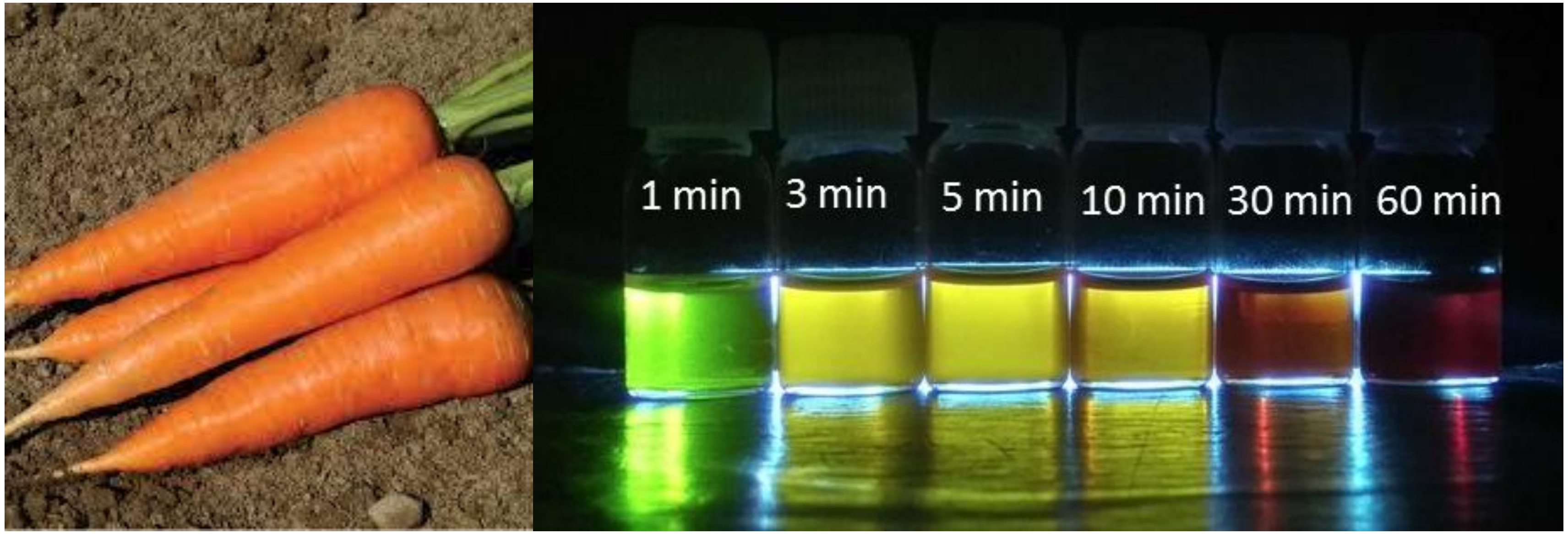
Particle in a box



Born Interretation: Restrictions on wavefunction

ψ must be a solution of the Schrodinger equation

ψ must be normalizable: ψ must be finite and $\rightarrow 0$ at boundaries/ $\pm\infty$

Ψ must be a continuous function of x,y,z

$d\Psi/dq$ must be must be continuous in q

Ψ must be single-valued

Ψ must be quadratically-intergrable
(square of the wavefunction should be integrable)

Origin of quantization

Quantum Mechanics

Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential (Particle in a box)
3. Hydrogen Atom

Free Particle

Time-independent Schrodinger equation

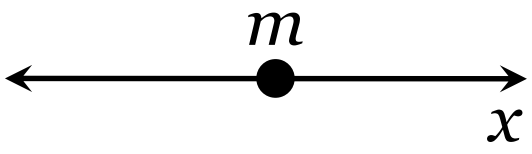
$$\hat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E \cdot \psi(x)$$

For a free particle *V(x)*=0
There are no external forces acting

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E \cdot \psi(x)$$

Free Particle



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

Second-order linear differential equation

Let us assume

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

Trial Solution

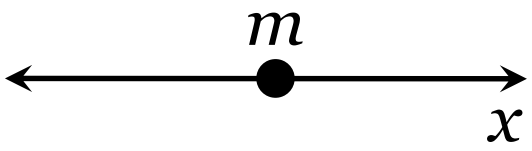
$$y(x) = A\sin kx + B\cos kx$$

$$\frac{d}{dx}y(x) = \frac{d}{dx}\left(A\sin kx + B\cos kx\right) = k\left(A\cos kx - B\sin kx\right)$$

$$\frac{d^2}{dx^2}y(x) = -k^2\left(A\sin kx + B\cos kx\right) = -k^2 y(x)$$

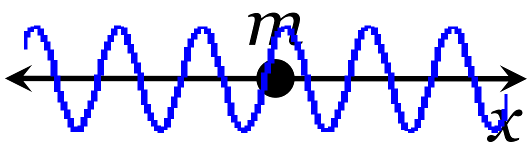
Free Particle

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



$$\frac{\hbar^2}{2m}k^2\psi(x) = E\cdot\psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

Free Particle



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

$$\frac{\hbar^2}{2m}k^2\psi(x) = E\cdot\psi(x) \quad\Rightarrow\quad E = \frac{\hbar^2k^2}{2m} \quad\Rightarrow\quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

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

There are no restrictions on k

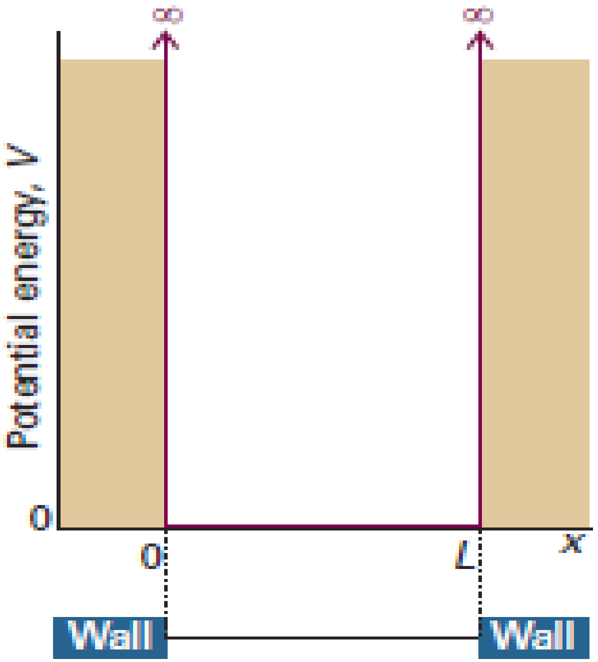
E can have any value

Energies of free particles are continuous

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

No Quantization **All energies are allowed**

Is this a good wavefunction?



