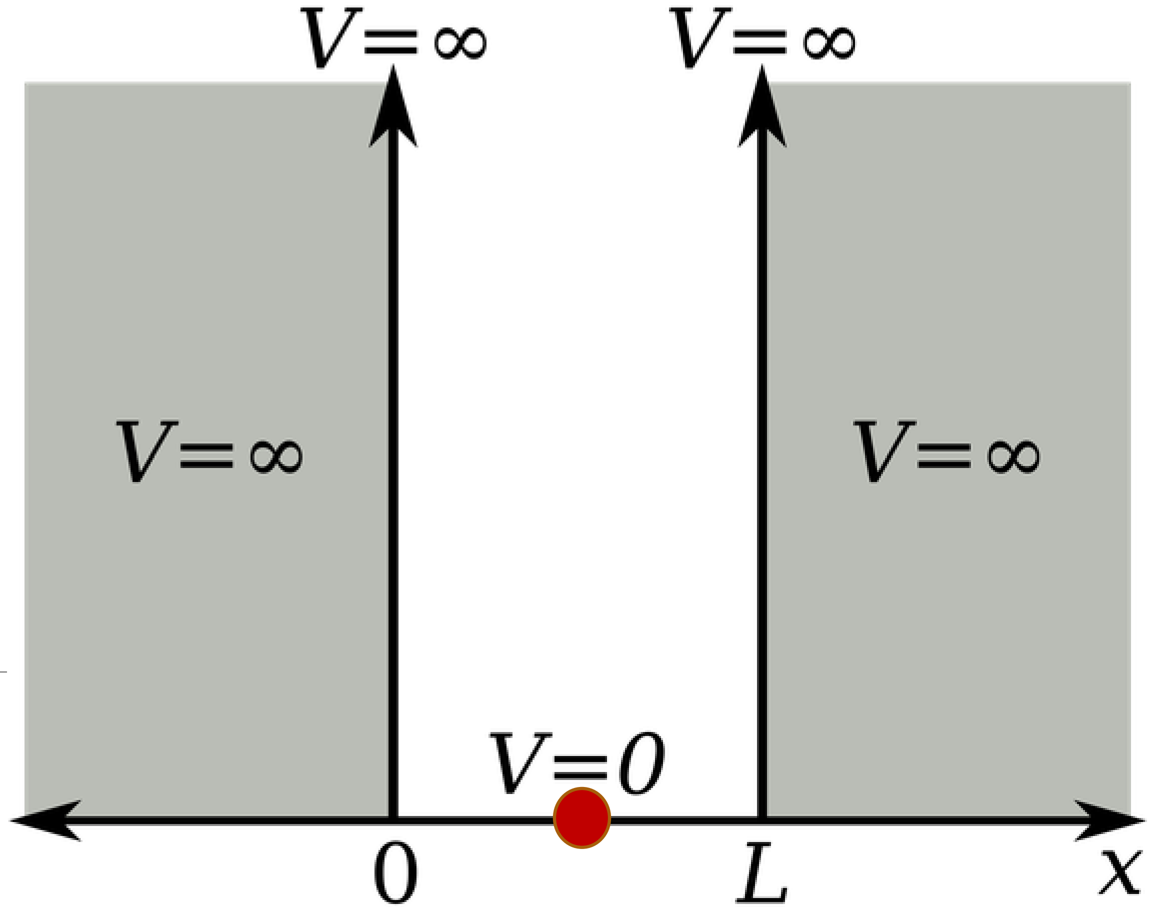
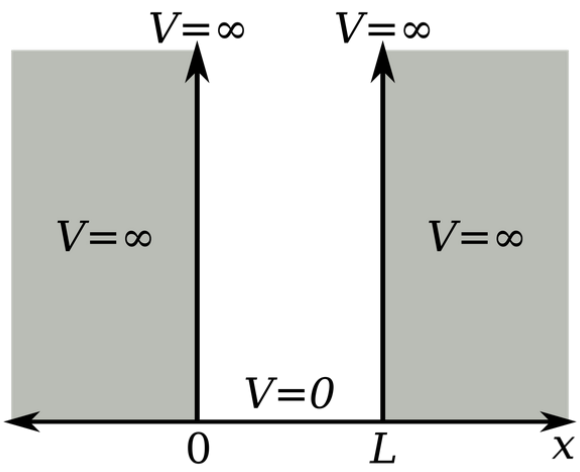
Particle in an one dimensional box



$V(x) = 0$ when $0 \le x \le L$

$= \infty$ at any other values of x

Particle in an one dimensional box



V(x) = 0 when 0≤x≤L

= ∞ at any other values of x

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

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

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

Normalization condition not satisfied

Ψ(x<0) = 0; Ψ(x>L) = 0

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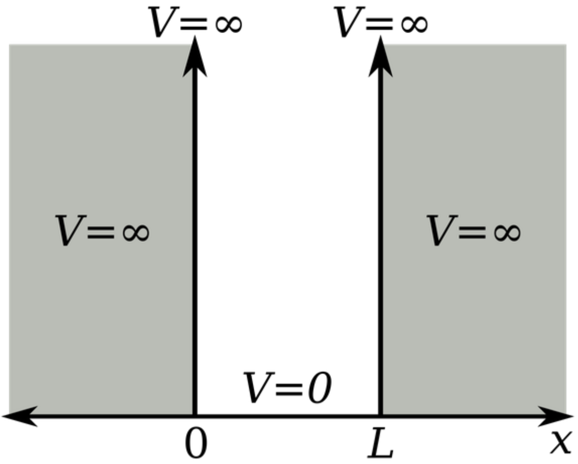


