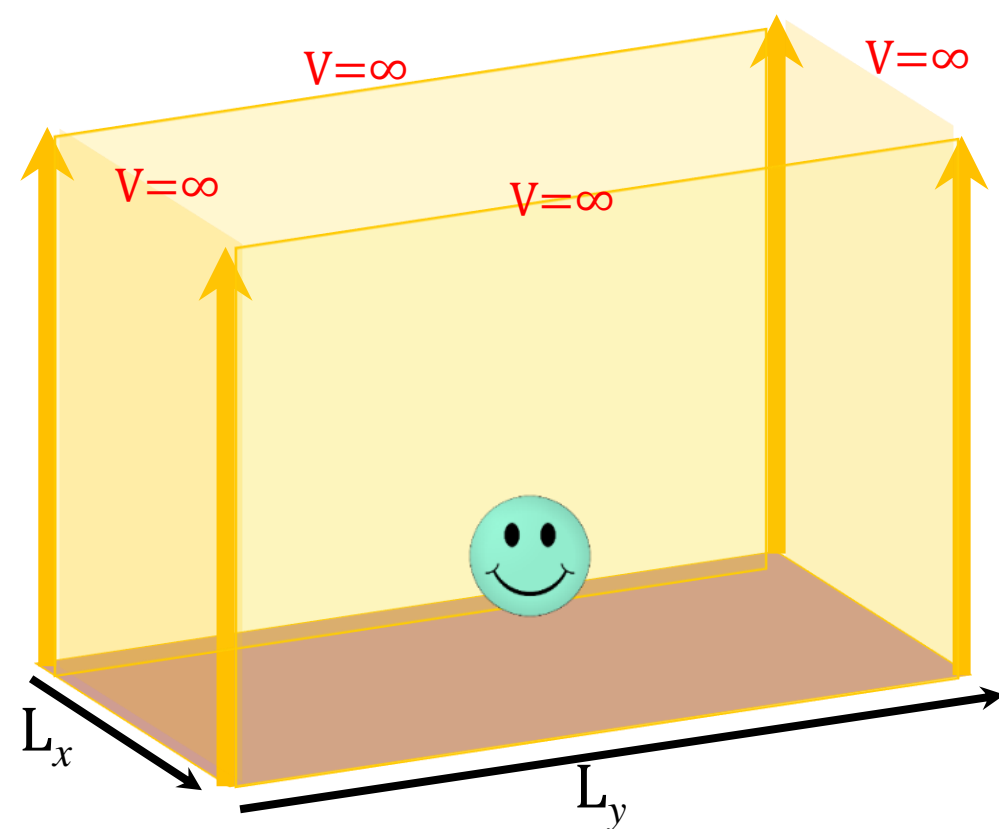


Particle in a two-dimensional box



$$\hat{V}(x, y) = 0 \text{ for } 0 \leq x \leq L_x \text{ and } 0 \leq y \leq L_y \\ = \infty \text{ Otherwise}$$

Boundary condition or trivial solution

$$\psi(x, y) = 0 \text{ for } x, y \leq 0 \text{ and } x \geq L_x \text{ \& } y \geq L_y$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} \right) = E \psi(x, y) \quad 0 \leq x \leq L_x \text{ and } 0 \leq y \leq L_y \quad (1)$$

$$\hat{H} = \hat{H}_x + \hat{H}_y$$

Using Separation of variables: $\psi(x, y) = X(x)Y(y) = XY \quad (2)$

$$\frac{\partial^2 \psi(x, y)}{\partial x^2} = X''Y \text{ and } \frac{\partial^2 \psi(x, y)}{\partial y^2} = XY''$$

• From (1)

$$X''Y + XY'' = -\frac{2mE}{\hbar^2} XY$$

$$\Rightarrow \frac{X''}{X} + \frac{Y''}{Y} = -\frac{2mE}{\hbar^2} \quad (3)$$

• 1st term is function of x only and second term function of y only

$$\frac{X''}{X} = -\frac{2mE}{\hbar^2} - \frac{Y''}{Y} = -k_x^2 \quad (4)$$

$$\frac{Y''}{Y} = -\frac{2mE}{\hbar^2} - \frac{X''}{X} = -\frac{2mE}{\hbar^2} + k_x^2 = -k_y^2 \quad (5)$$

Particle in a two-dimensional box

$$\frac{x''}{x} = -k_x^2 \quad \text{and} \quad \frac{y''}{y} = -k_y^2 \quad (6)$$

Possible solutions

$$X(x) = A_1 \sin(k_x x) + B_1 \cos(k_x x)$$

$$Y(y) = A_2 \sin(k_y y) + B_2 \cos(k_y y)$$

• **Boundary condition that** $\psi = 0$ *at* $x = 0$

$$\sin(x = 0) = 0 \text{ and } \cos(x = 0) = 1 \Rightarrow B_1 = 0$$

• **Boundary condition that** $\psi = 0$ *at* $y = 0$

$$\sin(y = 0) = 0 \text{ and } \cos(y = 0) = 1 \Rightarrow B_2 = 0$$

$$X(x) = A_1 \sin(k_x x)$$

$$\Rightarrow Y(y) = A_2 \sin(k_y y)$$

• **Boundary condition that** $\psi = 0$ *at* $x = L_x$ **and** $y = L_y$

$$X(x = L_x) = A_1 \sin(k_x L_x) = 0$$

$$Y(y = L_y) = A_2 \sin(k_y L_y) = 0$$

- If we take $A_1 = 0$ or $A_2 = 0$, then $\psi = 0$ for all x and y .
- This will be in conflict with the Born interpretation that the particle must be somewhere within the box

$$\Rightarrow A_1 \neq 0; \sin(k_x L_x) = 0$$

$$\Rightarrow k_x L_x = n_x \pi \Rightarrow k_x = \frac{n_x \pi}{L_x} \quad \text{where } n_x = 1, 2, \dots$$

• **Similarly**

$$\Rightarrow A_2 \neq 0; \sin(k_y L_y) = 0$$

$$\Rightarrow k_y L_y = n_y \pi \Rightarrow k_y = \frac{n_y \pi}{L_y} \quad \text{where } n_y = 1, 2, \dots$$

• **Therefore,**

$$X(x) = A_1 \sin\left(\frac{n_x \pi}{L_x} x\right); \quad Y(y) = A_2 \sin\left(\frac{n_y \pi}{L_y} y\right)$$

$$\psi_{n_x, n_y}(x, y) = A_1 A_2 \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \quad (10)$$

Particle in a two-dimensional box

$$\psi_{n_x, n_y}(x, y) = A_1 A_2 \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) = A \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right)$$

• Normalization of the wavefunction

$$\int_0^{L_x} \int_0^{L_y} \psi_{n_x, n_y}^*(x, y) \psi_{n_x, n_y}(x, y) dx dy = 1$$

$$A^2 \int_0^{L_x} \int_0^{L_y} \sin^2\left(\frac{n_x \pi}{L_x} x\right) \sin^2\left(\frac{n_y \pi}{L_y} y\right) dx dy = 1$$

Solving separately

$$\Rightarrow \int_0^{L_x} \sin^2\left(\frac{n_x \pi}{L_x} x\right) dx = \frac{1}{2} \int_0^{L_x} \left[1 - \cos\left(2 \frac{n_x \pi}{L_x} x\right)\right] dx = \frac{L_x}{2}$$

$$\Rightarrow \int_0^{L_y} \sin^2\left(\frac{n_y \pi}{L_y} y\right) dy = \frac{1}{2} \int_0^{L_y} \left[1 - \cos\left(2 \frac{n_y \pi}{L_y} y\right)\right] dy = \frac{L_y}{2}$$

Therefore,

$$A^2 \frac{L_x}{2} \frac{L_y}{2} = 1 \Rightarrow A = \frac{2}{\sqrt{L_x L_y}}$$

$$\psi_{n_x, n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) =$$

Now,

$$k_x^2 + k_y^2 = \frac{2mE}{\hbar^2}$$

$$\Rightarrow \left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2 = \frac{2mE_{n_x, n_y}}{\hbar^2}$$

$$E_{n_x, n_y} = \frac{\hbar^2}{2m} \left(\frac{n_x^2 \pi^2}{L_x^2} + \frac{n_y^2 \pi^2}{L_y^2} \right)$$