Particle in 1-D Box

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

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

For $x < 0$ and $x > \mathrm{L} \Rightarrow V = \infty$

$$\frac{d^2}{dx^2}\psi(x) = \frac{2m}{\hbar^2}\left(V - E\right)\cdot\psi(x) = \infty\cdot\psi(x)$$

$$\boxed{y(x<0)=0 \quad \text{and} \quad y(x>L)=0}$$

$$x = 0 \Rightarrow y(x) = 0$$

Wavefunction should be continuous:
Boundary condition

$$\boxed{y(x) = A\sin kx}$$

$$(B=0, \quad \cos x = \cos 0 = 1)$$

For $0 \le x \le \mathrm{L} \Rightarrow V = 0$

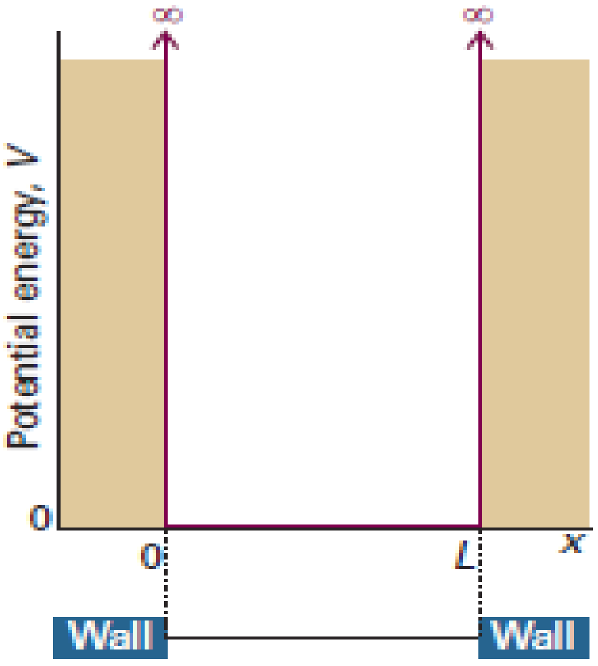
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\cdot\psi(x)$$

Zero

Trial Solution: $\boxed{y(x) = A\sin kx + B\cos kx}$

Energy: $E = \dfrac{\hbar^2 k^2}{2m}$

Particle in 1-D Box



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

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

$$\psi(x) = A\sin kx = A\sin\frac{n\pi}{L}x \quad n = 1, 2, 3, 4, \ldots..$$

$n \neq 0$, as wavefunction cannot be zero everywhere

For $x < 0$ and $x > \mathrm{L} \Rightarrow V = \infty$

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

$$\boxed{\psi(x<0) = 0 \quad \text{and} \quad \psi(x>L) = 0}$$

$x = L \Rightarrow \psi(L) = 0$ Boundary condition

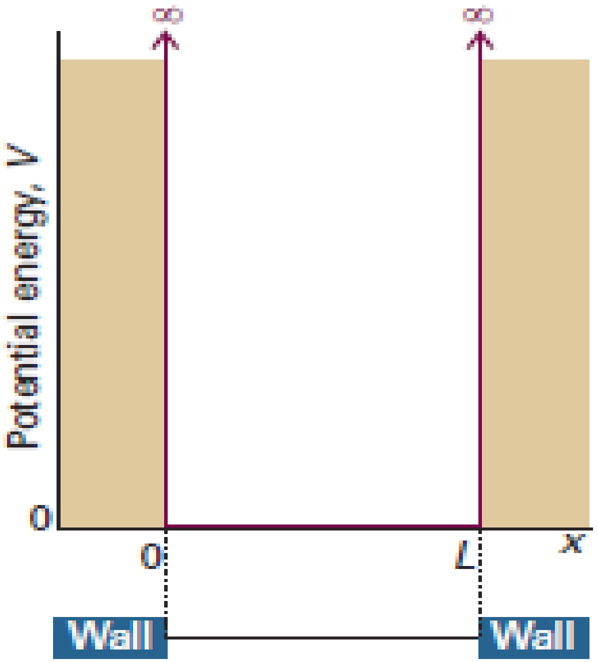
$$\sin kL = 0 \Rightarrow kL = n\pi \quad \mathrm{n}=1,2,3,4\ldots$$

For $0 \le x \le \mathrm{L} \Rightarrow V = 0$

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

Trial Solution: $\psi(x) = A\sin kx$

Energy: $E = \dfrac{\hbar^2 k^2}{2m}$



Particle in 1-D Box: Normalization

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

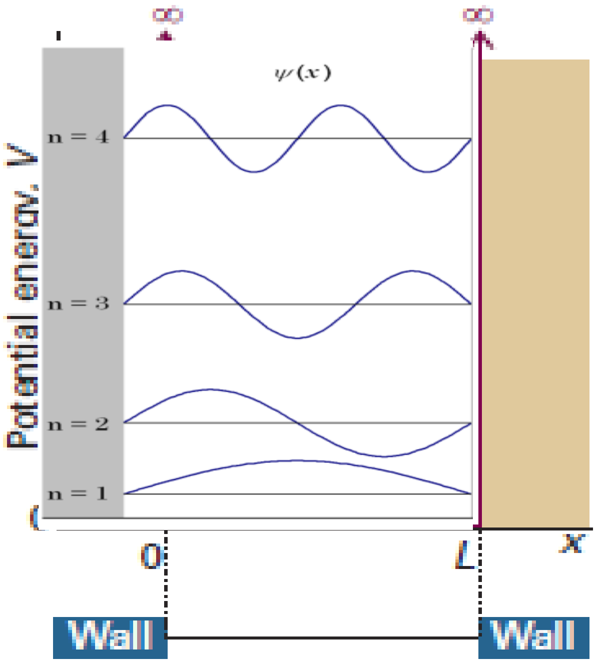
$$\psi(x) = A\sin kx = A\sin\frac{n\pi}{L}x \qquad n = 1, 2, 3, 4, \ldots..$$

