

Chapter 16

Quantum Particle in Three Dimensions

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Chem. 4300

Momentum and Kinetic Energy Operators in 3D

In 3D the components of the momentum operator are

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

and the vector operator is

$$\vec{\hat{p}} = \hat{p}_x \vec{e}_x + \hat{p}_y \vec{e}_y + \hat{p}_z \vec{e}_z = -i\hbar \vec{\nabla}$$

Kinetic energy operator in 3D is

$$\hat{K} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$$

Free particle in 3D

Time independent Schrödinger equation for free particle moving in 3D with $V(\vec{r}) = 0$ is

$$\hat{H}\psi(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\psi(\vec{r})$$

Eigenstate of \hat{H} is

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{-iEt/\hbar}$$

Wave function for free particle with momentum $\vec{p} = \hbar\vec{k}$ is

$$\Psi(\vec{r}, t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)} = \underbrace{Ae^{i\vec{p}\cdot\vec{r}/\hbar}}_{\psi(\vec{r})} e^{-iEt/\hbar}$$

Particle in Infinite 3D Well

Particle in Infinite 3D Well

Particle bound in infinite 3D well

$$V(x, y, z) = \begin{cases} 0 & 0 \leq x \leq L_x, \\ & 0 \leq y \leq L_y, \\ & 0 \leq z \leq L_z, \\ \infty & \text{otherwise.} \end{cases}$$

Separate variables and write

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

Plugging into time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}Y(y)Z(z)\frac{\partial^2 X(x)}{\partial x^2} - \frac{\hbar^2}{2m}X(x)Z(z)\frac{\partial^2 Y(y)}{\partial y^2} - \frac{\hbar^2}{2m}X(x)Y(y)\frac{\partial^2 Z(z)}{\partial z^2} = E\psi$$

Particle in Infinite 3D Well

Dividing both sides by $\psi(x, y, z)$ and rearranging gives

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} + k^2 = 0, \quad \text{where } k^2 = 2mE/\hbar^2$$

Rearranging to

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} = -\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} - \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} - k^2 = -k_x^2$$

Introduce separation constant $-k_x^2$, and obtain uncoupled ODE for $X(x)$

$$\frac{d^2 X(x)}{dx^2} + k_x^2 X(x) = 0$$

Particle in Infinite 3D Well

Leaves us with PDE that can be rearranged to

$$\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} - k^2 + k_x^2 = -k_y^2$$

Introduce separation constant $-k_y^2$ to obtain uncoupled ODE for $Y(y)$

$$\frac{d^2 Y(y)}{dy^2} + k_y^2 Y(y) = 0$$

Leaves us with uncoupled ODE for $Z(z)$

$$\frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} - k^2 + k_x^2 + k_y^2 = 0 \quad \text{or} \quad \frac{d^2 Z(z)}{dz^2} + k_z^2 Z(z) = 0$$

where $k^2 = k_x^2 + k_y^2 + k_z^2$.

Particle in Infinite 3D Well

$$\frac{d^2X(x)}{dx^2} + k_x^2X(x) = 0, \quad \frac{d^2Y(y)}{dy^2} + k_y^2Y(y) = 0, \quad \frac{d^2Z(z)}{dz^2} + k_z^2Z(z) = 0$$

3D boundary conditions constrain normalized ODEs solutions to

$$X(x) = \sqrt{\frac{2}{L_x}} \sin k_x x, \quad Y(y) = \sqrt{\frac{2}{L_y}} \sin k_y y, \quad Z(z) = \sqrt{\frac{2}{L_z}} \sin k_z z$$

k_x , k_y , and k_z have discrete values given by

$$k_x = \frac{n_x \pi}{L_x}, \quad k_y = \frac{n_y \pi}{L_y}, \quad k_z = \frac{n_z \pi}{L_z}, \quad \text{where } n_x, n_y, n_z = 1, 2, 3, \dots$$

and total energy

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

Degeneracy and density of states

When $L_x = L_y = L_z = L$, that is, box is cube, energy expression becomes

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

When different states lead to the same energy we say that those states are *degenerate states*.

Particle in a 3D Box has degenerate (identical energy) states

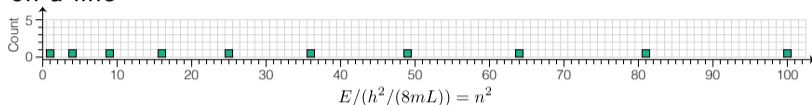
$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

Degeneracies play an important role in application of statistical mechanics to quantum mechanics.

