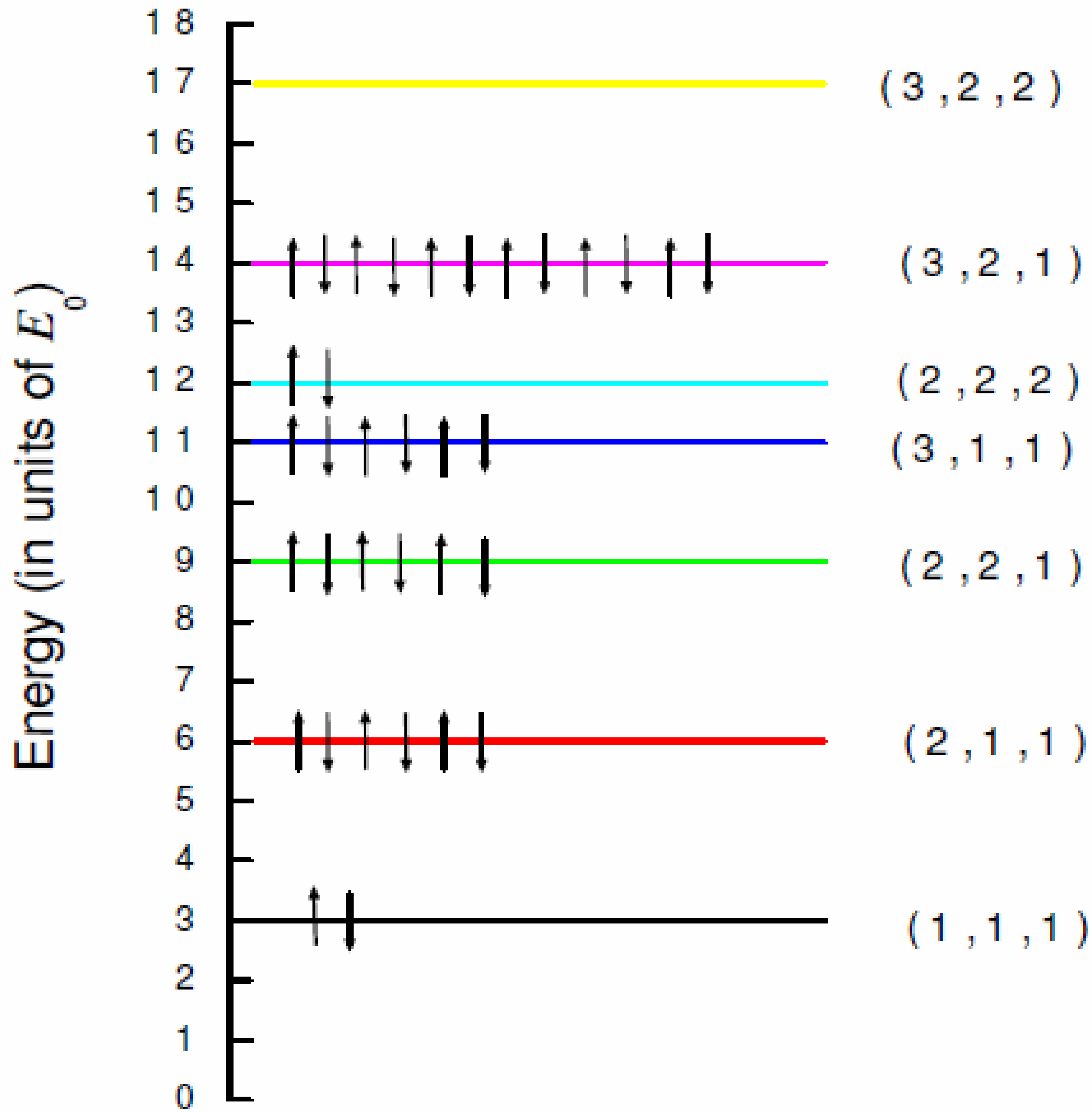
Particle in a three dimensional (3D) box

Reading Energy Diagram

$$E_0 = \frac{h^2}{8ma^2}$$

a **= side of cubic box**

Make sure that you keep track of the degeneracies. (Next Page)