$n \neq 0$, as wavefunction cannot be zero everywhere

$$\int_0^L \psi^*(x)\cdot\psi(x)\cdot dx = A^2\int_0^L \sin^2\frac{n\pi}{L}x\cdot dx = 1$$

$$\frac{1}{A^2} = \frac{1}{2}\int_0^L\left(1 - 2cos\frac{2n\pi}{L}x\right)dx \qquad = \frac{1}{2}\left[\int_0^L dx \; - \int_0^L\left(cos\frac{2n\pi}{L}x\right)dx\right] \qquad = \frac{L}{2} - 0$$

$$A = \sqrt{\frac{2}{L}} \qquad \psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$



Particle in 1-D Box: Wavefunctiona

$$(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad n = 1, 2, 3, 4, \ldots..$$

$n \neq 0$, as wavefunction cannot be zero everywhere

Orthogonality

$$\int_0^L \psi_1(x).\psi_2(x).dx = \frac{2}{L}\int_0^L \sin\frac{n_1\pi x}{L}.\sin\frac{n_2\pi x}{L}\,dx$$

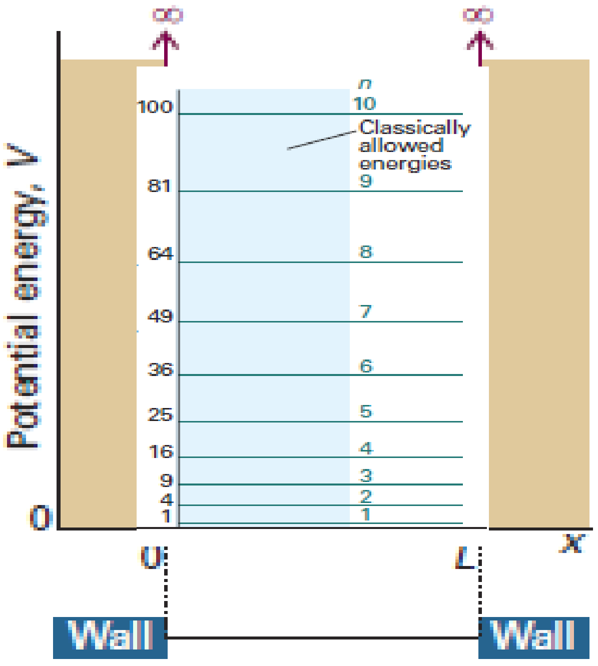
$$= \frac{1}{L}\int_0^L \left[\cos\frac{(n_1 - n_2)\pi x}{L} - \cos\frac{(n_1 + n_2)\pi x}{L}\right] dx$$

$$= 0$$

Is the first derivative continuous?

Not at $x = 0$ and $x = L$

Particle in 1-D Box: Energy



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad n = 1, 2, 3, 4, ...$$

$n \neq 0$, as wavefunction cannot be zero everywhere

- Energy is quantized!

Boundary conditions are the origin of quantization

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

$$\sin kL = 0 \quad \Rightarrow \quad \boxed{kL = n\pi} \quad \text{n=1,2,3,4...}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \qquad \text{n=1,2,3,4...}$$

- Energy separation increases with increasing values of n
- Lowest possible energy is non-zero: Zero point energy $E_1 = \dfrac{h^2}{8mL^2}$

$$h\nu = \Delta E = E_f - E_i = \frac{n_f^2 h^2}{8mL^2} - \frac{n_f^2 h^2}{8mL^2} = \left(n_f^2 - n_i^2\right)\frac{h^2}{8mL^2}$$

- Larger the box, smaller the energy of $h\nu$

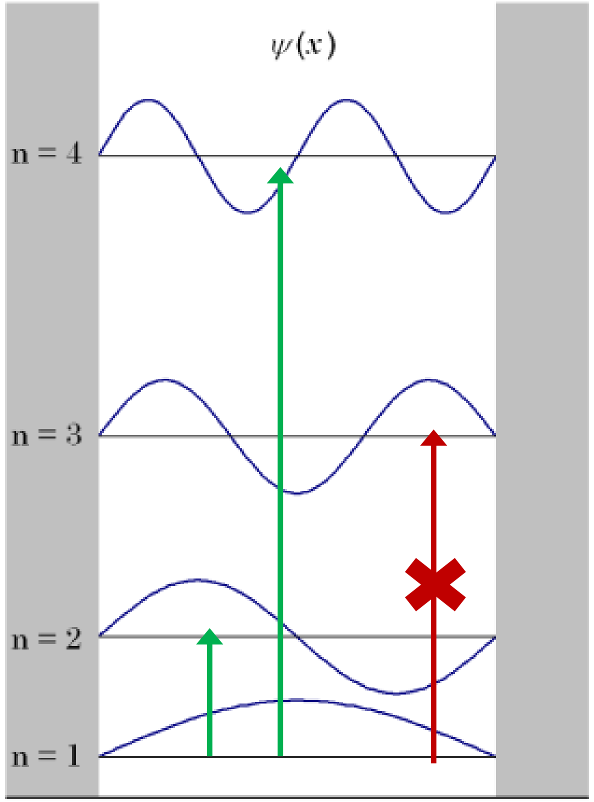
Particle in 1-D Box: Spectroscopy

Wavefunction: $y(x)=\sqrt{\frac{2}{L}}\sin\frac{np}{L}x$

n=1,3.. Symmetric wrt inversion (even function)

n=2,4.. Anti-Symmetric (odd function)