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

Particle in a two-dimensional box

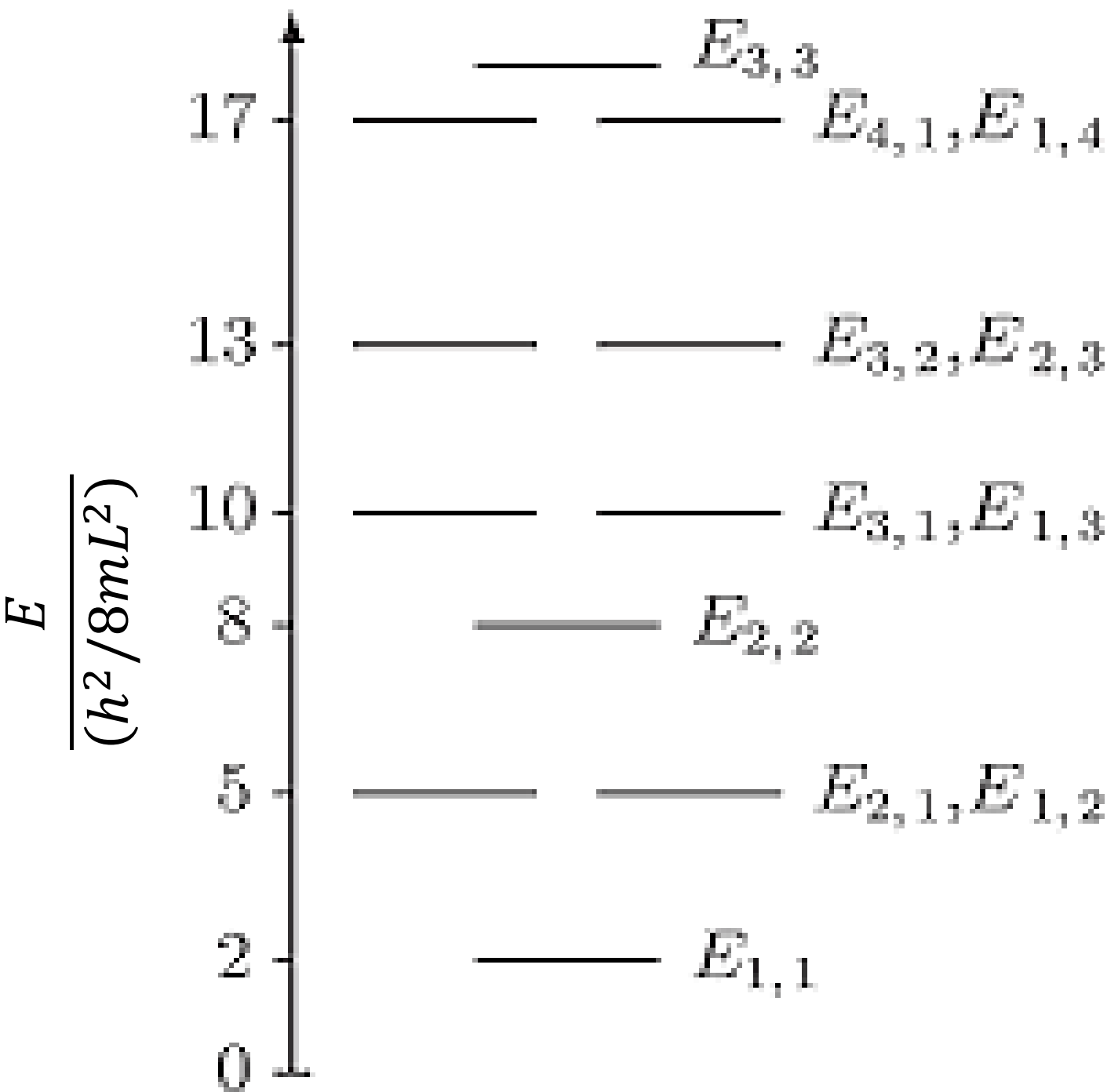
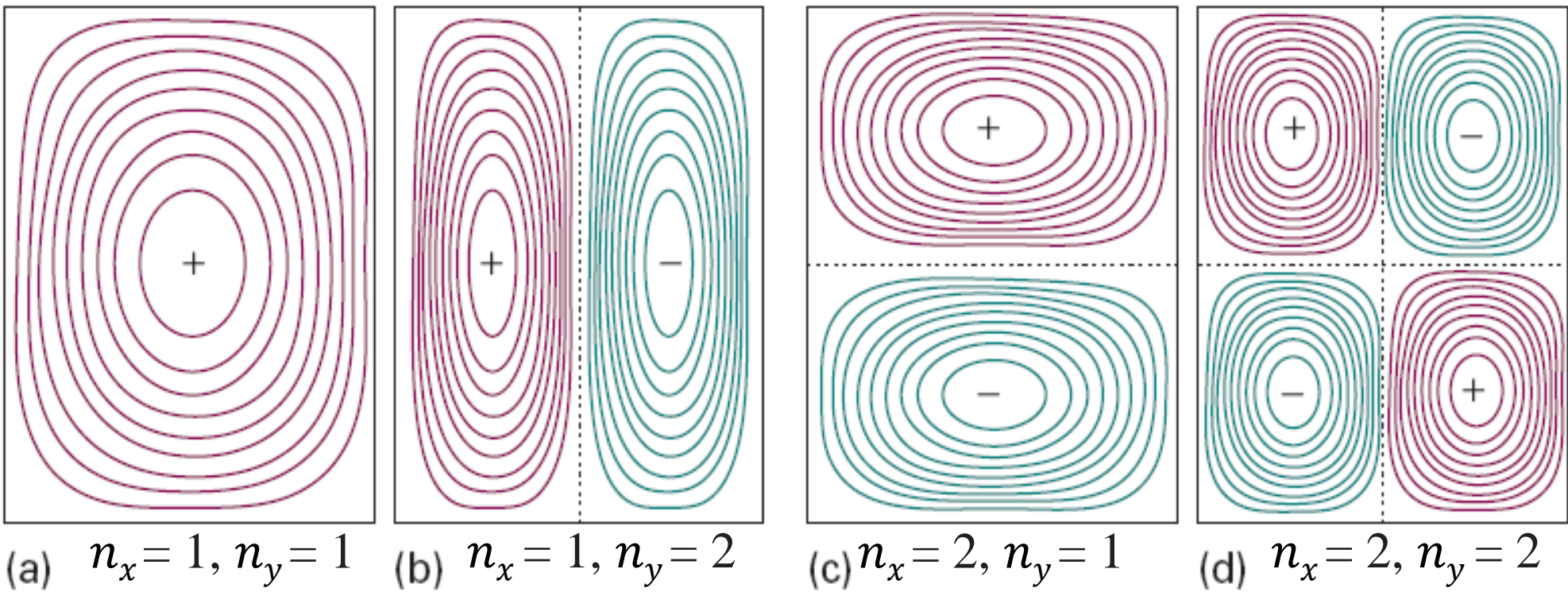
- If the particle is confined in a square box, $L_x = L_y = L$

$$E_{n_x, n_y} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2)$$

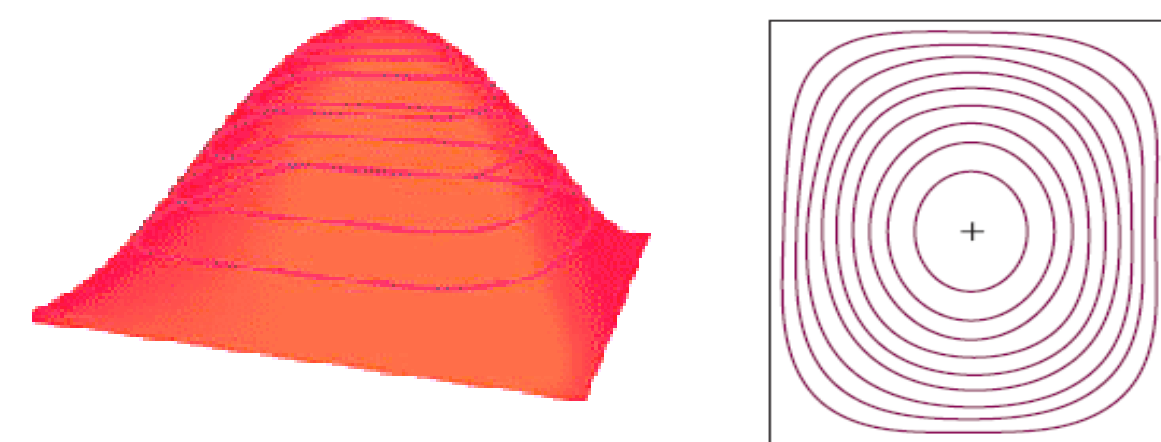
$$\psi_{n_x, n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right)$$