Quantum Numbers and Degeneracies of the Energy Levels for a Particle Confined to a Cubic Box*

n_1	n_2	n_3	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	Threefold
1	2	1	6	
2	1	1	6	
1	2	2	9	Threefold
2	1	2	9	
2	2	1	9	
1	1	3	11	Threefold
1	3	1	11	
3	1	1	11	
2	2	2	12	None

**Note*: $n^2 = n_1^2 + n_2^2 + n_3^2$.

Example:

Degeneracies of the first 4 energy levels of a particle in a 3D box with

a=b=1.5c

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

for $a = b = 1.5c$

$$E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2(2.25)\right]$$

	$n_x^2 + n_y^2 + 2.25n_z^2$	degeneracy
E_{111}	$1^2 + 1^2 + 2.25(1)^2 = 4.25$	1
E_{211}	$2^2 + 1^2 + 2.25(1)^2 = 7.25$	2
E_{121}	$1^2 + 2^2 + 2.25(1)^2 = 7.25$	
E_{221}	$2^2 + 2^2 + 2.25(1)^2 = 10.25$	1
E_{112}	$1^2 + 1^2 + 2.25(2)^2 = 11$	1

- A particle is confined to a three-dimensional box that has sides L_1, $L_2 = 2L_1$, and $L_3 = 3L_1$. Give the quantum numbers n_1, n_2, n_3 that correspond to the lowest ten quantum states of this box.

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + \frac{n_y^2}{4} + \frac{n_z^2}{9}\right)$$

	n_x	n_y	n_z	$E_1(n_x^2 + n_y^2/4 + n_z^2/9)$
①	1	1	1	$(1 + 1/4 + 1/9)E_1 = 49/36\,E_1$
②	1	1	2	$(1 + 1/4 + 4/9)E_1 = 61/36\,E_1$
③	1	2	1	$(1 + 1 + 1/9)E_1 = 76/36\,E_1$
④	1	1	3	$(1 + 1/4 + 1)E_1 = 81/36\,E_1$
⑤	1	2	2	$1 + 1 + 4/9)E_1 = 88/36\,E_1$
⑥	1	2	3	$(1 + 1 + 1)E_1 = 108/36\,E_1$
⑦	1	1	4	$(1 + 1/4 + 16/9)E_1 = 109/36\,E_1$
⑧	1	3	1	$(1 + 9/4 + 1/9)E_1 = 121/36\,E_1$
⑨	1	3	2	$(1 + 9/4 + 4/9)E_1 = 133/36\,E_1$
⑩	1	3	3	$(1 + 9/4 + 1)E_1 = 153/36\,E_1$
⑪	2	1	1	$(4 + 1/4 + 1/9)E_1 = 157/36\,E_1$

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

- **The Schrödinger equation in 3D**
- **V=0 (free particle)**

$$-\frac{\hbar^2}{2m}\nabla^2\psi=E\psi(x,y,z)$$

$$\nabla^2=\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}$$ ← **Laplacian Operator**

$$\Psi_{n_x,n_y,n_z}(x,y,z)=\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

Wavefunction →

$$\psi_{n_x}(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi}{a}x\right)$$

$$\psi_{n_y}(y)=\sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi}{b}y\right)$$

$$\psi_{n_z}(z)=\sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi}{c}z\right)$$

↓

$$\psi_{n_xn_yn_z}(x,y,z)=\sqrt{\frac{8}{L_xL_yL_z}}\,\sin\frac{n_x\pi x}{L_x}\cdot\sin\frac{n_y\pi y}{L_y}\cdot\sin\frac{n_z\pi z}{L_z},$$

Normalization of Wavefunction in cubic box

We know that the wavefunction will be

$$\psi(x,y,z) = A\sin\left(\frac{n_1\pi x}{L}\right)\sin\left(\frac{n_2\pi y}{L}\right)\sin\left(\frac{n_3\pi z}{L}\right)$$