V(x) = 0 when 0≤x≤L

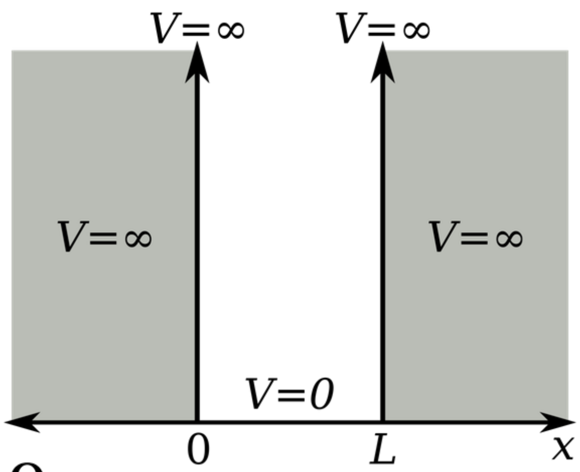
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$

Try with a trial solution:

Ψ(x) = A sin*kx*+ B cos*kx*

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

Particle in an one dimensional box



V(x) = 0 when 0≤x≤L

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

Boundary Condition $\quad x = 0 \quad \Rightarrow \quad \psi(x) = 0$

$$\psi(x) = A\sin kx \qquad \because \cos 0 = 1$$

Boundary Condition $\quad x = L \quad \Rightarrow \quad \psi(L) = 0$

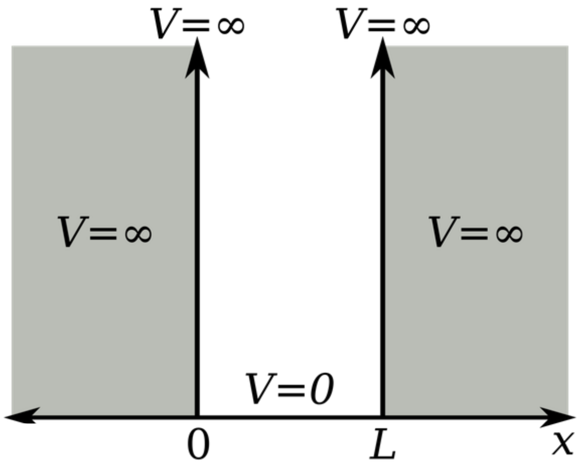
$$\psi(L) = 0 \quad \Rightarrow \quad A\sin kL = 0 \quad \Rightarrow \quad A = 0 \quad \text{or} \quad \sin kL = 0$$

But the wavefunction *ψ(x)* CANNOT be ZERO everywhere

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

Particle in an one dimensional box

V(x) = 0 when 0≤x≤L



Wavefunction $\psi(x) = A\sin kx$

Energy $E = \dfrac{\hbar^2 k^2}{2m}$ and $k = \dfrac{n\pi}{L}$

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

Particle in an one dimensional box

$$\psi(x) = A\sin kx$$

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad k = \frac{n\pi}{L}$$

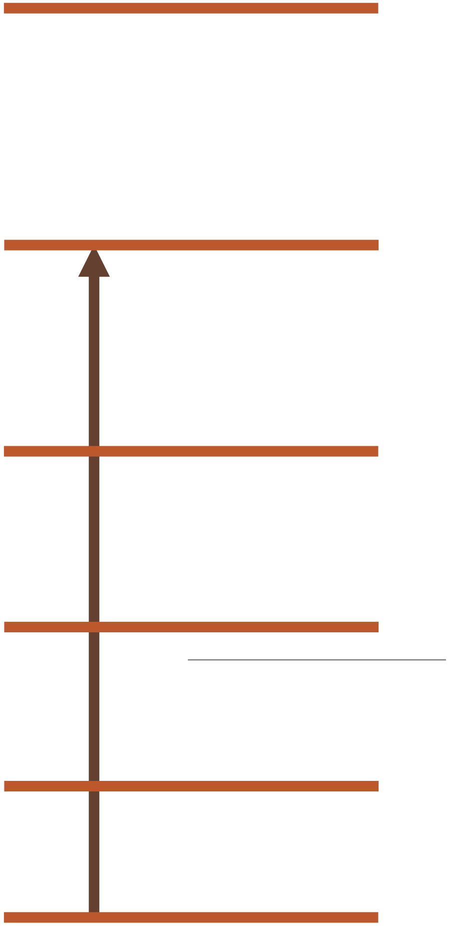
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad n=1,2,3,4\ldots$$

n	E_n /$(h^2/8mL^2)$	ΔE
6	36	
		11
5	25	
		9
4	16	
		7
3	9	
		5
2	4	
		3
1	1	

- Energy is no longer continuous but has discrete values;
- Quantization of energy
- Energy separation increases with increasing values of n