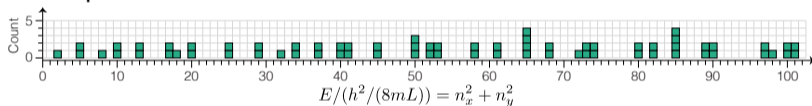
Degeneracy and density of states

Number of discrete states of an infinite well represented as histogram as function of energy for

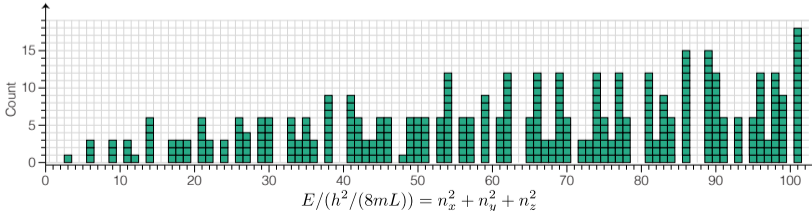
- 1D Particle on a line



- 2D Particle in a square



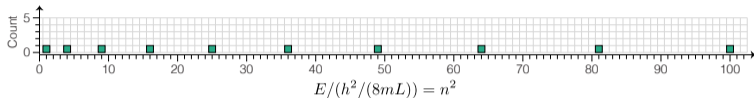
- 3D Particle in a cube



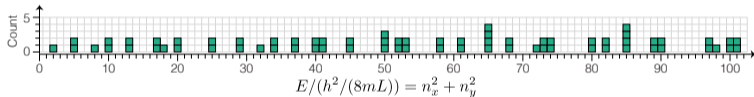
Degeneracy and density of states

Number of states in E to $E + dE$ is $g(E) dE$, where $g(E) \equiv$ density of states.

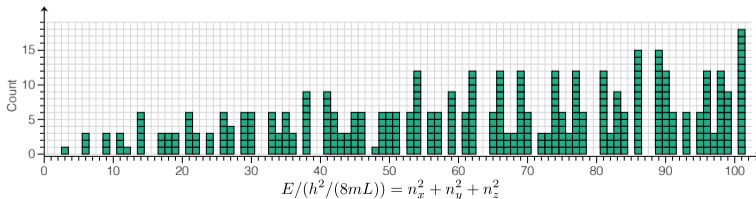
- Density of states in 1D in given dE **decreases** with increasing E



- Density of states in 2D in given dE **stays roughly constant** with increasing E



- Density of states in 3D in given dE **increases** with increasing E



Derive $g(E)$ for particle in 1D infinite well

For particle in 1D infinite well the energy is

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{one energy state for each } n$$

In 1D case, number of states associated with given energy interval, dE , is

$$g_{1D}(E) = \frac{dn}{dE}$$

Rearrange energy expression

$$n = \frac{\sqrt{8mL^2 E}}{h}$$

and calculate

$$g_{1D}(E) = \frac{dn}{dE} = \frac{1}{2} \left(\frac{8m}{h^2} \right)^{1/2} \frac{L}{\sqrt{E}}$$

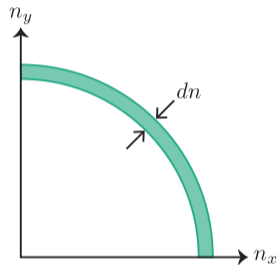
Density of states decreases with inverse square root of energy - Consistent with 1D energy histogram plot.

Derive $g(E)$ for particle in 2D infinite well

For particle in 2D infinite well the energy is

$$E_{n_x, n_y} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2) = \frac{h^2}{8mL^2} n^2 \quad \text{where} \quad n = \sqrt{n_x^2 + n_y^2} = \frac{\sqrt{8mLE}}{h}$$

- Defines circle passing through positive n_x and n_y quadrant.
- Take 1/4 of circle circumference ($2\pi r$) times dn as number of states that lie in annular region of n to $n + dn$



Calculate number of states associated with given dE in 2D as

$$g_{2D}(E) = \frac{1}{4} \frac{(2\pi n)dn}{dE} = \frac{(2\pi n)}{4} \frac{dn}{dE} = \frac{(\pi n)}{2} \frac{dn}{dE} = \frac{\pi}{4} \left(\frac{8m}{h^2} \right) L^2$$

Density of states is independent of energy – Consistent with 2D energy histogram plot.