Number of Nodes (zero crossings) = n-1



Transition $\psi_1 \rightarrow \psi_2$ is allowed when

Transition Moment Integral $\langle\psi_2|\mu|\psi_1\rangle \neq 0$ $\langle\psi_2|x|\psi_1\rangle \neq 0$

$\mu = e.x$

Antisymmetric

Non-zero integral: **Symmetric** integrand

If one wave function is symmetric, then the other should be antisymmetric

Selection rule: $\Delta n = 1, 3, 5, \ldots\ldots$

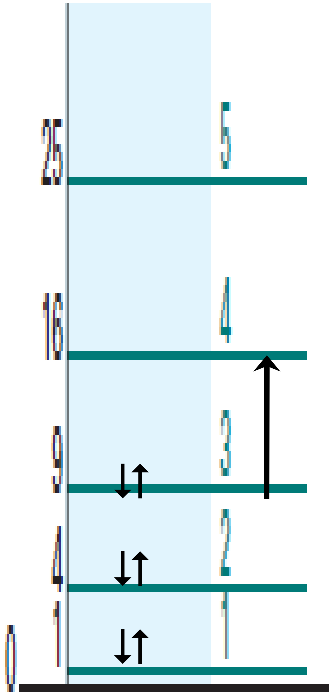
Odd to even, even to odd transitions are allowed

Particle in 1-D Box: Examples in Chemistry

Hexatriene: a linear molecule of length 7.3 Å
It absorbs at 258 nm
Use particle in a box model to explain the results.

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n = 1, 2, 3, 4, \ldots..$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \qquad \text{n=1,2,3,4...}$$



Six π electrons fill lower three levels

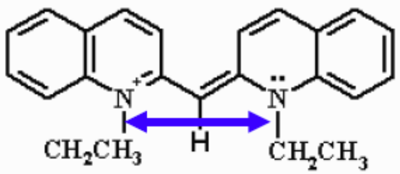
$$DE = E_f - E_i = \left(n_f^2 - n_i^2\right)\frac{h^2}{8mL^2} = \frac{hc}{l}$$

$$l = \frac{8mL^2c}{h}\left(n_f^2 - n_i^2\right) \approx 251\text{nm}$$

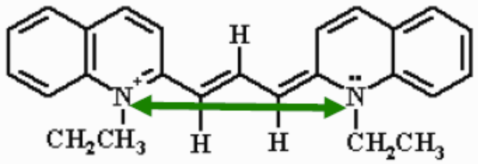
Compare with the experimental value of 258 nm
Particle in a box is a good first approximation

Particle in 1-D Box: Examples in Chemistry

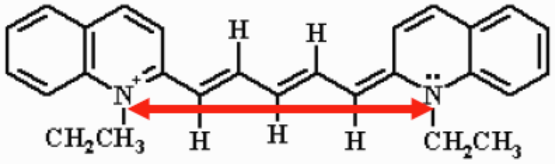
Electronic spectra of conjugated molecules



Dye A



Dye B



Dye C

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} \Rightarrow \lambda \propto L^2$$

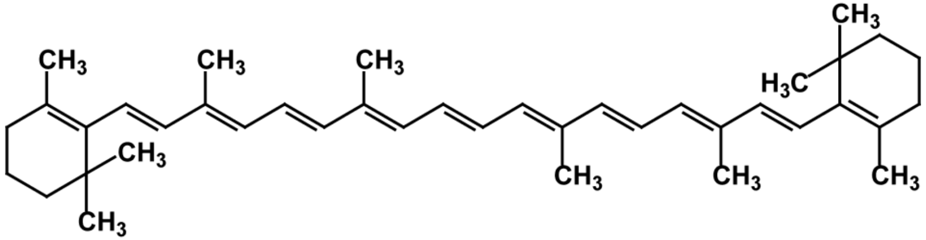
Increase in bridge length increase the emission wavelength.

Predicts correct trend and gets the wavelength almost right.

Particle in a box is a good first approximation

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, 4, \ldots..$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad n=1,2,3,4\ldots$$



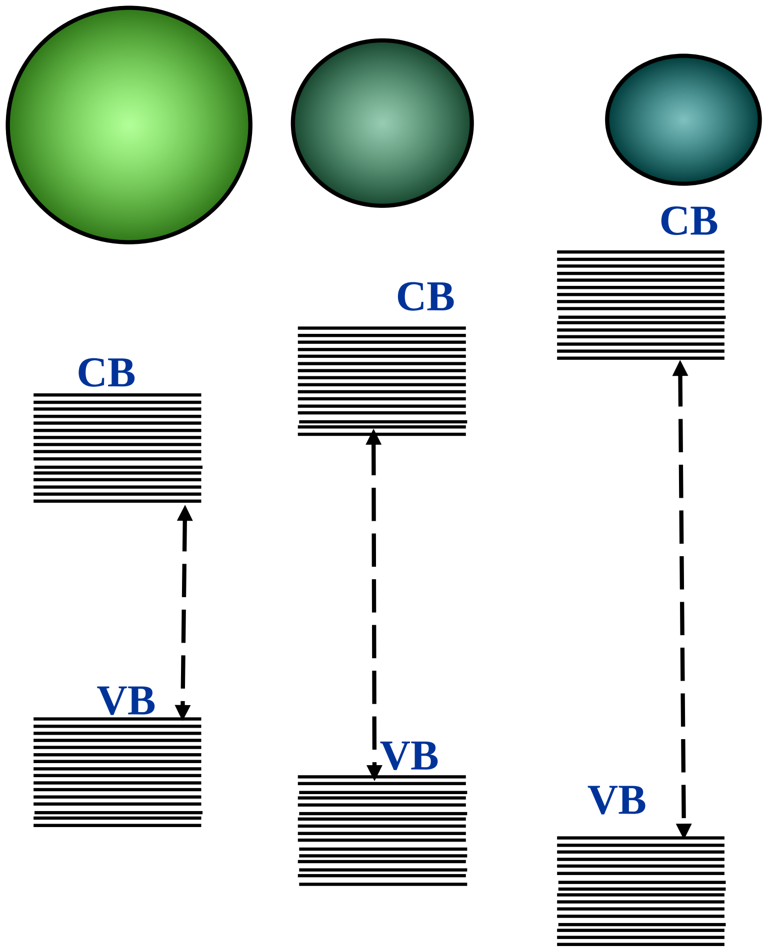
B-carotene is orange because of 11 conjugated double bonds