Particle in an one dimensional box

$$\psi(x) = A\sin kx$$



$$E = \frac{\hbar^2 k^2}{2m} \text{ and } k = \frac{n\pi}{L}$$

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

Spectroscopy:

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

Particle in an 1D box: Wavefunction

$$\psi(x) = A\sin kx \quad k = \frac{n\pi}{L}$$

Values of A:

$\Psi(x) = A \sin\frac{n\pi}{L}x$

Normalization Condition

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

$$\int_0^L \sin^2 kx\,.\,dx = [\frac{x}{2} - \frac{1}{4k} Sin\ 2kx\,]\,_0^L$$

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

So, $A^2 \,.\, \frac{L}{2} = 1;\ |A| = \sqrt{\frac{2}{L}}$

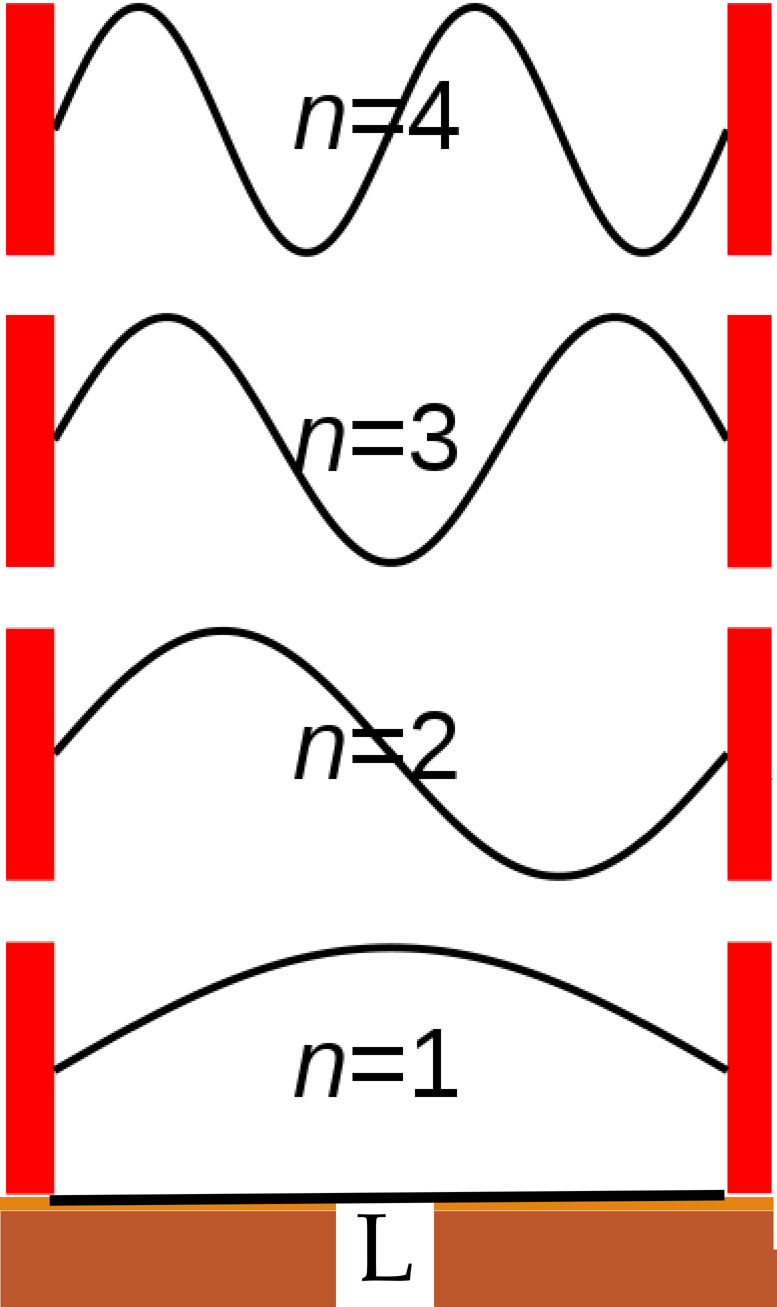
Particle in an 1D box: Wavefunction

$\boldsymbol{A = \pm\sqrt{\frac{2}{L}}}$,

A need not to be real, it could be complex
We could use any complex number with absolute value of $\sqrt{\frac{2}{L}}$ like A= $\sqrt{\frac{2}{L}}\, e^{i\propto}$
where $\propto$ is phase of A.
Considering zero phase of A,