n_x	n_y	E_{n_x, n_y}	ψ_{n_x, n_y}	Degree of degeneracy
1	1	$E_{1,1} = \frac{2h^2}{8mL^2}$	$\psi_{1,1}$	Non-degenerate
1	2	$E_{1,2} = \frac{5h^2}{8mL^2}$	$\psi_{1,2}$	2-fold
2	1	$E_{2,1} = \frac{5h^2}{8mL^2}$	$\psi_{2,1}$	
2	2	$E_{2,2} = \frac{h^2}{mL^2}$	$\psi_{2,2}$	Non-degenerate
1	3	$E_{1,3} = \frac{10h^2}{8mL^2}$	$\psi_{1,3}$	2-fold
3	1	$E_{3,1} = \frac{10h^2}{8mL^2}$	$\psi_{3,1}$	

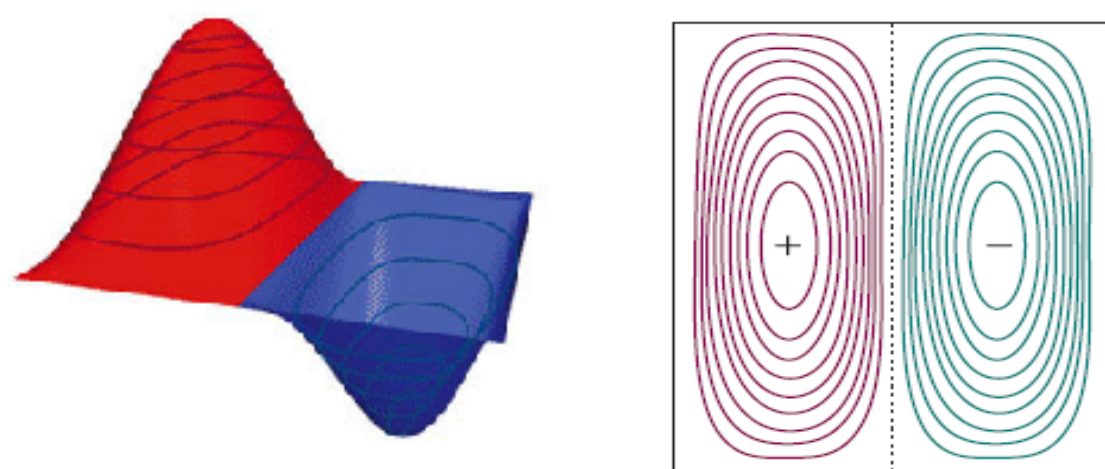
The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude.



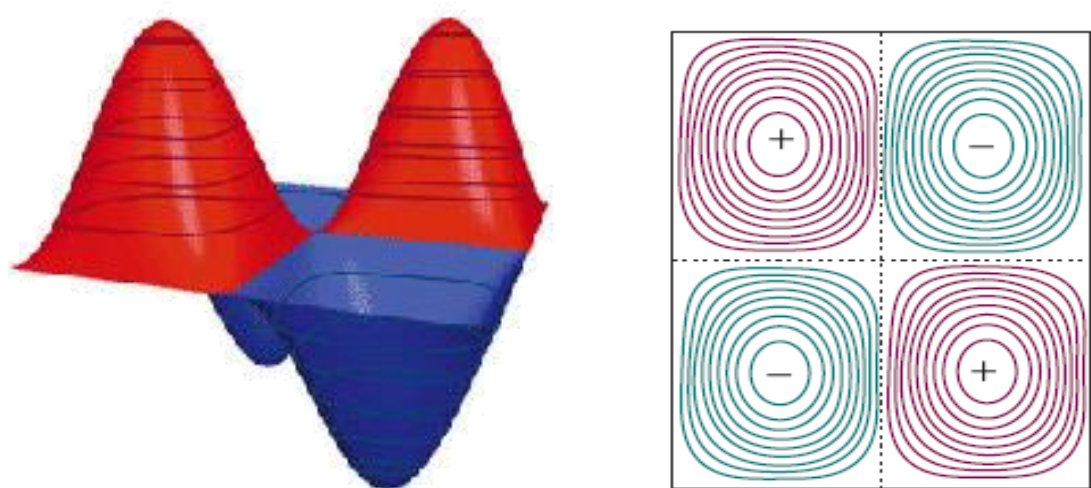
Particle in a two-dimensional box



$$n_x = 1, n_y = 1$$

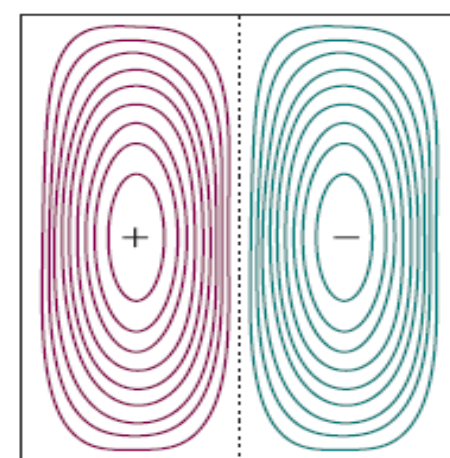


$$n_x = 1, n_y = 2$$



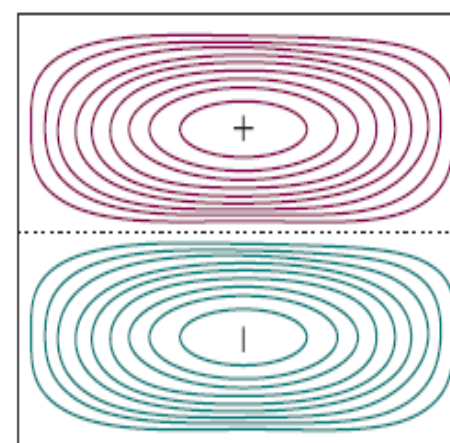
$$n_x = 2, n_y = 2$$

• Degeneracy



$$n_x = 1, n_y = 2$$

$$\psi_{1,2} = \frac{2}{L} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{2\pi}{L}y\right); \quad E_{1,2} = \frac{5h^2}{8mL^2}$$