Derive $g(E)$ for particle in 3D infinite well

Imagine spherical shell in 3D space of n_x , and n_y , and n_z with radius of

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\sqrt{8mLE}}{h}$$

and thickness of dn associated with states in interval $E + dE$.

- Take 1/8 of surface area of sphere ($4\pi r^2$) times dn as number of states that lie in n to $n + dn$

$$g_{3D}(E) = \frac{1}{8} \frac{(4\pi n^2)dn}{dE} = \frac{\pi n^2}{2} \frac{dn}{dE}$$

- Substituting expressions for n and dn/dE gives

$$g_{3D}(E) = \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} L^3 \sqrt{E}$$

- Density of states increase with square root of energy – Consistent with 3D energy histogram plot.

Quantum Theory of Angular Momentum

Quantum Theory of Angular Momentum

Angular momentum of particle with respect to origin is

$$\vec{\hat{L}} = \vec{\hat{r}} \times \vec{\hat{p}} = \vec{\hat{r}} \times (-i\hbar \vec{\nabla}) = -i\hbar \vec{\hat{r}} \times \vec{\nabla}$$

Recalling procedure for expanding cross product

$$\vec{\hat{r}} \times \vec{\hat{p}} = \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

Operators do not commute. Be careful with order when expanding.

$$\vec{\hat{L}} = \vec{\hat{r}} \times \vec{\hat{p}} = \underbrace{\vec{e}_x \begin{vmatrix} \hat{y} & \hat{z} \\ \hat{p}_y & \hat{p}_z \end{vmatrix}}_{L_x} - \underbrace{\vec{e}_y \begin{vmatrix} \hat{x} & \hat{z} \\ \hat{p}_x & \hat{p}_z \end{vmatrix}}_{L_y} + \underbrace{\vec{e}_z \begin{vmatrix} \hat{x} & \hat{y} \\ \hat{p}_x & \hat{p}_y \end{vmatrix}}_{L_z}$$

and we find

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

Angular Momentum of a Single Particle

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

Unlike linear momentum operators which all commute:

$$[\hat{p}_x, \hat{p}_y] = 0, \quad [\hat{p}_y, \hat{p}_z] = 0, \quad [\hat{p}_z, \hat{p}_x] = 0$$

Not true for \hat{L}_x , \hat{L}_y , and \hat{L}_z .

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad \text{and} \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y.$$

Notice cyclic permutation of subscripts, $x \rightarrow y \rightarrow z \rightarrow x \dots$.

Commutators tell us \hat{L}_x , \hat{L}_y , and \hat{L}_z are incompatible observables.

$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2} |\langle L_z \rangle|.$$

Quantum Theory of Angular Momentum

The total angular momentum operator is

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

It commutes with all 3 components, \hat{L}_x , \hat{L}_y , and \hat{L}_z

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

- \hat{L}^2 commutes with \hat{L}_x , \hat{L}_y , and \hat{L}_z . (But \hat{L}_x , \hat{L}_y , and \hat{L}_z don't commute with each other.)
- \hat{L}^2 eigenstate cannot simultaneously be eigenstate of \hat{L}_x , \hat{L}_y , and \hat{L}_z .
- \hat{L}^2 eigenstate can only be eigenstate of \hat{L}^2 and \hat{L}_x , or \hat{L}^2 and \hat{L}_y , or \hat{L}^2 and \hat{L}_z .

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- *We cannot simultaneously know all 3 components of angular momentum vector in QM.*
 - At best, we can know angular momentum vector length and one vector component.
 - Convention is to work with eigenstates of \hat{L}^2 and \hat{L}_z

Eigenvalues of angular momentum operators

Meet the Raising and Lowering operators \hat{L}_+ and \hat{L}_-

Start with

$$\hat{L}^2\psi = \lambda\psi \quad \text{and} \quad \hat{L}_z\psi = \mu\psi$$

λ and μ are yet-to-be-determined eigenvalues. Introduce related raising and lowering operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \text{and} \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y \quad \leftarrow \text{What do these operators do?}$$

Similar approach taken for harmonic oscillator

$$\text{If } \psi' = \hat{L}_+\psi \quad \text{then} \quad \hat{L}_z\psi' = \hat{L}_z(\hat{L}_+\psi) = \hat{L}_z\hat{L}_+\psi.$$