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

Particle in an 1D box: Wavefunction



$\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{4\pi}{L}x;\ n=4;$

peaks@ x=L/8, 3L/8, 5L/8, 7L/8

$\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{3\pi}{L}x;\ n=3;$

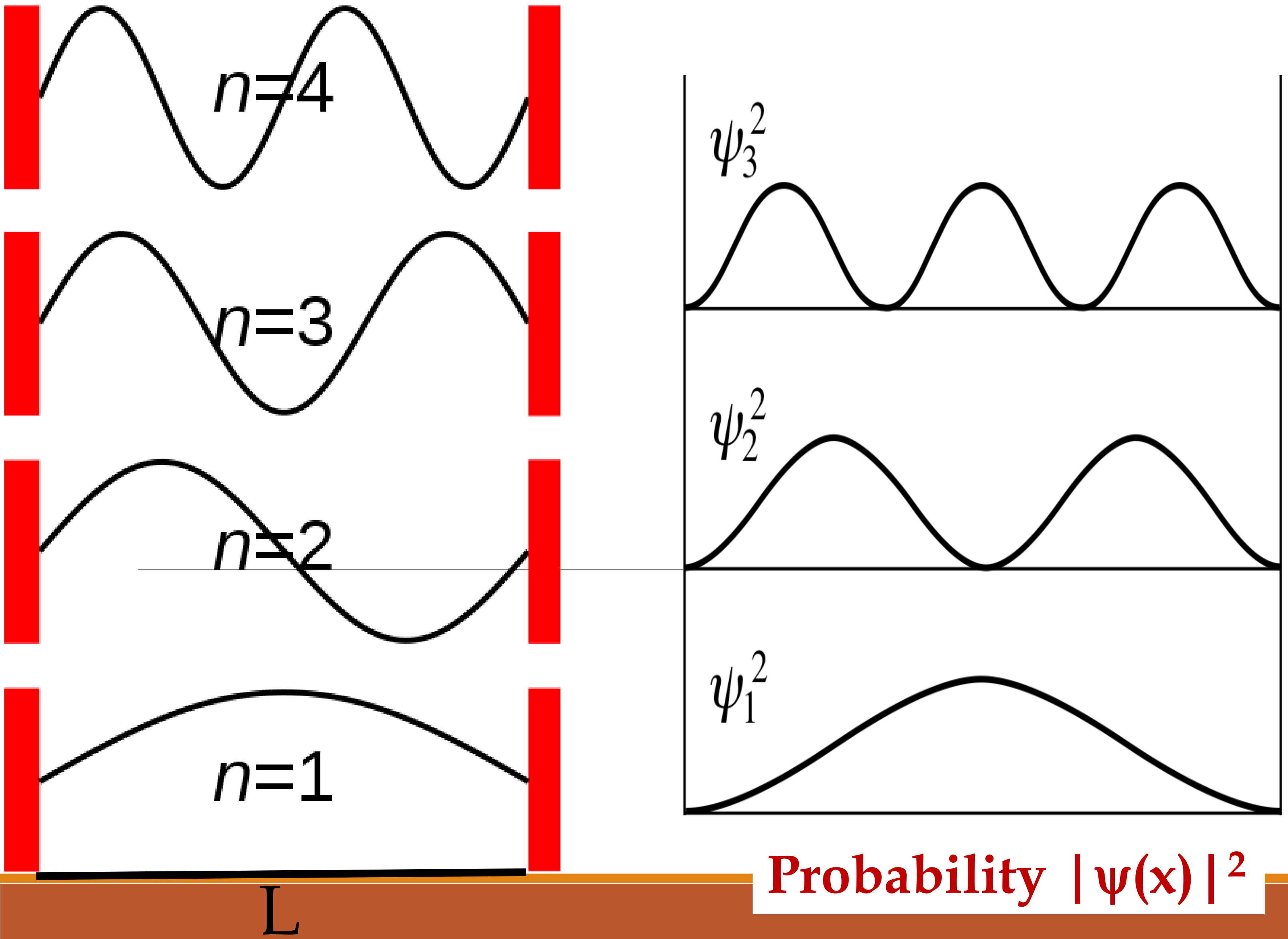
peaks@ x=L/6, L/2, 5L/6

$\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{2\pi}{L}x;\ n=2;$

peaks@ x=L/4, 3L/4

$\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi}{L}x;\ n=1;$ peak@ x=L/2

Particle in an 1D box: Wavefunction



Probability $|\psi(x)|^2$

Expectation values: Position

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

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

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

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

Expectation values: Momentum

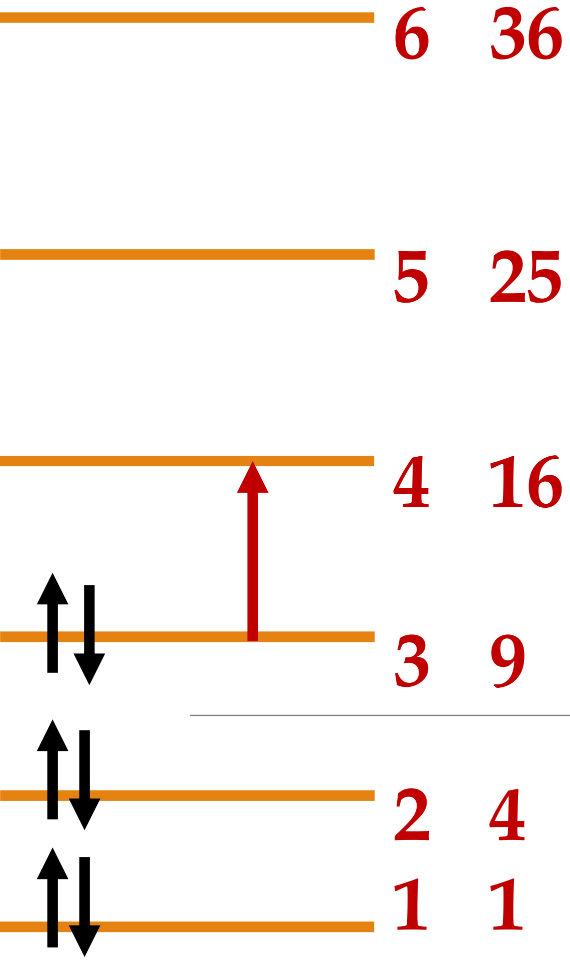
$$\langle p_x \rangle = \int \psi^* \cdot \left(-i\hbar \frac{\partial}{\partial x} \right) \cdot \psi \cdot dx$$