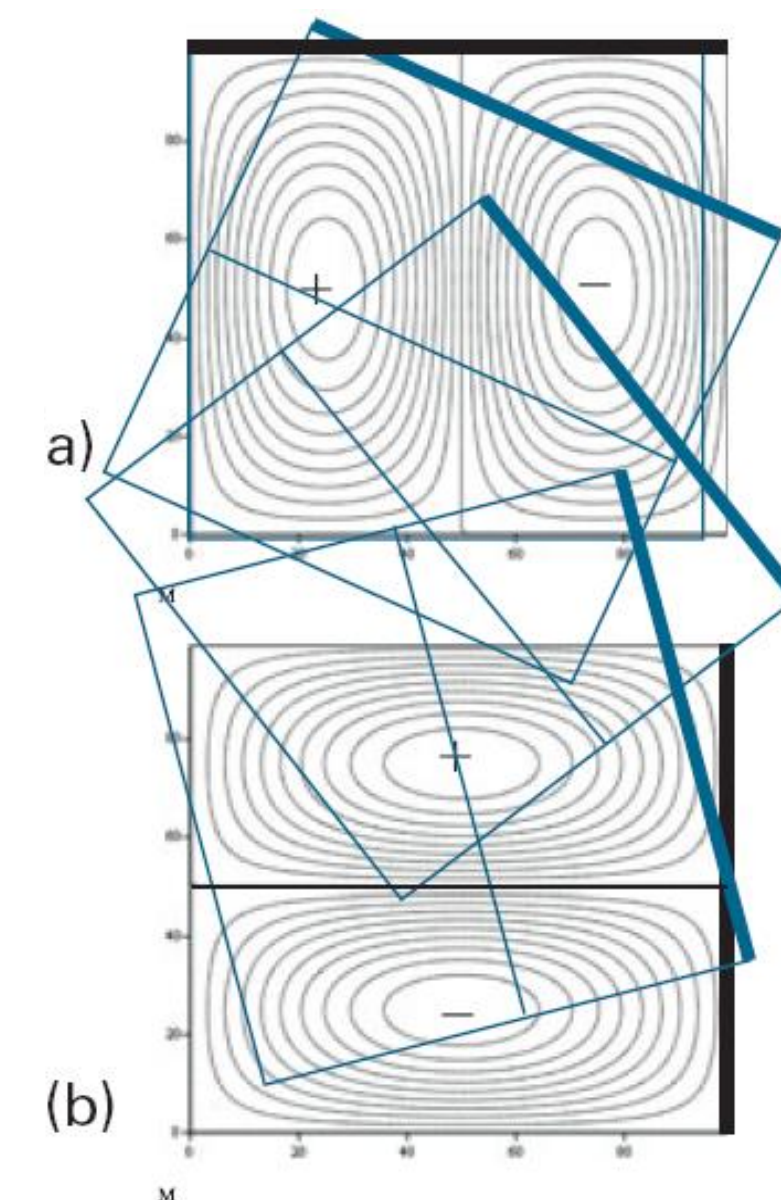


$$n_x = 2, n_y = 1$$

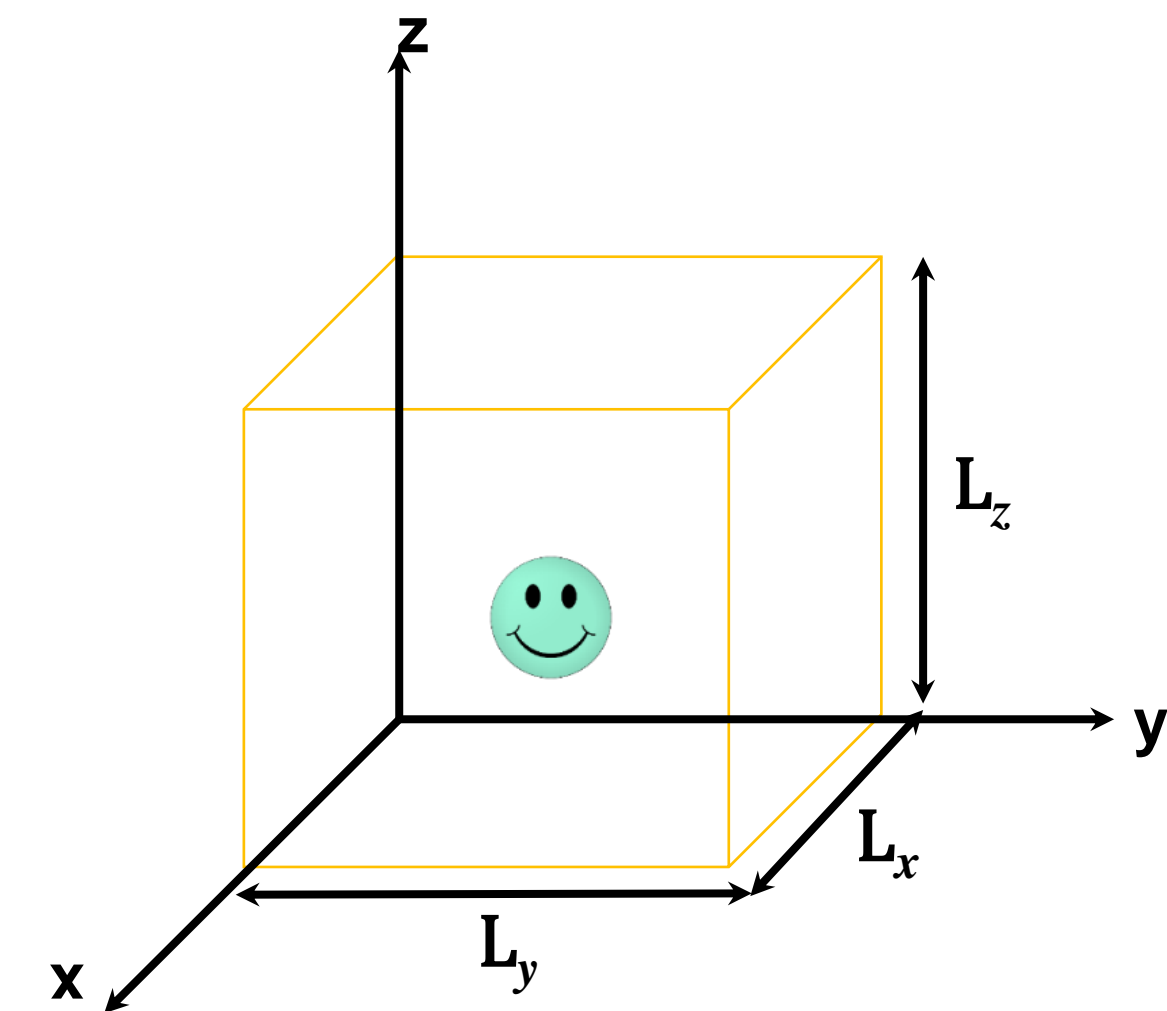
$$\psi_{2,1} = \frac{2}{L} \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right); \quad E_{2,1} = \frac{5h^2}{8mL^2}$$

- The occurrence of degeneracy is related to the symmetry of the system

- Because the box is square, we can convert one wavefunction into the other simply by rotating the plane by 90° .
- Interconversion by rotation through 90° is not possible when the plane is not square, and $\psi_{1,2}$ and $\psi_{2,1}$ are then not degenerate.



Particle in a three-dimensional box



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

$$\psi_{n_x, n_y, n_z}(x, y, z) = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right)$$
$$0 \leq x \leq L_x, 0 \leq y \leq L_y, 0 \leq z \leq L_z$$

$$\hat{V}(x, y, z) = 0 \text{ for } 0 \leq x \leq L_x, 0 \leq y \leq L_y$$
$$\text{and } 0 \leq z \leq L_z$$
$$= \infty \text{ Otherwise}$$

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

Boundary conditions or trivial solution

$$\psi(x, y, z) = 0 \text{ for } x, y, z \leq 0 \text{ and } x \geq L_x, y \geq L_y \text{ \& } z \geq L_z$$