Little math slight of hand gives

$$\hat{L}_z\psi' = \hat{L}_z\hat{L}_+\psi \underbrace{-\hat{L}_+\hat{L}_z\psi + \hat{L}_+\hat{L}_z\psi}_{\text{zero}} = \underbrace{(\hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z)}_{[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+} \psi + \hat{L}_+\hat{L}_z\psi = \hbar\hat{L}_+\psi + \hat{L}_+\mu\psi$$

$$\text{Then } \hat{L}_z\psi' = \hbar\hat{L}_+\psi + \hat{L}_+\mu\psi = \underbrace{(\hbar + \mu)}_{\text{eigenvalue of } \psi'} \hat{L}_+\psi \quad \leftarrow \quad \hat{L}_+ \text{ increase } \mu \text{ (eigenvalue of } \hat{L}_z) \text{ by } \hbar$$

$$\text{Summary: } \hat{L}_z\psi = \mu\psi, \quad \hat{L}_+\psi = \psi', \quad \text{and} \quad \hat{L}_z\psi' = (\mu + \hbar)\psi'$$

What are eigenvalues of angular momentum operators \hat{L}^2 and \hat{L}_z ?

- Similarly, \hat{L}_- on eigenstate of \hat{L}_z makes new eigenstate with eigenvalue reduced by \hbar .
- \hat{L}_+ and \hat{L}_- are called the *raising* and *lowering operators*, respectively.
- \hat{L}^2 gives square of total angular momentum, $\hat{L}^2\psi = \lambda\psi$
- \hat{L}_z gives z component of angular momentum, $\hat{L}_z\psi = \mu\psi$
- \hbar has units of angular momentum, $\hbar = 1.054571800139113 \times 10^{-34} \text{m}^2 \cdot \text{kg/s}$

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- \hat{L}_+ cannot create new \hat{L}_z eigenstate with eigenvalue greater than total angular momentum.
 - No single component of vector cannot exceed total length of vector.

If ψ_{\max} is eigenstate of \hat{L}_z with highest possible eigenvalue, $\ell\hbar$, then

$$\hat{L}_+\psi_{\max} = 0, \quad \text{while} \quad \hat{L}_z\psi_{\max} = \ell\hbar\psi_{\max} \quad \text{and} \quad \hat{L}^2\psi_{\max} = \lambda\psi_{\max}$$

where ℓ and λ are to be determined.

What are eigenvalues of angular momentum operators \hat{L}^2 and \hat{L}_z ?

Determine ℓ and λ from

$$\hat{L}_+ \psi_{\max} = 0, \quad \text{while} \quad \hat{L}_z \psi_{\max} = \ell \hbar \psi_{\max} \quad \text{and} \quad \hat{L}^2 \psi_{\max} = \lambda \psi_{\max}$$

Start by applying \hat{L}^2 to ψ_{\max} ,

$$\hat{L}^2 \psi_{\max} = \left(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \right) \psi_{\max} = \lambda \psi_{\max}.$$

Next, use identity

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

Prove $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}_- \hat{L}_+ + \hbar \hat{L}_z$

$$\hat{L}_x^2 + \hat{L}_y^2 = \underbrace{\left(\frac{\hat{L}_+ + \hat{L}_-}{2}\right)}_{\hat{L}_x} \underbrace{\left(\frac{\hat{L}_+ + \hat{L}_-}{2}\right)}_{\hat{L}_x} + \underbrace{\left(\frac{\hat{L}_+ - \hat{L}_-}{2i}\right)}_{\hat{L}_y} \underbrace{\left(\frac{\hat{L}_+ - \hat{L}_-}{2i}\right)}_{\hat{L}_y}$$

$$\hat{L}_x^2 + \hat{L}_y^2 = \frac{(\hat{L}_+^2 + \hat{L}_- \hat{L}_+ + \hat{L}_+ \hat{L}_- + \hat{L}_-^2)}{4} + \frac{(\hat{L}_+^2 - \hat{L}_- \hat{L}_+ - \hat{L}_+ \hat{L}_- + \hat{L}_-^2)}{-4} = \frac{1}{2} (\hat{L}_- \hat{L}_+ + \hat{L}_+ \hat{L}_-).$$