We apply the normalization rule

$$1 = \int_{-\infty}^{+\infty} \psi^*(\vec{r})\psi(\vec{r})dV$$

$$1 = A^2\int_{x=0}^{L}\int_{y=0}^{L}\int_{z=0}^{L}\sin^2\left(\frac{n_1\pi x}{L}\right)\sin^2\left(\frac{n_2\pi y}{L}\right)\sin^2\left(\frac{n_3\pi z}{L}\right)dxdydz$$

$$1 = A^2\int_{x=0}^{L}\sin^2\left(\frac{n_1\pi x}{L}\right)dx\int_{y=0}^{L}\sin^2\left(\frac{n_2\pi y}{L}\right)dy\int_{z=0}^{L}\sin^2\left(\frac{n_3\pi z}{L}\right)dz$$

$$1 = A^2\left(\frac{L}{2}\right)^3$$

$$A = \left(\frac{2}{L}\right)^{3/2}$$

A particle of mass m is in a 3D cube with sides L. It is in the third excited state, corresponding to $n^2 = 11$.
(a) Calculate the energy of the particle.
(b) The possible combinations of n_1, n_2, and n_3
(c) The wavefunctions for these states.

Sample Problem

2.1 Solution

2.1.1 Part (a)

Just plug in $n^2 = 11$ to the 3D box's energy.

$$E = \frac{11\hbar^2\pi^2}{2mL^2}$$

2.1.2 Part (b) and Part (c)

We'll need

$$n^2 = n_1^2 + n_2^2 + n_3^2$$

There are three ways to do this

$$11 = (3^2 + 1^2 + 1^2) = (1^2 + 3^2 + 1^2) = (1^2 + 1^2 + 3^2)$$

Corresponding to the three states and their wavefunctions

$$n_1 = 3; n_2 = 1; n_3 = 1 \quad \rightarrow \quad \psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{3\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

$$n_1 = 1; n_2 = 3; n_3 = 1 \quad \rightarrow \quad \psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{3\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

$$n_1 = 1; n_2 = 1; n_3 = 3 \quad \rightarrow \quad \psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{3\pi z}{L}\right)$$

A particle with mass m moves in a 3D box with edges $L_1 = L$, $L_2 = 2L$, and $L_3 = 2L$. Find the energies of the six lowest states. Which ones are degenerate?

1.1 Solution

We get the wavenumbers the usual way, using the boundary conditions.

$$k_1 = \frac{n_1 \pi}{L} = \sqrt{\frac{2mE_1}{\hbar^2}}$$

$$k_2 = \frac{n_2 \pi}{2L} = \sqrt{\frac{2mE_2}{\hbar^2}}$$

$$k_3 = \frac{n_3 \pi}{2L} = \sqrt{\frac{2mE_3}{\hbar^2}}$$

Solving for the energies gives

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2$$

$$E_2 = \frac{\hbar^2 \pi^2}{2mL^2} \frac{n_2^2}{4}$$

$$E_3 = \frac{\hbar^2 \pi^2}{2mL^2} \frac{n_3^2}{4}$$

(next page)

Or

$$E = E_1 + E_2 + E_3 = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{4} \right)$$

The ground state is when $n_1 = n_2 = n_3 = 1$ leading to

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{1^2}{4} + \frac{1^2}{4}\right) = \frac{3\hbar^2\pi^2}{4mL^2}$$

There is a twofold degeneracy in the first excited state: $n_1 = n_2 = 1; n_3 = 2$ or $n_1 = n_3 = 1; n_2 = 2$

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{2^2}{4} + \frac{1^2}{4}\right) = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{1^2}{4} + \frac{2^2}{4}\right) = \frac{9\hbar^2\pi^2}{8mL^2}$$

The second excited state is unique and will be $n_1 = 1; n_2 = n_3 = 2$.

