s} (\approx 1.7 \times 10^7 \text{ mi/hr})$$

Thus, the minimum speed of an electron confined to an atom is quite high.

Let's perform the same calculation on a macroscopic system.

Consider a 1 gram particle in a 10 cm box.

Calculate (a) the Zero Point Energy (i.e. minimum energy)

(b) the minimum speed of the particle

$$m = 1 \times 10^{-3} \text{ kg}$$

$$a = 0.10 \text{ m}$$

$$\hbar = 6.63 \times 10^{-34} \text{ J-s}$$

$$E_1 = \frac{\hbar^2}{8ma^2} = \frac{(6.63 \times 10^{-34} \text{ J-s})^2}{8(1 \times 10^{-3} \text{ kg})(0.1 \text{ m})^2} = 5.50 \times 10^{-63} \text{ J}$$

$$E_1 = \frac{mv_1^2}{2} \rightarrow v_1 = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2(5.50 \times 10^{-63} \text{ kg} \cdot \text{m}^2/\text{s}^2)}{1 \times 10^{-3} \text{ kg}}} = 3.3 \times 10^{-30} \text{ m/s}$$

Thus, the minimum energy and speed of a macroscopic particle are completely negligible.

Probability Distribution of a Macroscopic Particle

Consider a 1 gram particle in a 10 cm box moving at 1 cm/s.

Calculate the quantum number, n , which represents the number of maxima in the probability, ψ^2 .

$$E = \frac{1}{2}mv^2 = \frac{1}{2}(1 \times 10^{-3} \text{ kg})(0.01 \text{ m/s})^2 = 5.0 \times 10^{-8} \text{ J}$$

$$m = 1 \times 10^{-3} \text{ kg}$$

$$a = 0.10 \text{ m}$$

$$v = 0.01 \text{ m/s}$$

$$h = 6.63 \times 10^{-34} \text{ J-s}$$

$$E = \frac{n^2 h^2}{8ma^2} \rightarrow n^2 = \frac{8ma^2 E}{h^2} = \frac{8(1 \times 10^{-3} \text{ kg})(0.1 \text{ m})^2 (5.0 \times 10^{-8} \text{ J})}{(6.63 \times 10^{-34} \text{ J.s})^2}$$

$$n^2 = 9.1 \times 10^{54} \rightarrow n = 3 \times 10^{27}$$

Thus, the probability distribution is uniform throughout the box, as predicted by classical mechanics.

PIB Properties

Normalization of the Wavefunctions

$$\psi_n = A \sin\left(\frac{n\pi}{a}x\right) \quad 0 \leq x \leq a$$

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha}\sin(2\alpha x)$$

$$1 = \int_0^a \psi_n^2 dx = \int_0^a \left[A \sin\left(\frac{n\pi}{a}x\right) \right]^2 dx = A^2 \int_0^a \sin^2(\alpha x) dx \quad \alpha = \frac{n\pi}{a}$$

$$= A^2 \left[\frac{1}{2}x - \frac{1}{4\alpha}\sin(2\alpha x) \right]_0^a = A^2 \left[\left(\frac{1}{2}a - \frac{1}{4\alpha}\sin\left(2\frac{n\pi}{a}a\right) \right) - \left(0 - \frac{1}{4\alpha}\sin(0) \right) \right]$$

$$1 = A^2 \left(\frac{a}{2} \right) \longrightarrow A = \left(\frac{2}{a} \right)^{1/2} = \sqrt{\frac{2}{a}}$$

Probability of finding the particle in a particular portion of the box

Calculate the probability of finding a particle with $n=1$ in the region of the box between 0 and $a/4$

$$\psi_1 = A \sin\left(\frac{\pi x}{a}\right)$$

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$P(0 \leq x \leq a/4) = A^2 \int_0^{a/4} \sin^2(\alpha x) dx \quad \alpha = \pi/a$$

$$= A^2 \left[\frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x) \right]_0^{a/4} = A^2 \left[\left(\frac{1}{2} \cdot \frac{a}{4} - \frac{1}{4(\pi/a)} \sin\left(2\frac{\pi}{a} \frac{a}{4}\right) \right) - \left(0 - \frac{1}{4(\pi/a)} \sin(0) \right) \right]$$

$$P(0 \leq x \leq a/4) = \frac{2}{a} \left(\frac{a}{8} - \frac{a}{4\pi} \right) = \frac{1}{4} - \frac{1}{2\pi} = 0.091$$

This is significantly lower than the classical probability, 0.25.