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

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

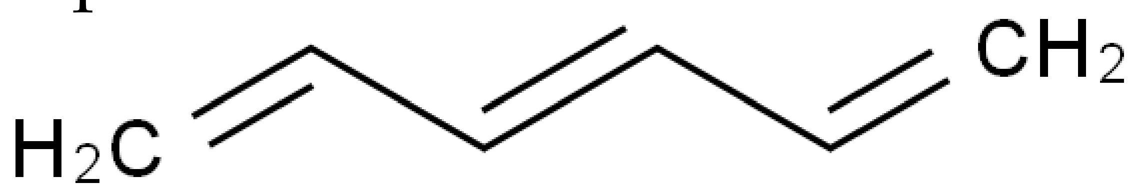
$$= 0$$

Application in Chemistry



Six π electron fill lower three levels

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



$$\Delta E = \frac{h^2}{8mL^2}(n_f^2 - n_i^2) = \frac{hc}{\lambda}$$

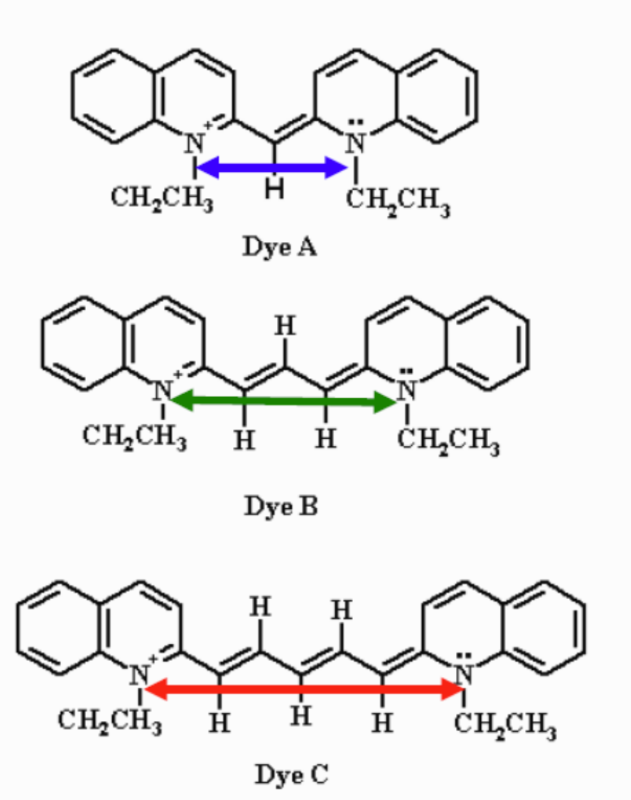
M=mass of electron; L=length of the molecule