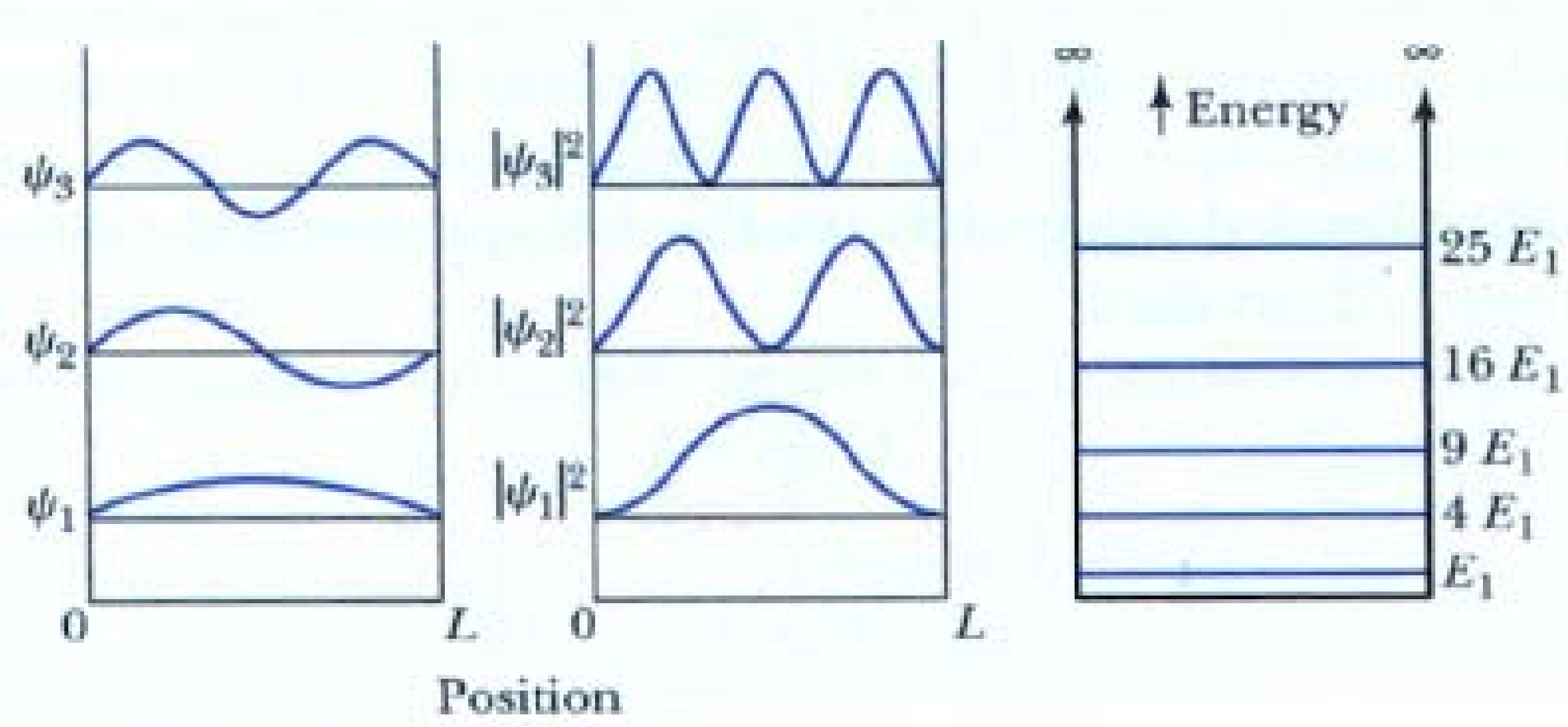
$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{2^2}{4} + \frac{2^2}{4}\right) = \frac{3\hbar^2\pi^2}{mL^2}$$

Again, there is a twofold degeneracy in the third excited state $n_1 = 1; n_2 = 2; n_3 = 3$ or $n_1 = 1; n_2 = 3; n_3 = 2$

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{2^2}{4} + \frac{3^2}{4}\right) = \frac{\hbar^2\pi^2}{2mL^2}\left(1^2 + \frac{3^2}{4} + \frac{2^2}{4}\right) = \frac{17\hbar^2\pi^2}{8mL^2}$$