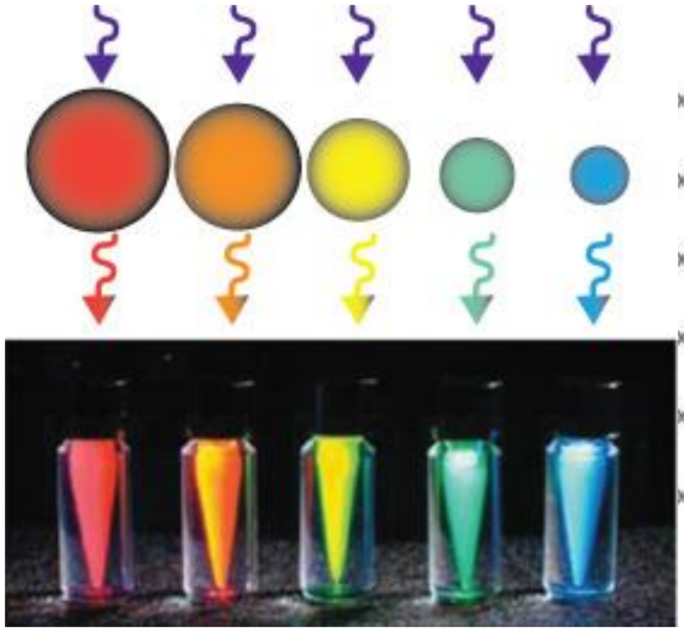
Particle in 1-D Box: Examples in Chemistry

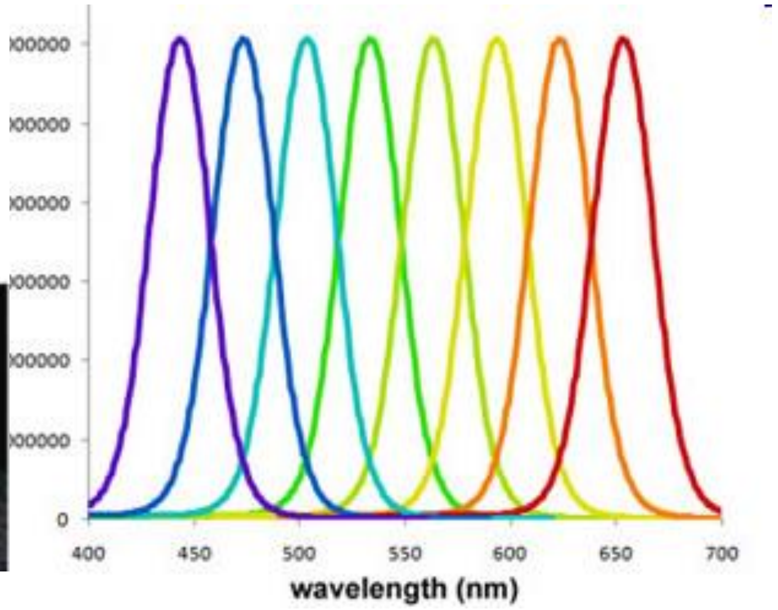
$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n = 1, 2, 3, 4, \ldots..$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \qquad n=1,2,3,4\ldots$$

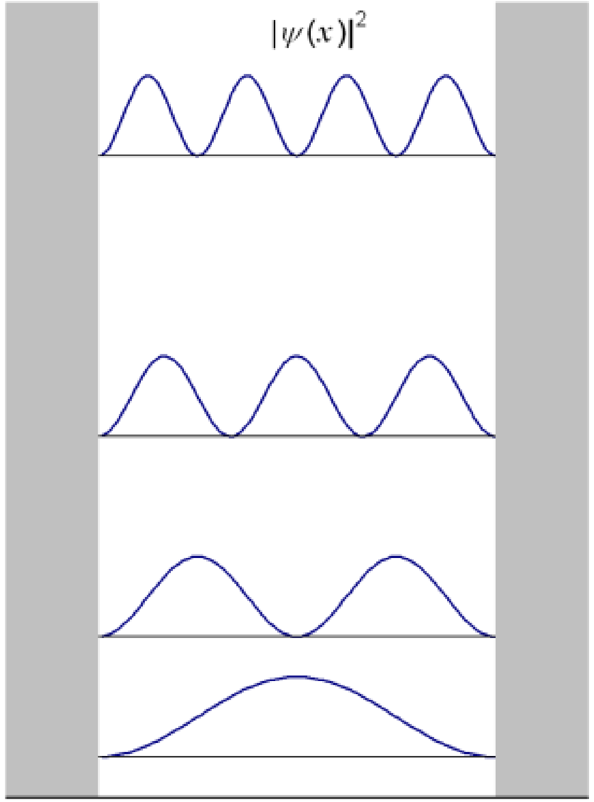
Quantum Dots – Quasi-particle (exciton) in a Box!