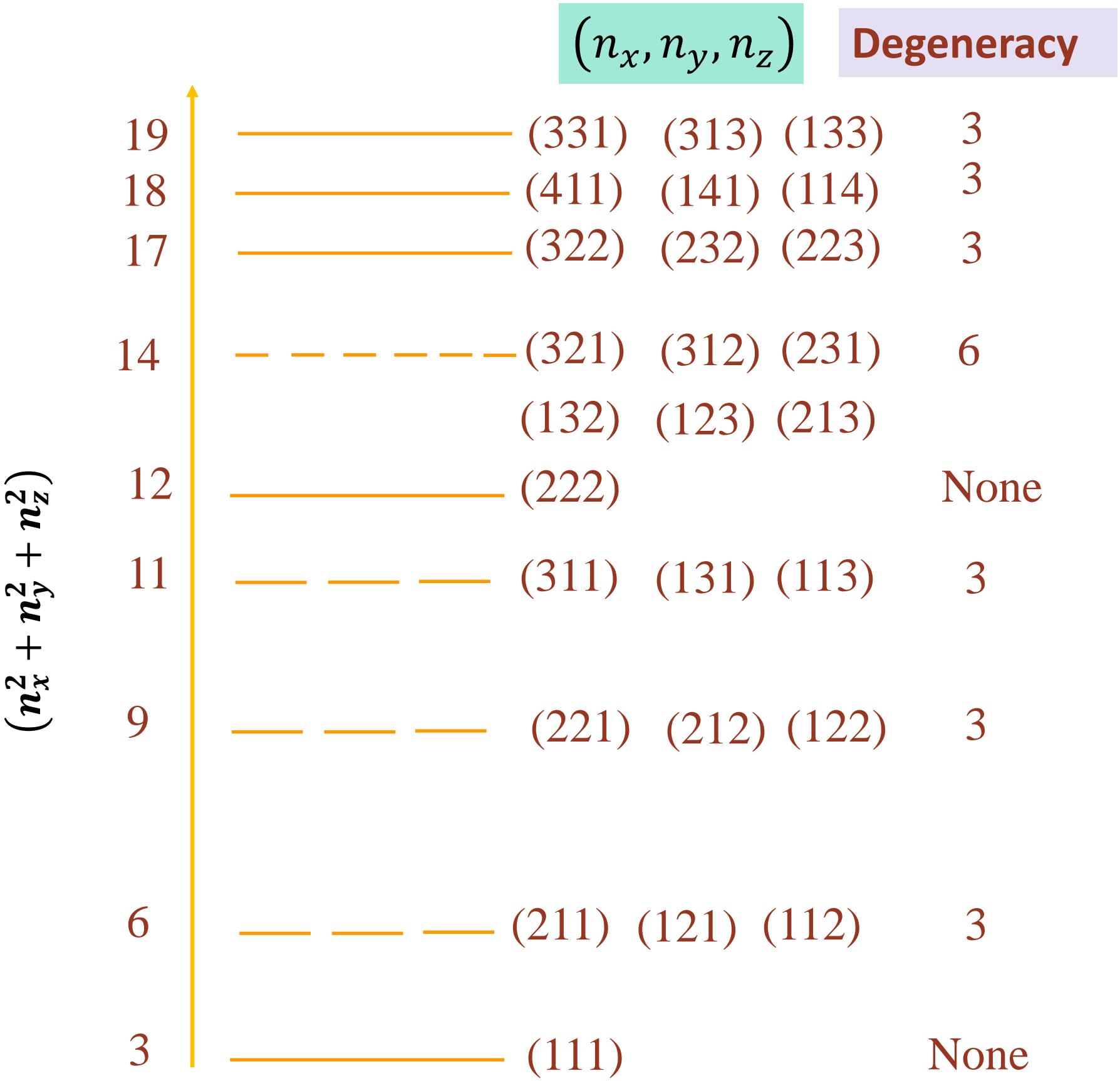
Particle in a three-dimensional box

• If the particle is confined in a cubical box: $L_x = L_y = L_z = L$

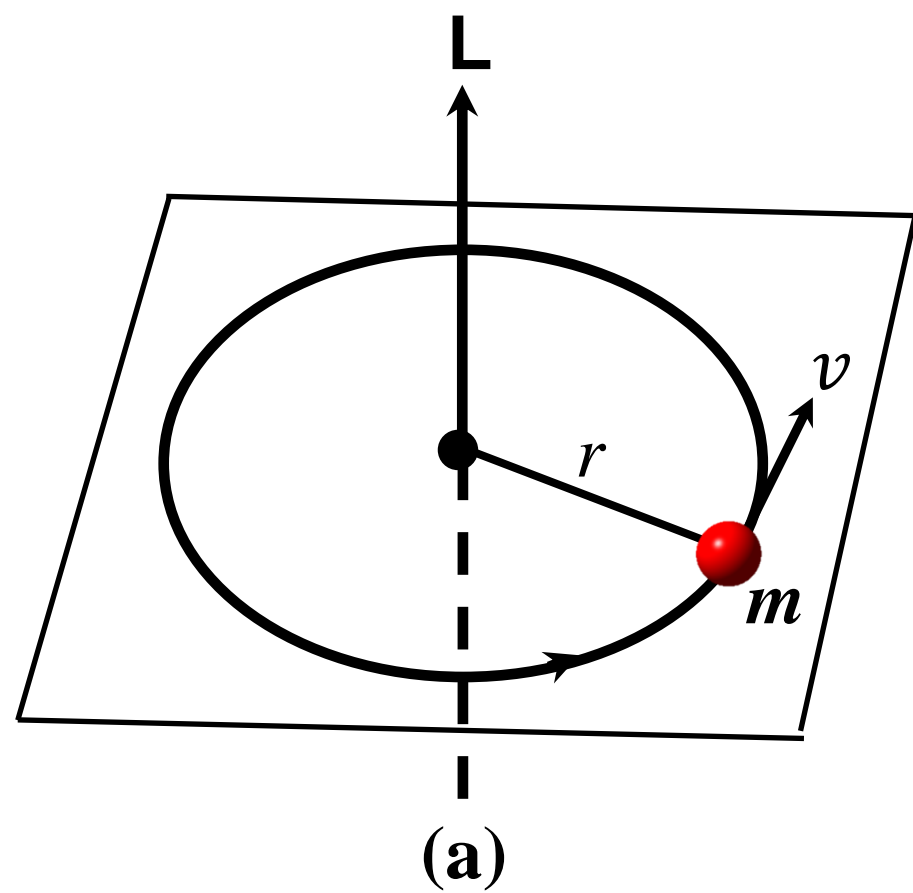
$$\psi_{n_x,n_y,n_z}(x,y,z) = \frac{2\sqrt{2}}{\sqrt{L^3}} \sin\left(\frac{n_x\pi}{L}x\right) \sin\left(\frac{n_y\pi}{L}y\right) \sin\left(\frac{n_z\pi}{L}z\right)$$
$$0 \leq x \leq L, \ 0 \leq y \leq L, \ 0 \leq z \leq L$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

n_x, n_y, n_z	E_{n_x,n_y,n_z}	ψ_{n_x,n_y,n_z}	Degree of degeneracy
111	$E_{1,1,1} = \frac{3h^2}{8mL^2}$	$\psi_{1,1,1}$	Non-degenerate
211	$E_{2,1,1} = \frac{6h^2}{8mL^2}$	$\psi_{2,1,1}$	3-fold
121	$E_{1,2,1} = \frac{6h^2}{8mL^2}$	$\psi_{1,2,1}$	
112	$E_{1,1,2} = \frac{6h^2}{8mL^2}$	$\psi_{1,1,2}$	

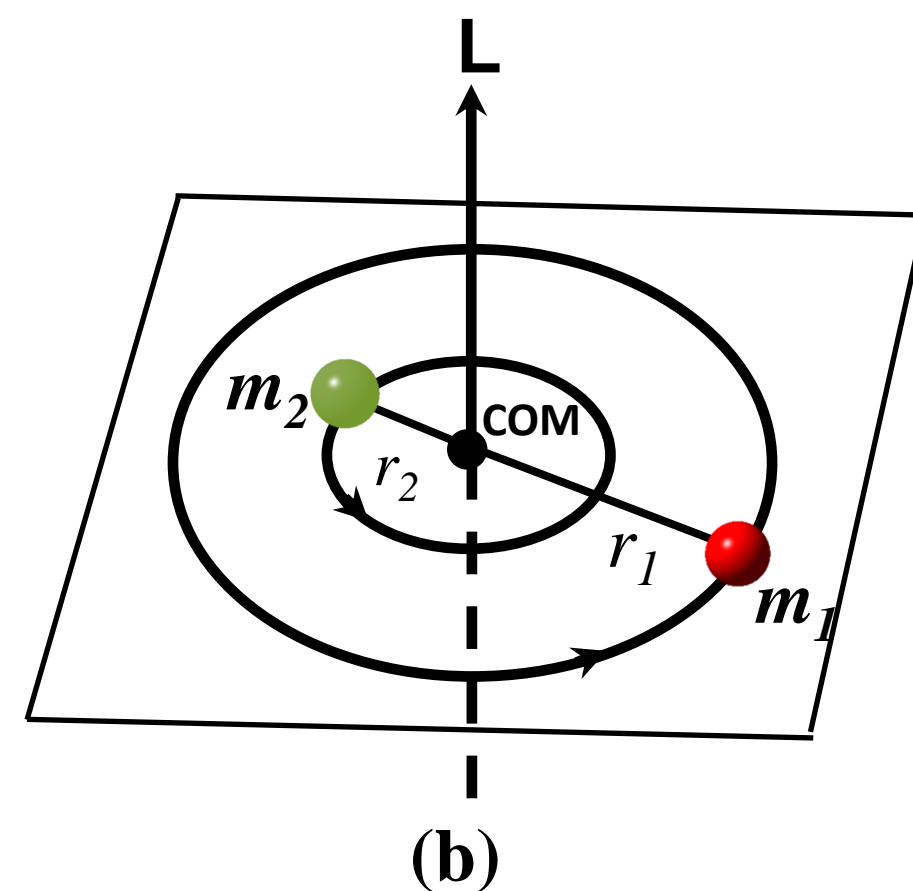


Particle on a ring/sphere: Quantization of rotations



- Particle moving around an axis will possess **angular momentum** ($L = I\omega = mvr = pr$) and **rotational kinetic energy** ($K = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$)