$$\lambda = \frac{1758}{(n_f^2 - n_i^2)}\ \text{nm}$$

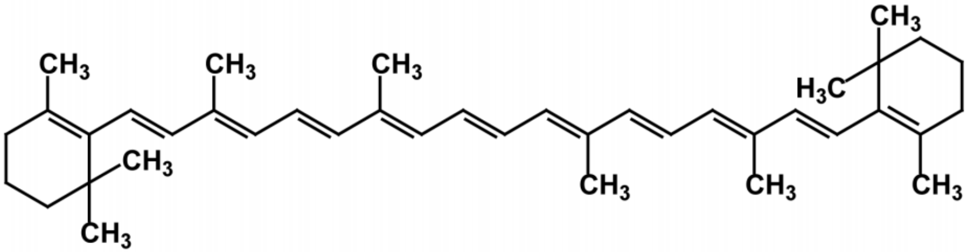
$$\lambda = 251\ \text{nm}$$

Application in Chemistry

Electronic spectra of conjugated molecules



$$\frac{h^2}{8mL^2}\left(n_f^2 - n_i^2\right) = \frac{hc}{\lambda}$$



B-carotene is orange because of 11 conjugated double bonds

Particle in an 2D box

$$\widehat{H}\cdot\psi(x,y)=\widehat{H}\cdot\left(\psi(x)\cdot\psi(y)\right)$$

$$=\left[\widehat{H}_x+\widehat{H}_y\right]\left(\psi(x)\cdot\psi(y)\right)$$

$$=\psi(y)\cdot\widehat{H}_x\cdot\psi(x)+\psi(x)\cdot\widehat{H}_y\cdot\psi(y)$$

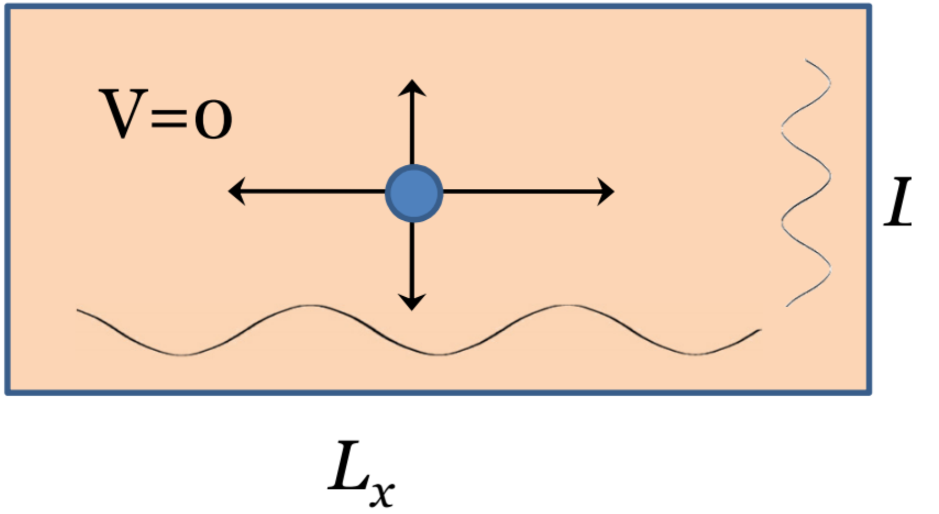
$$=\psi(y)\cdot E_x\cdot\psi(x)+\psi(x)\cdot E_y\cdot\psi(y)$$

$$=E_x\cdot\psi(x)\cdot\psi(y)+E_y\cdot\psi(x)\cdot\psi(y)$$

$$=\left(E_x+E_y\right)\cdot\left(\psi(x)\cdot\psi(y)\right)$$

$$=\left(E_x+E_y\right)\cdot\left(\psi(x,y)\right)$$

Particle in an 2D box



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

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

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

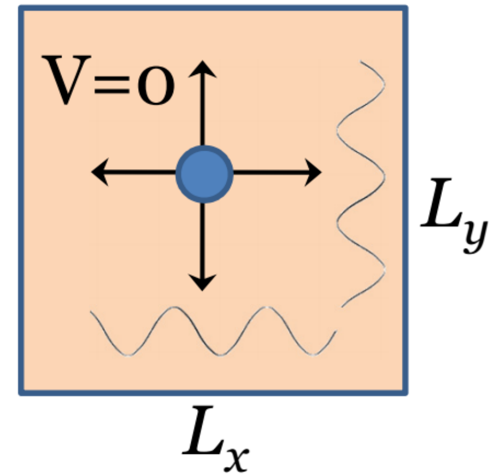
$$E_{n_x,n_y}=E_{n_x}+E_{n_y}$$

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

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

Particle in an 2D box: Square

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$
$$= \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x\cdot\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}y$$
$$= \frac{2}{L}\sin\frac{n\pi}{L}x\cdot\sin\frac{n\pi}{L}y$$



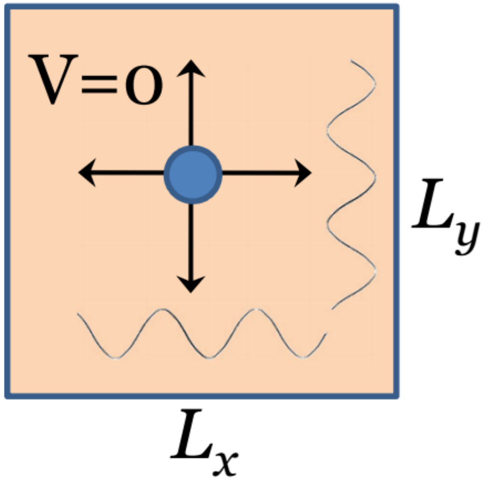
Square Box
$\Rightarrow L_x = L_y = L$

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

Particle in an 2D box: Square

$$\psi_{1,2} = \psi_1 \cdot \psi_2 = \frac{2}{L}\sin\frac{\pi}{L}x \cdot \sin\frac{2\pi}{L}y$$

$$E_{1,2} = E_1 + E_2 = \frac{5h^2}{8mL^2}$$



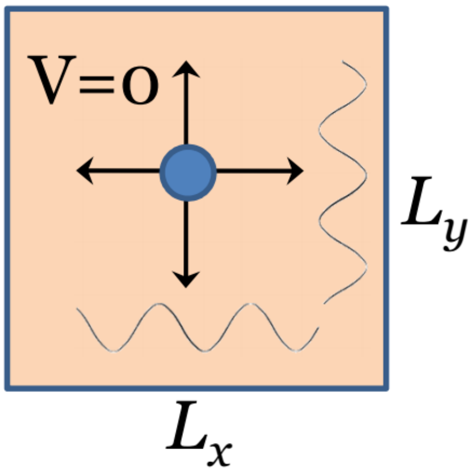
Square Box
$\Rightarrow L_x = L_y = L$

$$\psi_{2,1} = \psi_2 \cdot \psi_1 = \frac{2}{L}\sin\frac{2\pi}{L}x \cdot \sin\frac{\pi}{L}y$$