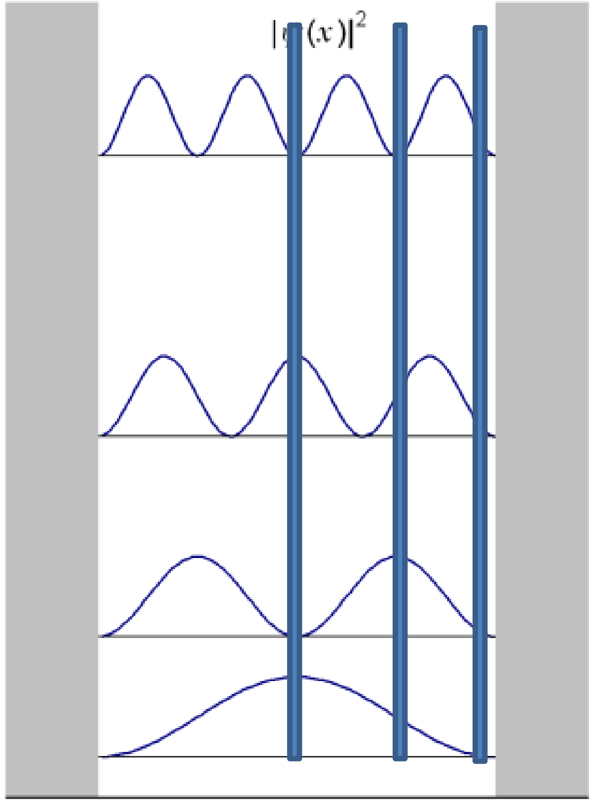
Expectation value: Position



$$\langle x \rangle = \int \psi^* \cdot x \cdot \psi \cdot dx$$

Expectation value: Position

Probability in a thin strip for different n and x values



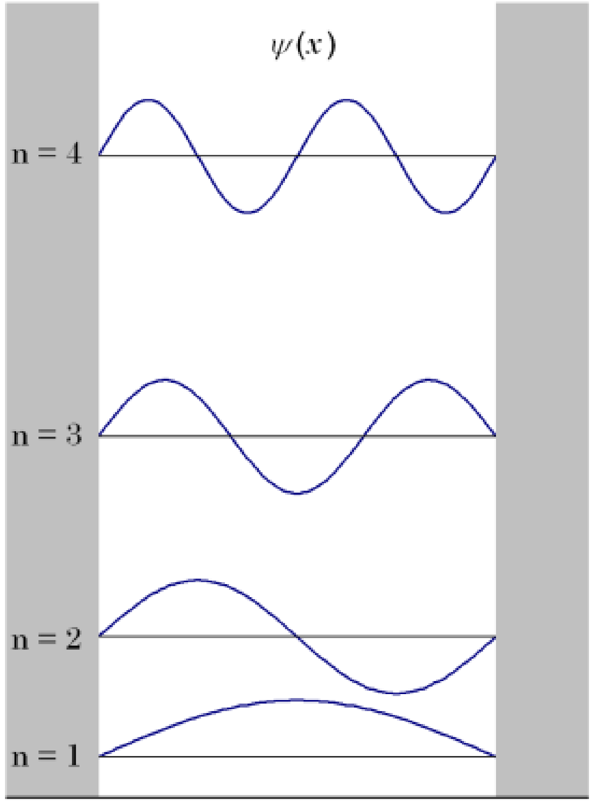
$$\langle x \rangle = \int \psi^* \cdot x \cdot \psi \cdot dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L} x \cdot x \cdot \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L} x \cdot dx$$

$$= \frac{2}{L} \int_0^L x \cdot \sin^2 \frac{n\pi}{L} x \cdot dx$$

$$= \frac{L}{2}$$

Expectation value: Momentum



$$\langle p_x \rangle = \int \psi^* \cdot \boxed{\left(-i\hbar \frac{\partial}{\partial x}\right)} \cdot \psi \cdot dx$$

Eigenfunctions:
Equal magnitude,
opposite direction

$$= -i\hbar \int_0^L \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L}x \cdot \frac{\partial}{\partial x} \cdot \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L}x \cdot dx$$

$$\psi_n = \sqrt{\frac{2}{L}} \cdot \frac{1}{i}\left[e^{\frac{in\pi x}{L}} - e^{\frac{-in\pi x}{L}}\right]$$

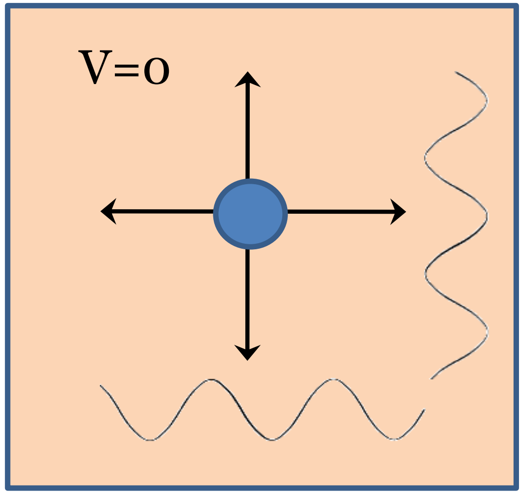
$$= \frac{-2i\hbar n\pi}{L^2} \int_0^L \sin\frac{n\pi}{L}x \cdot \cos\frac{n\pi}{L}x \cdot dx$$

$$= 0$$

Equal probability for propagation in the two directions

Particle in a 2-D box

Separation of variables



L_y

L_x

Square Box
$\Rightarrow L_x = L_y = L$

$$H = H_x + H_y$$

$$y(x,y) = y(x) \times y(y)$$

$$= \sqrt{\frac{2}{L}} \sin \frac{np}{L} x \times \sqrt{\frac{2}{L}} \sin \frac{np}{L} y$$