Orthogonality of the Wavefunctions

Two wavefunctions are orthogonal if: $\int \psi_i^* \psi_j d\tau = 0 \quad i \neq j$

We will show that the two lowest wavefunctions of the PIB

are orthogonal: $\psi_1 = A \sin\left(\frac{\pi x}{a}\right) \quad \psi_2 = A \sin\left(\frac{2\pi x}{a}\right)$

$$\int_0^a \psi_2 \psi_1 dx = \int_0^a A \sin\left(\frac{2\pi x}{a}\right) A \sin\left(\frac{\pi x}{a}\right) dx = A^2 \int_0^a \sin(\alpha x) \sin(\beta x) dx \quad \alpha = \frac{2\pi}{a} \quad \beta = \frac{\pi}{a}$$

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)}$$

$$\int_0^a \psi_2 \psi_1 dx = A^2 \left(\frac{\sin[(\alpha - \beta)a]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)a]}{2(\alpha + \beta)} \right) - A^2 (0 - 0) \quad (\alpha + \beta)a = \frac{3\pi}{a}a = 3\pi$$

$$(\alpha - \beta)a = \frac{\pi}{a}a = \pi$$

$$\int_0^a \psi_2 \psi_1 dx = A^2 \left(\frac{\sin[\pi]}{2(\alpha - \beta)} - \frac{\sin[3\pi]}{2(\alpha + \beta)} \right) = 0 \quad \text{Thus, } \psi_1 \text{ and } \psi_2 \text{ are orthogonal}$$

Using the same method as above, it can be shown that:

$$\int \psi_i^* \psi_j d\tau = 0 \quad \text{For all } i \neq j$$

Thus, the PIB wavefunctions are orthogonal.

If they have also been normalized, then
the wavefunctions are **orthonormal**:

$$\int \psi_i^* \psi_j d\tau = \delta_{ij}$$

or

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Positional Averages

We will calculate the averages for ψ_1 and present the general result for ψ_n

$$\psi_1 = A \sin\left(\frac{\pi x}{a}\right) = A \sin(\alpha x) \quad \alpha = \frac{\pi}{a} \quad A = \sqrt{\frac{2}{a}}$$

$$\sin(\alpha a) = \sin\left(\frac{\pi}{a} a\right) = 0 \quad \sin(2\alpha a) = \sin\left(2 \frac{\pi}{a} a\right) = 0$$

$$\cos(\alpha a) = \cos\left(\frac{\pi}{a} a\right) = -1 \quad \cos(2\alpha a) = \cos\left(2 \frac{\pi}{a} a\right) = +1$$

<X>

$$\begin{aligned} \langle x \rangle &= \langle \psi_1 | x | \psi_1 \rangle = \int_0^a \psi_1^* x \psi_1 dx = \int_0^a A \sin\left(\frac{\pi x}{a}\right) x A \sin\left(\frac{\pi x}{a}\right) dx \\ &= A^2 \int_0^a x \sin^2(\alpha x) dx \quad \alpha = \frac{\pi}{a} \end{aligned}$$

$$\langle x \rangle = A^2 \int_0^a x \sin^2(\alpha x) dx$$

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\langle x \rangle = \frac{2}{a} \left[\left(\frac{a^2}{4} - \frac{a \sin(2\alpha a)}{4\alpha} - \frac{\cos(2\alpha a)}{8\alpha^2} \right) - \left(0 - 0 - \frac{\cos(0)}{8\alpha^2} \right) \right]$$

$$\langle x \rangle = \frac{2}{a} \left[\left(\frac{a^2}{4} - \frac{1}{8\alpha^2} \right) - \left(-\frac{1}{8\alpha^2} \right) \right]$$

$$\langle x \rangle = \frac{a}{2}$$

General Case: $\langle x \rangle = \frac{a}{2}$

This makes sense because ψ^2 is symmetric about the center of the box.

$$\langle x^2 \rangle$$

$$\begin{aligned}\langle x^2 \rangle &= \langle \psi_1 | x^2 | \psi_1 \rangle = \int_0^a \psi_1^* x^2 \psi_1 dx = \int_0^a A \sin\left(\frac{\pi x}{a}\right) x^2 A \sin\left(\frac{\pi x}{a}\right) dx \\ &= A^2 \int_0^a x^2 \sin^2(\alpha x) dx \quad \alpha = \frac{\pi}{a}\end{aligned}$$

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

$$\langle x^2 \rangle = \frac{2}{a} \left[\left(\frac{a^3}{6} - \left(\frac{a^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha a) - \frac{a \cos(2\alpha a)}{4\alpha^2} \right) - (0 - 0 - 0) \right]$$

$$\langle x^2 \rangle = \frac{2}{a} \left(\frac{a^3}{6} - \frac{a}{4 \left(\frac{\pi}{a} \right)^2} \right) = \frac{a^2}{3} - \frac{a^2}{2\pi^2} = \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) a^2 \approx 0.28a^2$$

$$\langle x^2 \rangle = \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) a^2 \approx 0.28a^2$$

compared to the classical result

$$\langle x^2 \rangle = \frac{a^2}{2} \approx 0.33a^2$$

General Case: $\langle x^2 \rangle = \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right) a^2$

Note that the general QM value reduces to the classical result in the limit of large n, as required by the Correspondence Principle.