From $[\hat{L}_+, \hat{L}_-] = \hat{L}_+ \hat{L}_- - \hat{L}_- \hat{L}_+ = 2\hbar \hat{L}_z$ get $\hat{L}_+ \hat{L}_- = 2\hbar \hat{L}_z + \hat{L}_- \hat{L}_+$

$$\hat{L}_x^2 + \hat{L}_y^2 = \frac{1}{2} (\hat{L}_- \hat{L}_+ + 2\hbar \hat{L}_z + \hat{L}_- \hat{L}_+) = \hat{L}_- \hat{L}_+ + \hbar \hat{L}_z$$

Similar approach to prove $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}_+ \hat{L}_- - \hbar \hat{L}_z$

What are eigenvalues of angular momentum operators \hat{L}^2 and \hat{L}_z ?

$$\hat{L}_+ \psi_{\max} = 0, \quad \text{while} \quad \hat{L}_z \psi_{\max} = \ell \hbar \psi_{\max} \quad \text{and} \quad \hat{L}^2 \psi_{\max} = \lambda \psi_{\max}$$

Use these equations to determine values of ℓ and λ .

Start by applying \hat{L}^2 to ψ_{\max} ,

$$\hat{L}^2 \psi_{\max} = \left(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \right) \psi_{\max} = \lambda \psi_{\max}.$$

Next, use identity

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

and obtain

$$\hat{L}^2 \psi_{\max} = \left(\hat{L}_- \hat{L}_+ + \hbar \hat{L}_z + \hat{L}_z^2 \right) \psi_{\max} = \left(0 + \ell \hbar^2 + \ell^2 \hbar^2 \right) \psi_{\max} = \ell(\ell + 1) \hbar^2 \psi_{\max} = \lambda \psi_{\max},$$

learn that $\lambda = \ell(\ell + 1) \hbar^2$.

What are eigenvalues of angular momentum operators \hat{L}^2 and \hat{L}_z ?

Similarly,

$$\hat{L}_- \psi_{\min} = 0, \quad \text{while} \quad \hat{L}_z \psi_{\min} = \ell' \hbar \psi_{\min} \quad \text{and} \quad \hat{L}^2 \psi_{\min} = \lambda \psi_{\min}$$

As before,

$$\hat{L}^2 \psi_{\min} = \left(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \right) \psi_{\min} = \lambda \psi_{\min}.$$

giving

$$\hat{L}^2 \psi_{\min} = \left(\hat{L}_+ \hat{L}_- - \hbar \hat{L}_z + \hat{L}_z^2 \right) \psi_{\min} = \left(0 - \ell' \hbar^2 + (\ell' \hbar)^2 \right) \psi_{\min} = \ell'(\ell' - 1) \hbar^2 \psi_{\min} = \lambda \psi_{\min}$$

learn that

$$\lambda = \ell'(\ell' - 1) \hbar^2 = \ell(\ell + 1) \hbar^2 \leftarrow \text{Since } \hat{L}^2 \psi = \lambda \psi \text{ for all } \psi$$

can only be true if $\ell' = -\ell$.

- $\hat{L}^2 \psi = \ell(\ell + 1) \hbar^2 \psi$, thus, $\ell(\ell + 1) \hbar^2$ is eigenvalue of \hat{L}^2
- Eigenvalues of \hat{L}_z range from $-\ell \hbar$ for ψ_{\min} to $+\ell \hbar$ for ψ_{\max} , and increase in steps of \hbar

What are eigenvalues of angular momentum operators \hat{L}^2 and \hat{L}_z ?

Using raising and lowering operators, determined behavior and eigenvalues of \hat{L}^2 and \hat{L}_z without explicit expression for ψ .

$$\hat{L}^2\psi = \ell(\ell + 1)\hbar^2\psi$$

and

$$\hat{L}_z\psi = m\hbar\psi \quad \text{where } m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$$

- If there are N steps between $m = -\ell$ and $m = \ell$ then $\ell = -\ell + N$ gives $\ell = N/2$.
- ℓ must have an integer or half-integer value,

$$\ell = 0, 1/2, 1, 3/2, \dots$$

- Notice that maximum eigenvalue of \hat{L}_z is smaller than total angular momentum, i.e., $\ell\hbar < \sqrt{\ell(\ell + 1)}\hbar$. This is due to uncertainty in \hat{L}_x and \hat{L}_y .