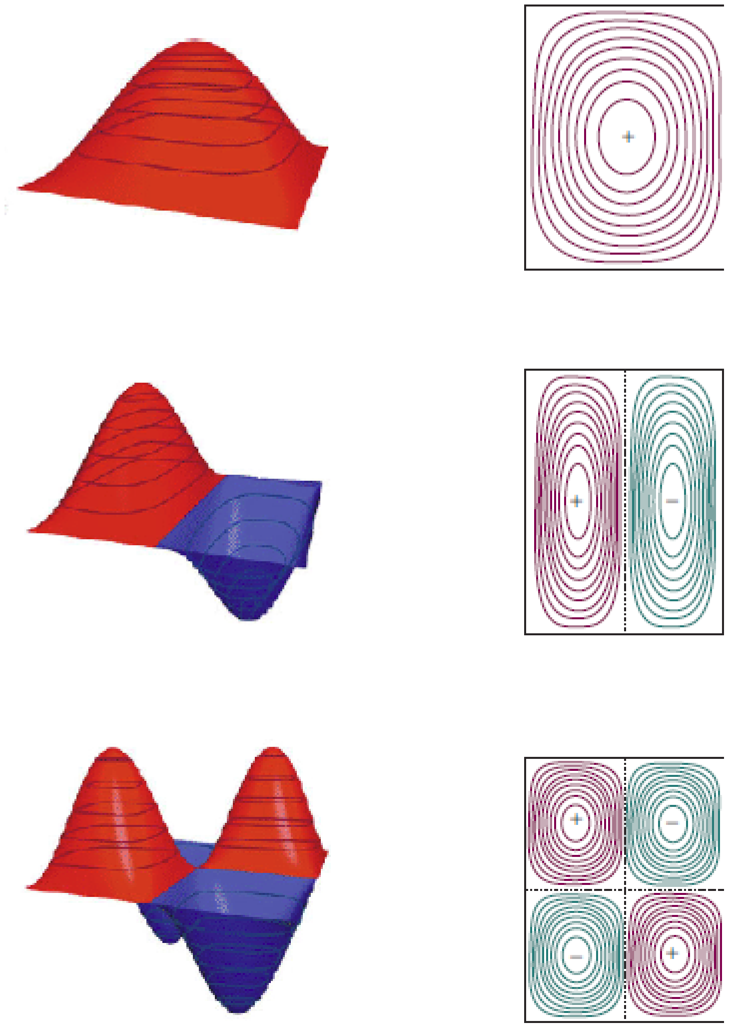
$$= \frac{2}{L} \sin \frac{np}{L} x \times \sin \frac{np}{L} y$$

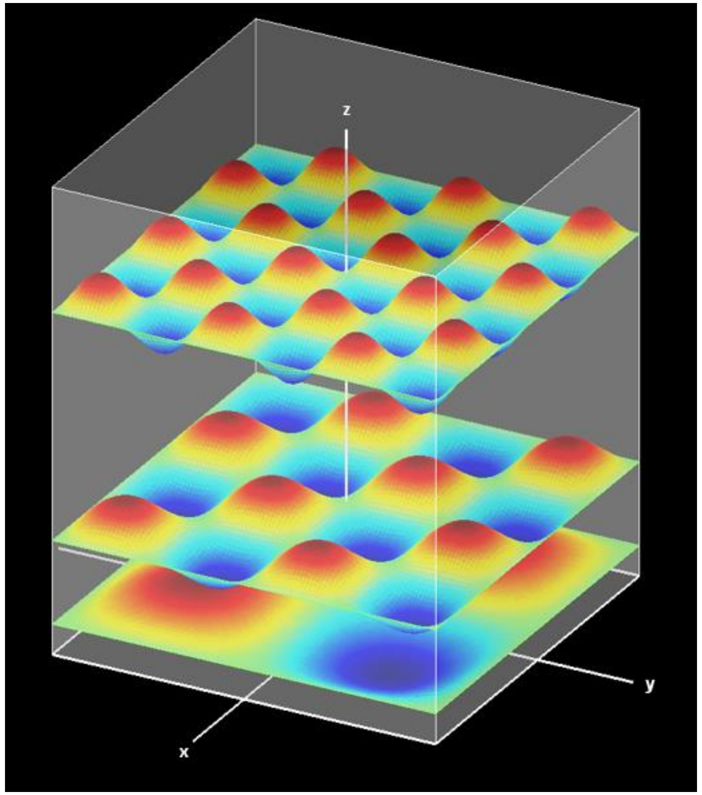
$$E_{n_x, n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2}$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right) \qquad n_x, n_y = 1,2,3,4\ldots$$

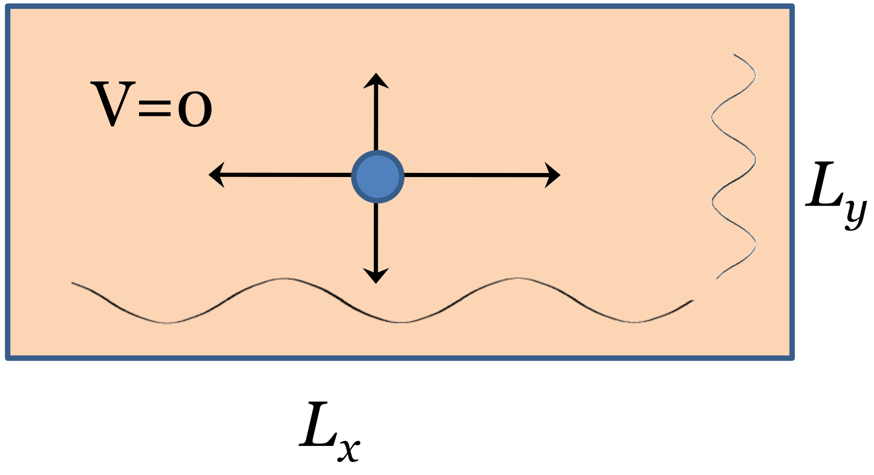
Particle in a 2-D box: Wavefuntiona





Number of nodes = n_x+n_y-2

Rectangular box



$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2}$$

$$\boxed{= \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)} \quad n_x, n_y = 1,2,3,4\ldots$$

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

$$= \sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x \times \sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$

$$= \frac{2}{\sqrt{L_x L_y}}\sin\frac{n\pi}{L_x}x \times \sin\frac{n\pi}{L_y}y$$

(1, 2) and (2, 1) levels, for example,
have same energy in square box, but not in rectangular box