Momentum Averages

Preliminary

$$\hat{p} \equiv \frac{\hbar}{i} \frac{d}{dx} \quad \hat{p}^2 \equiv -\hbar^2 \frac{d^2}{dx^2}$$

$$\psi_1 = A \sin\left(\frac{\pi}{a} x\right) = A \sin(\alpha x) \quad \alpha = \frac{\pi}{a} \quad A = \sqrt{\frac{2}{a}}$$

$$\frac{d\psi_1}{dx} = \frac{d}{dx}(A \sin(\alpha x)) = A\alpha \cos(\alpha x)$$

$$\frac{d^2\psi_1}{dx^2} = \frac{d}{dx}(A\alpha \cos(\alpha x)) = -A\alpha^2 \sin(\alpha x)$$

$$\sin(\alpha a) = \sin\left(\frac{\pi}{a} a\right) = 0 \quad \sin(2\alpha a) = \sin\left(2\frac{\pi}{a} a\right) = 0$$

$$\cos(\alpha a) = \cos\left(\frac{\pi}{a} a\right) = -1 \quad \cos(2\alpha a) = \cos\left(2\frac{\pi}{a} a\right) = 1$$

< p >

$$\hat{p} \equiv \frac{\hbar}{i} \frac{d}{dx}$$

$$\begin{aligned}\langle p \rangle &= \langle \psi_1 | \hat{p} | \psi_1 \rangle = \int_0^a \psi_1^* \frac{\hbar}{i} \frac{d\psi_1}{dx} dx = \int_0^a A \sin(\alpha x) \frac{\hbar}{i} \frac{dA \sin\left(\frac{\pi x}{a}\right)}{dx} dx \quad \alpha = \frac{\pi}{a} \\ &= \int_0^a A \sin(\alpha x) \frac{\hbar}{i} A \alpha \cos(\alpha x) dx = A^2 \left(\frac{\hbar}{i} \right) \alpha \int_0^a \sin(\alpha x) \cos(\alpha x) dx \\ &\quad \int \sin(\alpha x) \cos(\alpha x) dx = \frac{1}{2\alpha} \sin^2(\alpha x)\end{aligned}$$

$$\langle p \rangle = A^2 \left(\frac{\hbar}{i} \right) \alpha \left[\left(\frac{1}{2\alpha} \sin^2(\alpha a) \right) - \left(\frac{1}{2\alpha} \sin^2(0) \right) \right] = A^2 \left(\frac{\hbar}{i} \right) \alpha [0 - 0]$$

< p > = 0 (General case is the same)

On reflection, this is not surprising.

The particle has equal probabilities of moving in the + or - x-direction, and the momenta cancel each other.

$$\langle p^2 \rangle$$

$$\hat{p}^2 \equiv -\hbar^2 \frac{d^2}{dx^2}$$

$$\langle p^2 \rangle = \langle \psi_1 | \hat{p}^2 | \psi_1 \rangle = \int_0^a \psi_1^* (-\hbar^2) \frac{d^2 \psi_1}{dx^2} dx = \int_0^a A \sin(\alpha x) (-\hbar^2) \frac{d^2 \sin(\alpha x)}{dx^2} dx \quad \alpha = \frac{\pi}{a}$$

$$= \int_0^a A \sin(\alpha x) (-\hbar^2) (-A\alpha^2) \sin(\alpha x) dx = A^2 \hbar^2 \alpha^2 \int_0^a \sin^2(\alpha x) dx$$

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$\langle p^2 \rangle = A^2 \hbar^2 \alpha^2 \left[\left(\frac{a}{2} - \frac{1}{4\alpha} \sin(2\alpha a) \right) - \left(0 - \frac{1}{4\alpha} \sin(0) \right) \right] = \left(\frac{2}{a} \right) \hbar^2 \alpha^2 \left[\frac{a}{2} \right]$$

$$\langle p^2 \rangle = \hbar^2 \alpha^2 = \frac{\pi^2 \hbar^2}{a^2}$$

General Case: $\langle p^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{a^2}$

Standard Deviations and the Uncertainty Principle

Heisenberg Uncertainty Principle: $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

$$\langle x \rangle = \frac{a}{2} = 0.50a$$

$$\langle p \rangle = 0$$

$$\langle x^2 \rangle \approx 0.28a^2$$

$$\langle p^2 \rangle = \frac{\pi^2 \hbar^2}{a^2}$$

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{0.28a^2 - (0.50a)^2} \approx 0.17a$$

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\langle p^2 \rangle - 0} = \frac{\pi \hbar}{a} \approx 3.14 \frac{\hbar}{a}$$

$$\sigma_x \sigma_p \approx (0.17a) \left(3.14 \frac{\hbar}{a} \right) \approx 0.53\hbar$$