⇒ If no torque is applied, L is conserved



- In a rigid rotor (rigid diatomic molecule), two particles rotate about their COM such that $m_1r_1 = m_2r_2$.

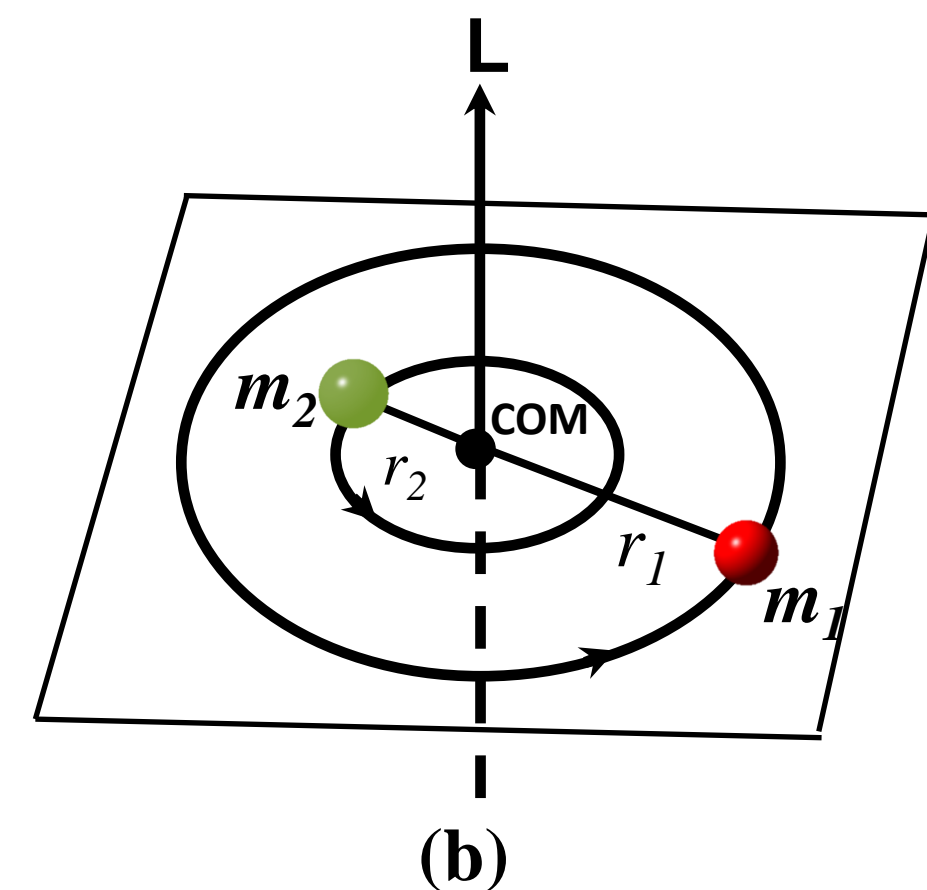
- The equilibrium distance $r = r_1 + r_2$ such that

$$r_1 = \frac{m_2}{m_1+m_2}r \text{ and } r_2 = \frac{m_1}{m_1+m_2}r$$

- Moment of inertia: $I = m_1r_1^2 + m_2r_2^2 = \frac{m_1m_2}{m_1+m_2}r^2 = \mu r^2$

- Rotational kinetic energy: $K = \frac{1}{2}m_1r_1^2\omega^2 + \frac{1}{2}m_2r_2^2\omega^2$

$$= \frac{1}{2}I\omega^2 = \frac{L^2}{2I} = \frac{L^2}{2\mu r^2}$$



- Since there is no potential energy, the Hamiltonian operator for a rigid rotor can be written as

$$\hat{H} = \hat{K} = \frac{\hat{L}^2}{2I} = -\frac{\hbar^2}{2\mu r^2} \nabla^2 \quad (r \text{ constant})$$

- For rotational motion, it is more convenient to use spherical coordinates and write the Schrödinger equation

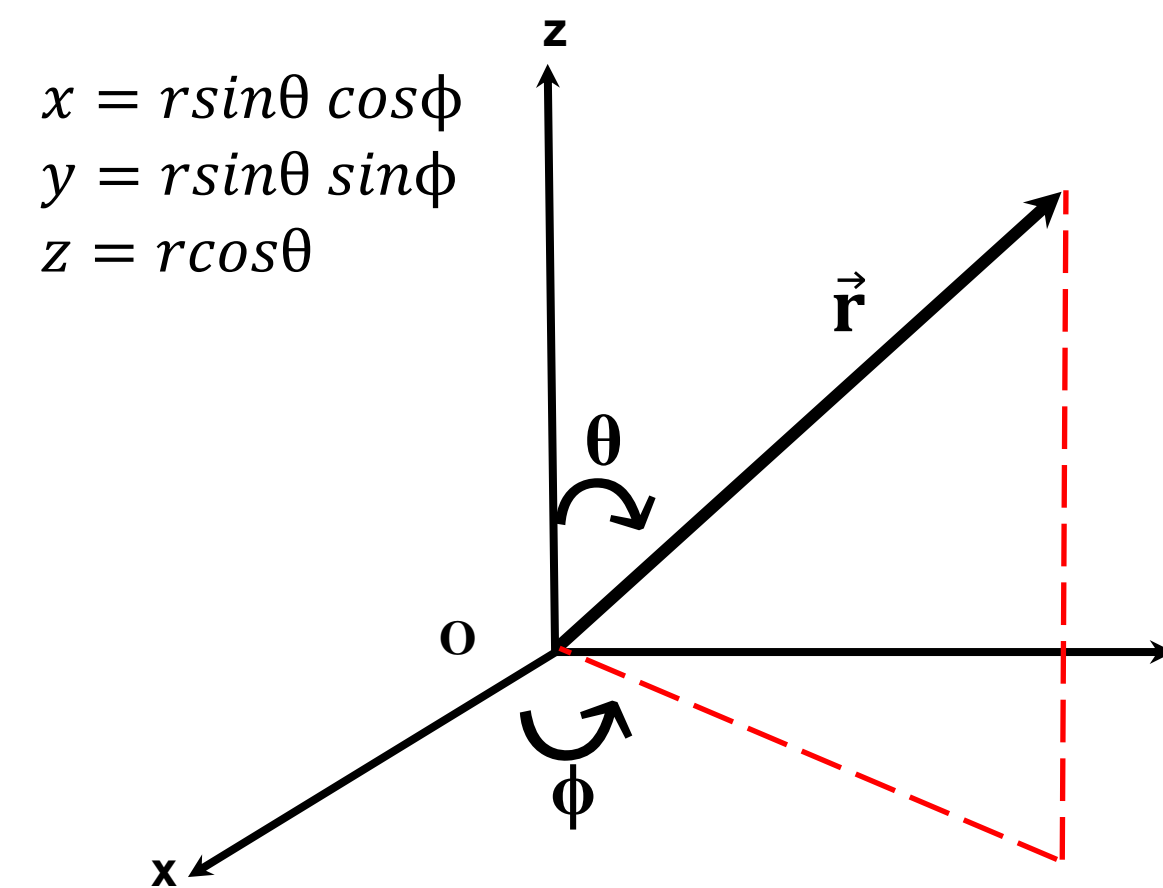
$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