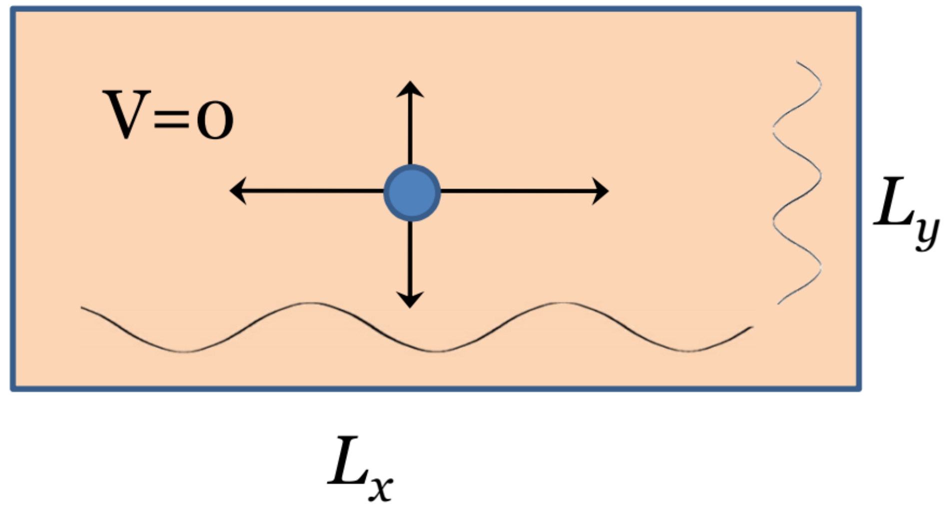
$$E_{2,1} = E_2 + E_1 = \frac{5h^2}{8mL^2}$$

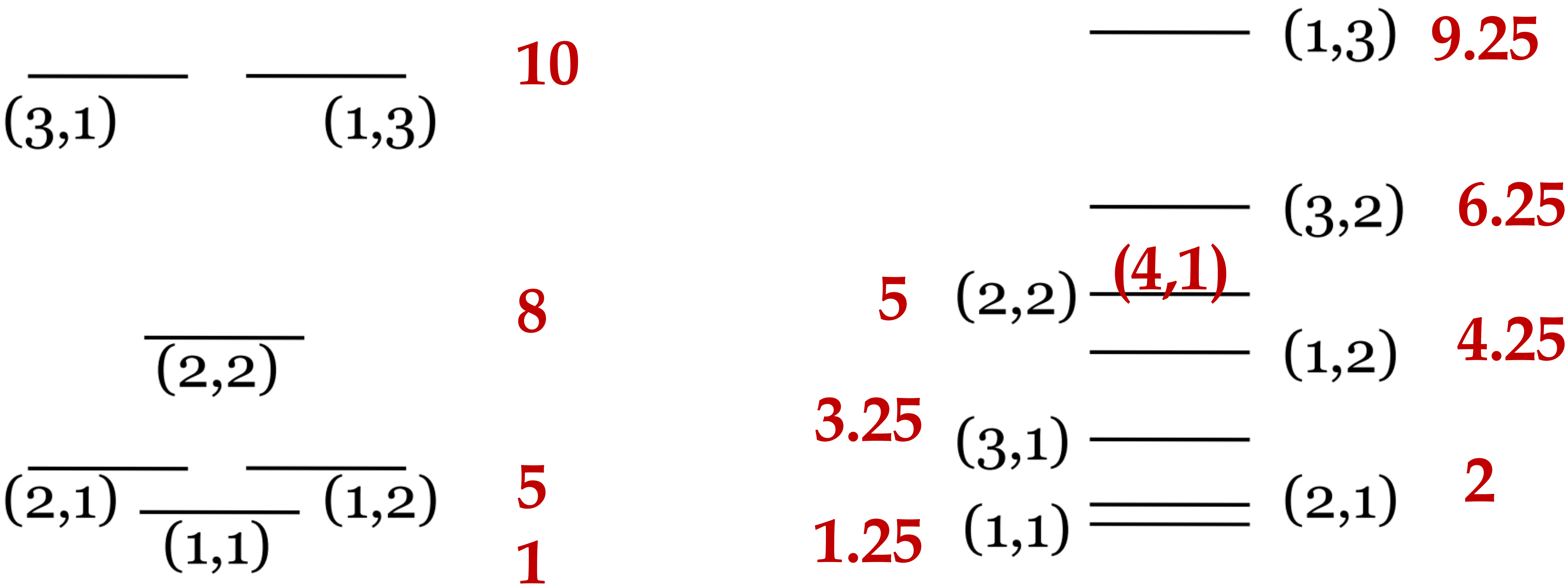
$E_{1,2} = E_{2,1}$; $\Psi_{1,2}$ and $\Psi_{2,1}$ are degenerate wavefunctions