Symmetry and degeneracy go hand in hand

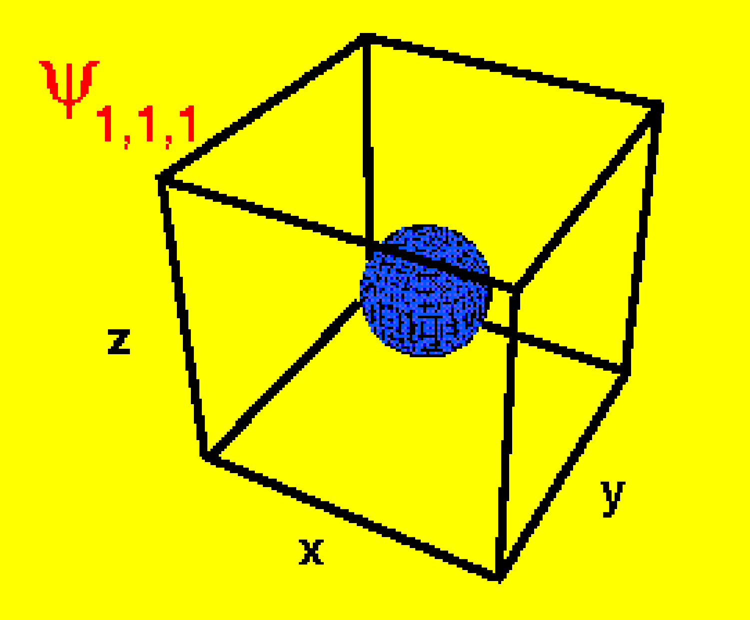
3D box

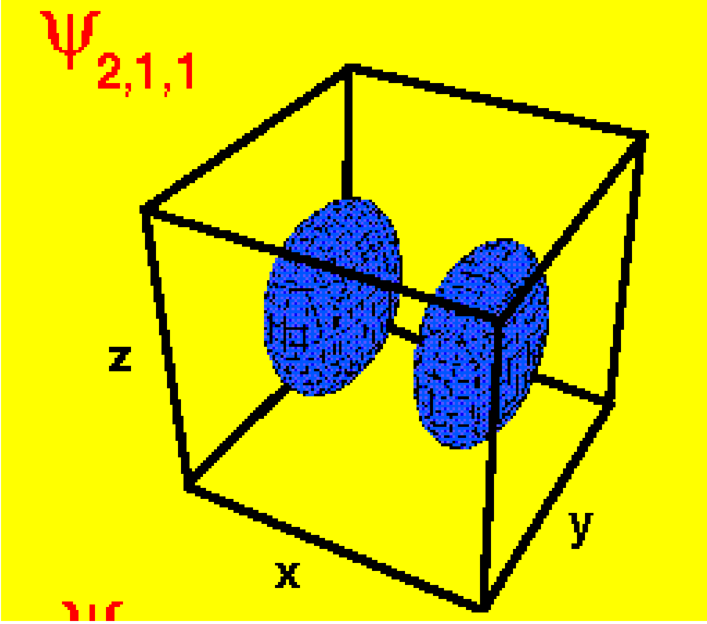
$$y(x,y,z) = y(x) \times y(y) \times y(z)$$

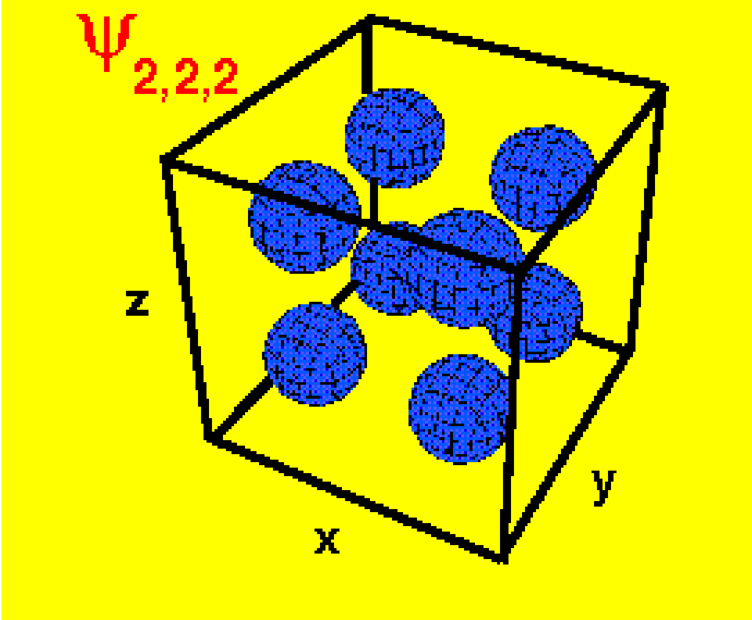
$$= \sqrt{\frac{2}{L_x}} \sin \frac{n_x p}{L_x} x \times \sqrt{\frac{2}{L_y}} \sin \frac{n_y p}{L_y} y \times \sqrt{\frac{2}{L_z}} \sin \frac{n_z p}{L_z} z$$

$$E_{n_x, n_y, n_z} = E_{n_x} + E_{n_y} + E_{n_z}$$

$$= \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2} + \frac{n_z^2 h^2}{8mL_z^2} \quad n_x, n_y, n_z = 1,2,3,4 \ldots$$







Particle in a box: Take home messages

- Schrodinger equation is **exactly solvable**
- Boundary conditions: **Quantization**
- More **nodes** in wavefunction, higher is the associated **energy**
- Eigenfunction of **linear momentum** operator
- **Simple** model, finds **application** in Chemistry
- Increase in dimensionality: **Separation of variable**
- **Symmetry** and **degeneracy** go hand in hand
- Beyond 3D functions
- Testing ground for more **sophisticated treatment**

What happens if the potential barrier is finite?