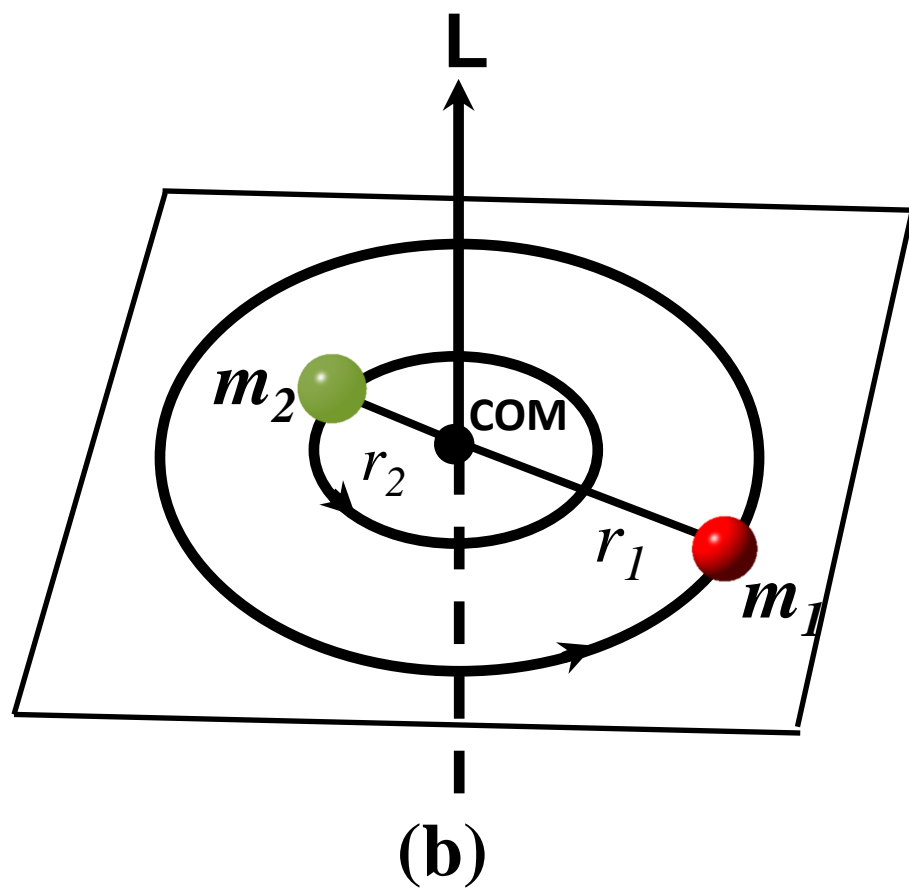
$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad \text{[Laplacian operator]}$$

- Since for rigid rotor, $r = r_1 + r_2 = \text{const.}$, we can ignore the derivatives w.r.t. r in ∇^2 and also the wavefunction will be function of two variables θ and ϕ .

$$-\frac{\hbar^2}{2\mu r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(\theta, \phi) = E \psi(\theta, \phi)$$

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(\theta, \phi) = E \psi(\theta, \phi)$$





- The Schrödinger equation thus obtained is a standard differential equation whose solutions are spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$. Thus,

$$\hat{H}Y_\ell^{m_\ell}(\theta, \phi) = EY_\ell^{m_\ell}(\theta, \phi)$$

$$E = \frac{\ell(\ell+1)\hbar^2}{2I} \text{ where } \ell = 0, 1, 2 \dots$$

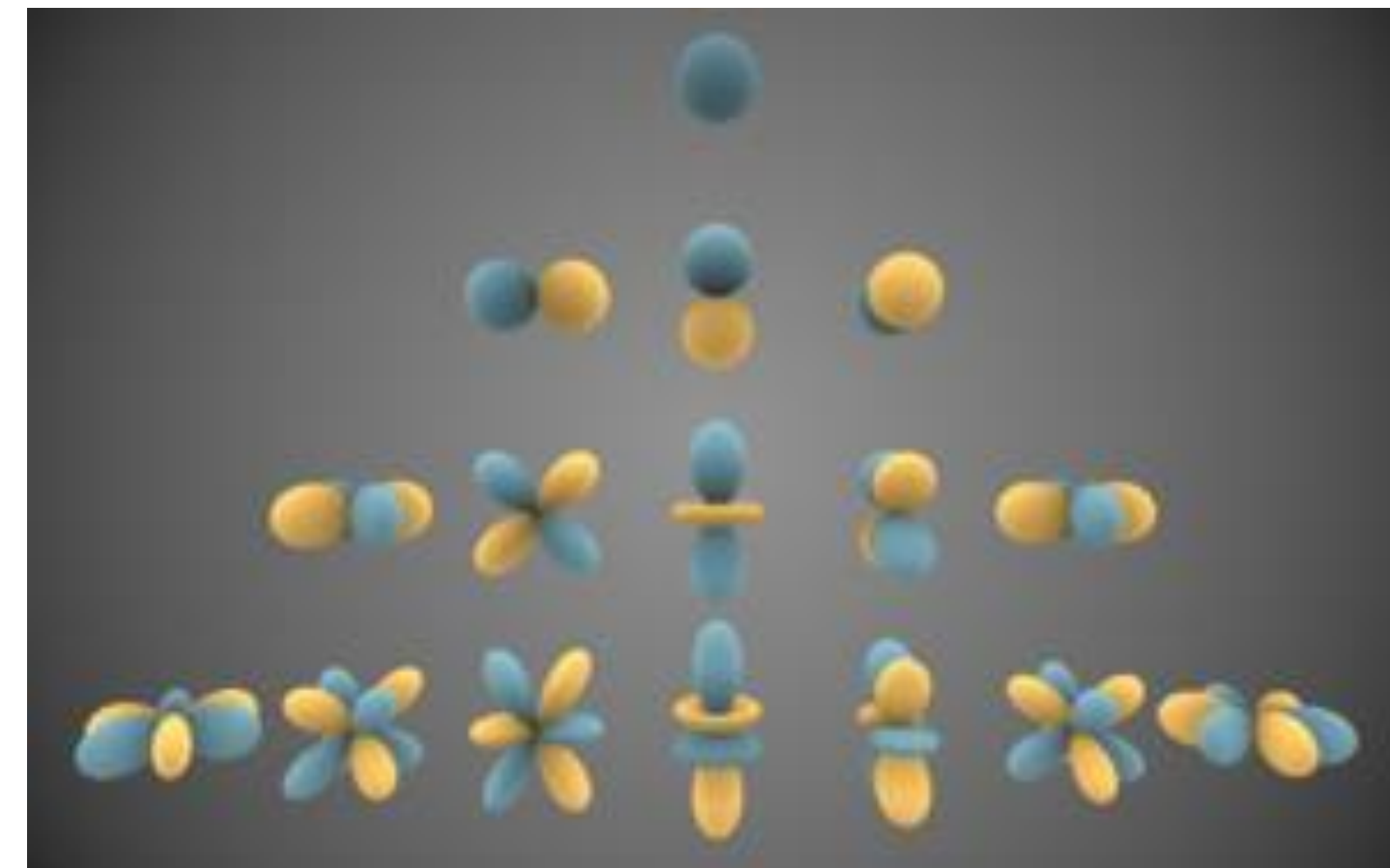
$$\hat{H}Y_\ell^{m_\ell}(\theta, \phi) = \frac{\ell(\ell+1)\hbar^2}{2I} Y_\ell^{m_\ell}(\theta, \phi)$$

where ℓ is **angular momentum quantum number** and m_ℓ is referred to as **magnetic quantum number**

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2I}$$

- Note that there is no zero-point energy for rigid rotor

$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$	$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$	$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$	$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi}$
$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$	



https://en.wikipedia.org/wiki/Spherical_harmonics

Construction of operator for square of the angular momentum

- So far, we neglected the fact that the angular momentum is a vector quantity.