Particle in an 2D box Symmetry/Energy

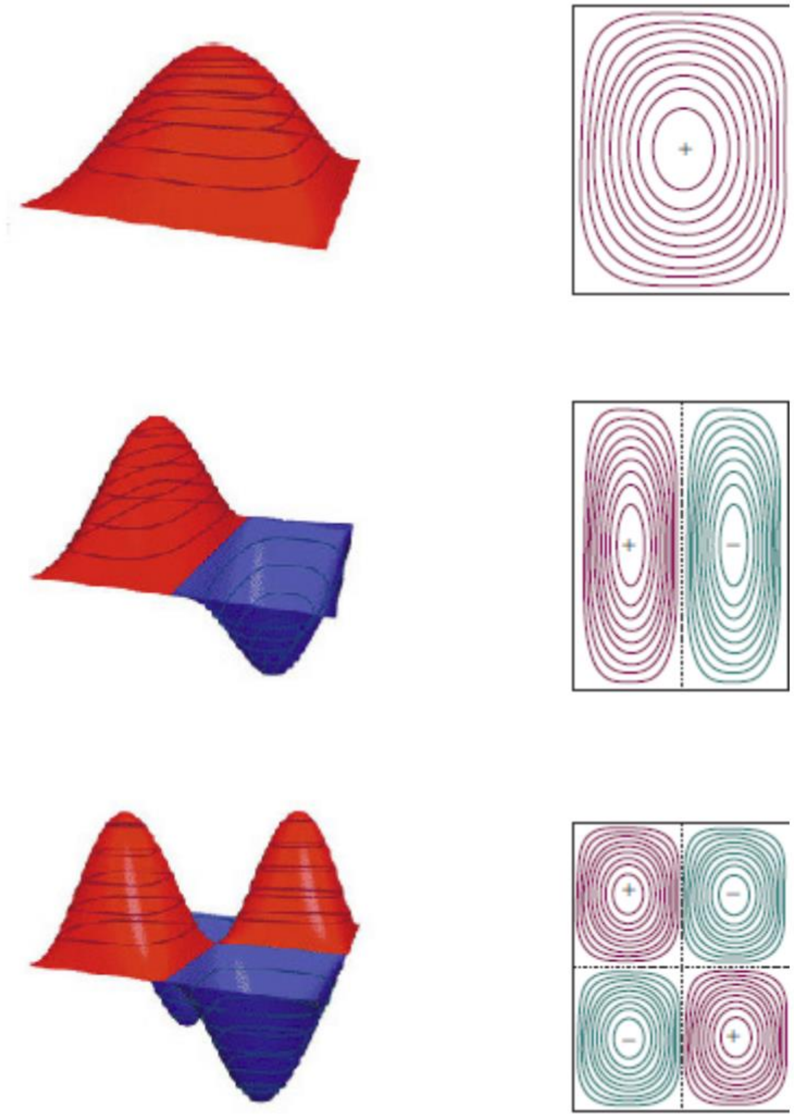


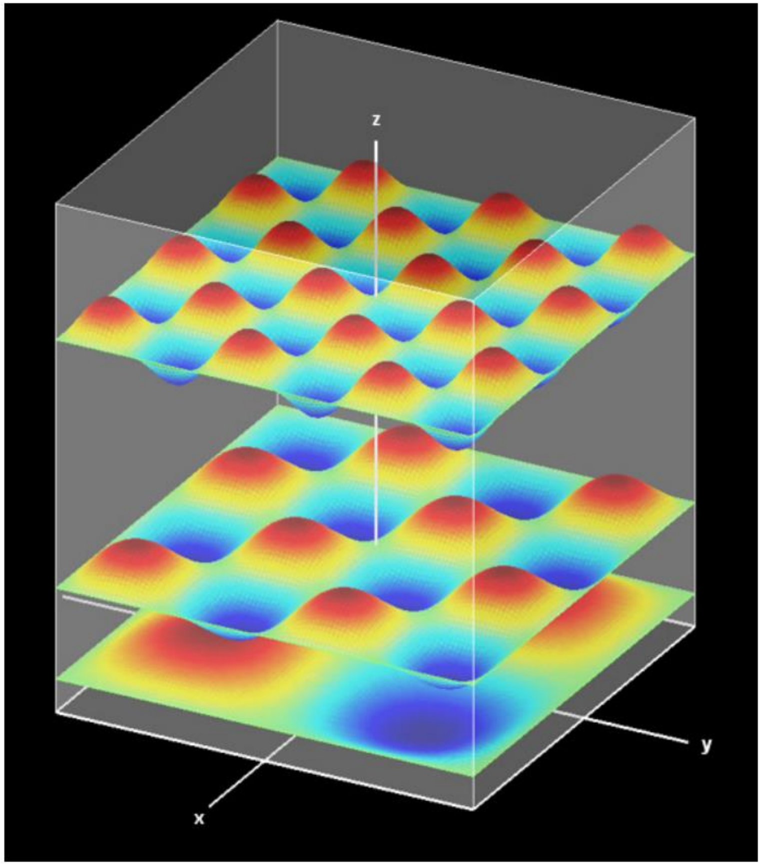
$L_x=2L_y$





Particle in an 2D box: Wavefunction





Number of nodes = n_x+n_y-2

Particle in an 3D box

$$\psi(x,y,z)=\psi(x)\cdot\psi(y)\cdot\psi(z)$$

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

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

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