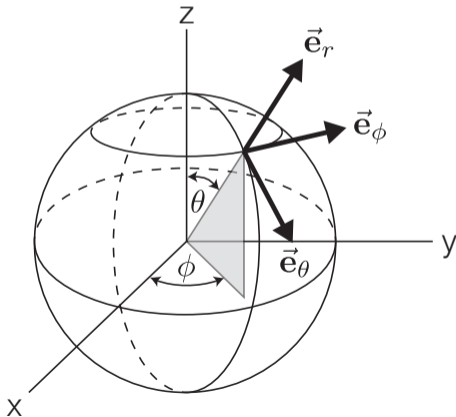
Eigenstates of angular momentum operators

Eigenstates of angular momentum operators \hat{L}^2 and \hat{L}_z

To determine eigenstates of \hat{L}^2 and \hat{L}_z , go back to

$$\vec{L} = \vec{r} \times \vec{p} = -i\hbar \vec{r} \times \vec{\nabla}$$

To go further we are better off working in spherical coordinates,



Eigenstates of angular momentum operators \hat{L}^2 and \hat{L}_z

In spherical coordinates

$$\vec{e}_r = \sin \theta \cos \phi \hat{e}_x + \sin \theta \sin \phi \vec{e}_y + \cos \theta \vec{e}_z,$$

$$\vec{e}_\theta = \cos \theta \cos \phi \hat{e}_x + \cos \theta \sin \phi \vec{e}_y - \sin \theta \vec{e}_z,$$

$$\vec{e}_\phi = -\sin \phi \hat{e}_x + \cos \phi \vec{e}_y,$$

or the inverse

$$\vec{e}_x = \sin \theta \cos \phi \hat{e}_r + \cos \theta \cos \phi \vec{e}_\theta - \sin \phi \vec{e}_\phi,$$

$$\vec{e}_y = \sin \theta \sin \phi \hat{e}_r + \cos \theta \sin \phi \vec{e}_\theta + \cos \phi \vec{e}_\phi,$$

$$\vec{e}_z = \cos \theta \hat{e}_r - \sin \theta \vec{e}_\theta,$$

and can express $\vec{\nabla}$ as

$$\vec{\nabla} = \vec{e}_r \frac{\partial}{\partial r} + \vec{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \vec{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}.$$

Eigenstates of angular momentum operators \hat{L}^2 and \hat{L}_z

After some quantum algebra, we obtain

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

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

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

Similarly, one can show that

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

Eigenstates of angular momentum operators \hat{L}^2 and \hat{L}_z

To determine eigenfunction of both \hat{L}^2 and \hat{L}_z , start with

$$\hat{L}_z \psi(\theta, \phi) = \frac{\hbar}{i} \frac{\partial \psi(\theta, \phi)}{\partial \phi} = m\hbar \psi(\theta, \phi)$$

Use separation of variables: $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$

Substituting into the partial differential equation,

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} \Theta(\theta)\Phi(\phi) = \frac{\hbar}{i} \Theta(\theta) \frac{\partial \Phi(\phi)}{\partial \phi} = m\hbar \Theta(\theta)\Phi(\phi)$$

and simplifying gives

$$\frac{d\Phi(\phi)}{d\phi} = im\Phi(\phi) \quad \text{which rearranges to} \quad \frac{d\Phi(\phi)}{\Phi(\phi)} = imd\phi$$

and integrates to

$$\Phi(\phi) = Ae^{im\phi}$$

Since we require wave functions to be single valued we must have

$$\Phi(\phi) = \Phi(\phi + 2\pi) \quad \text{or} \quad Ae^{im\phi} = Ae^{im(\phi+2\pi)}$$

which leads to the constraint $e^{im2\pi} = 1$ requiring $m = 0, \pm 1, \pm 2, \dots$

Eigenstates of angular momentum operators \hat{L}^2 and \hat{L}_z

Next we consider

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

Substituting the expression for \hat{L}^2 gives

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

Substituting $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ into this PDE and dividing both sides by $\psi(\theta, \phi)$

$$\frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \ell(\ell + 1) \sin^2 \theta = -\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = m^2,$$

Identify m^2 as separation constant for this PDE. No need to go further.

Recognize this PDE from Chapter 8 (Classical Waves) as having spherical harmonic wave solutions

$$Y_{\ell,m}(\theta, \phi) = (-1)^m \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}} P_{\ell}^m(\cos \theta) e^{im\phi}$$