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$$

$$\mathbf{L} \cdot \mathbf{L} = L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\therefore \hat{p}_x = -i\hbar \frac{\partial}{\partial x}; \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}; \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z},$$

$$\therefore \hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad \hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \quad \hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

⇒ The operator for the square of the angular momentum

$$\hat{L}^2 = |\hat{L}|^2 = \hat{L} \cdot \hat{L} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

•

\hat{L}^2 and its eigenfunctions

- It is often more convenient to use the angular momentum operators in spherical coordinates r, θ, ϕ

$$\hat{L}_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad \hat{L}_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \quad \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$\Rightarrow \nabla^2 = -\frac{\hat{L}^2}{r^2 \hbar^2}$$

- Since $\hat{H} = \hat{K} = \frac{\hat{L}^2}{2I} = -\frac{\hbar^2}{2\mu r^2} \nabla^2$ (r constant) and $\hat{H} Y_\ell^{m_\ell}(\theta, \phi) = \frac{\ell(\ell+1)\hbar^2}{2I} Y_\ell^{m_\ell}(\theta, \phi)$, we can write

$$\hat{L}^2 Y_\ell^{m_\ell}(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_\ell^{m_\ell}(\theta, \phi)$$

$\Rightarrow Y_\ell^{m_\ell}(\theta, \phi)$ are the eigenfunctions of \hat{L}^2 and \hat{H}

$$\Rightarrow [\hat{L}^2, \hat{H}] = 0$$

\Rightarrow Simultaneous measurement of L^2 and ‘energy’ with infinite precision is possible for a rigid rotor

- It can be shown that

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}$$

- Consider the operator $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$

$$\hat{L}_z Y_\ell^{m_\ell}(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} \Theta(\theta) e^{im_\ell \phi} = -i\hbar (im_\ell) Y_\ell^{m_\ell}(\theta, \phi)$$

$$\hat{L}_z Y_\ell^{m_\ell}(\theta, \phi) = m_\ell \hbar Y_\ell^{m_\ell}(\theta, \phi) \quad |L_z| = m_\ell \hbar$$

$\Rightarrow Y_\ell^{m_\ell}(\theta, \phi)$ are also the eigenfunctions of \hat{L}_z as well as of \hat{L}^2 and \hat{H}

$$\Rightarrow [\hat{L}_z, \hat{H}] = 0$$

\Rightarrow Simultaneous measurement of \hat{L}_z , L^2 and ‘energy’ with infinite precision is possible for a rigid rotor

- Limits on m_ℓ

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \Rightarrow \hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$$

$$\begin{aligned} (\hat{L}_x^2 + \hat{L}_y^2) Y_\ell^{m_\ell}(\theta, \phi) &= (\hat{L}^2 - \hat{L}_z^2) Y_\ell^{m_\ell}(\theta, \phi) \\ &= [\ell(\ell + 1) - m_\ell^2] \hbar^2 Y_\ell^{m_\ell}(\theta, \phi) \end{aligned}$$

$\therefore \hat{L}_x$ and \hat{L}_y are Hermitian, their eigenvalues will be real

\therefore The square of the eigenvalues will be real and nonnegative

$$\Rightarrow [\ell(\ell + 1) - m_\ell^2] \hbar^2 \geq 0$$

$$\Rightarrow [\ell(\ell + 1) - m_\ell^2] \geq 0$$

$$\Rightarrow |m_\ell| \leq \ell$$

\therefore The only possible values of m_ℓ are

$$m_\ell = 0, \pm 1, \pm 2, \dots \pm \ell$$

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2I} \Rightarrow \text{Each energy level is } (2\ell + 1)\text{-fold degenerate}$$

Construction of operator for square of the angular momentum

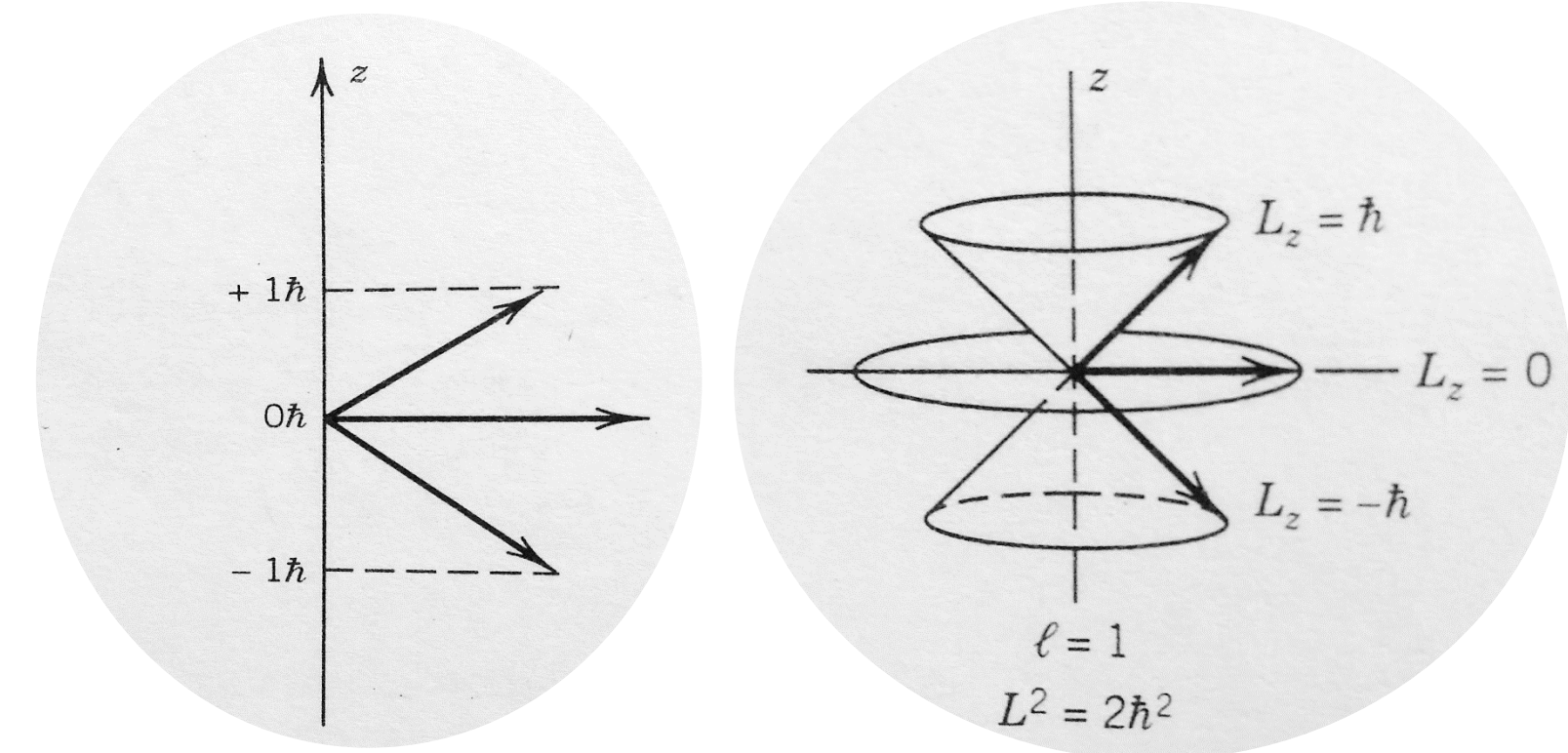
- Example 1: For $\ell=1$, what are the values of $|L|$ and L_z ?

$$|L| = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{2}\hbar$$

$$m_\ell = 0, \pm 1$$

$$|L_z| = m_\ell \hbar = 0, \pm \hbar$$

The angular momentum is same ($\sqrt{2}\hbar$), but its projection on z-axis depends on m_ℓ



- **Example 2:** For $\ell=2$, what are the values of $|L|$ and L_z ?

$$|L| = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{6}\hbar$$

$$m_\ell = 0, \pm 1, \pm 2$$

$$|L_z| = m_\ell \hbar = 0, \pm \hbar, \pm 2\hbar$$