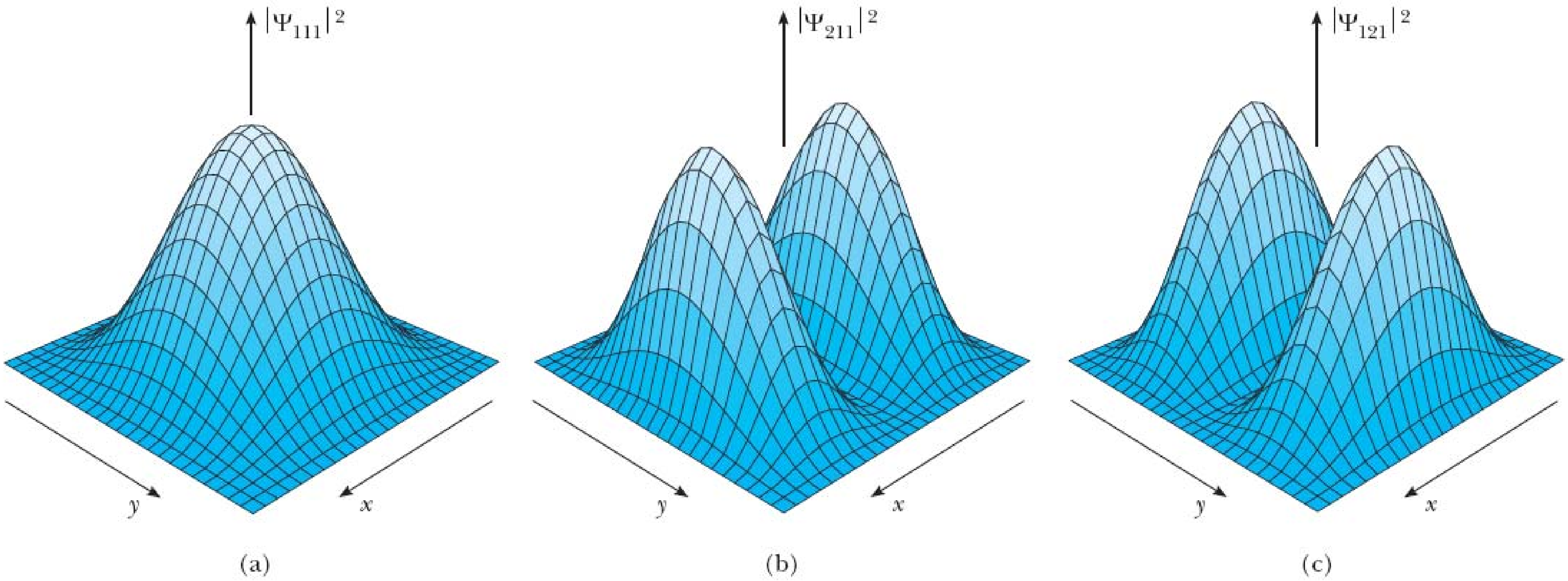
These are the lowest six states. 1 ground + 2 first excited + 1 second excited + 2 third excited = 6.

Wavefunctions and Probability Density



Particle in a 1-D box

Wavefunction for Particle in a box (in 3D)



Particle in a 2D box

$$E_{n_1} + E_{n_2} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2\right) = E_{n_1 n_2}$$

(Think about degeneracy in a square box)

$$\Psi_{n_1 n_2}(x,y) = X_{n_1}(x).Y_{n_2}(y)$$

Examples of quantum numbers, wave functions and energies:

$n_1 = 1, n_2 = 1$	$\psi_{11}(x,y) = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)$	$E_{11} = \frac{h^2}{8mL^2}(1^2 + 1^2) = \frac{h^2}{4mL^2}$
$n_1 = 2, n_2 = 1$	$\psi_{21}(x,y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)$	$E_{21} = \frac{h^2}{8mL^2}(2^2 + 1^2) = \frac{5h^2}{8mL^2}$
$n_1 = 1, n_2 = 2$	$\psi_{12}(x,y) = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$	$E_{12} = \frac{h^2}{8mL^2}(1^2 + 2^2) = \frac{5h^2}{8mL^2}$
$n_1 = 2, n_2 = 2$	$\psi_{22}(x,y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$	$E_{22} = \frac{h^2}{8mL^2}(2^2 + 2^2) = \frac{h^2}{mL^2}$
$n_1 = 3, n_2 = 2$	$\psi_{32}(x,y) = \frac{2}{L}\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$	$E_{32} = \frac{h^2}{8mL^2}(3^2 + 2^2) = \frac{13h^2}{8mL^2}$
$n_1 = 2, n_2 = 3$	$\psi_{23}(x,y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{3\pi y}{L}\right)$	$E_{23} = \frac{h^2}{8mL^2}(2^2 + 3^2) = \frac{13h^2}{8mL^2}$

ψ_{11}

ψ_{21}

ψ_{22}