Quantum Particle in Three Dimensions

Chapter 16

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Free particle in 3D

A free particle moving in 3D with no forces acting on it, that is, $V(\vec{r}) = 0$, time independent Schrödinger equation is

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

$\psi(\vec{r})$ is stationary state eigenstate of $\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2$

Total wave function is

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

For particle with momentum $\vec{p} = \hbar\vec{k}$ wave function is

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

Free particle in 3D

In 3D momentum operator is vector operator

$$\vec{\hat{p}} = \hat{p}_x \vec{e}_x + \hat{p}_y \vec{e}_y + \hat{p}_z \vec{e}_z,$$

where

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

Kinetic energy operator in 3D is

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

Particle in Infinite 3D Well

Particle bound in infinite 3D well

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

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

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2} + k^2 = 0$$

$k^2 = 2mE/\hbar^2$

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 $Z(z)$

$$\frac{1}{Z(z)}\frac{d^2 Z(z)}{dz^2} + k_z^2 = 0$$

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

Particle in Infinite 3D Well

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

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

Similarly, we find total energy

$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m}$$

becomes

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

Degeneracy and density of states

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

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

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

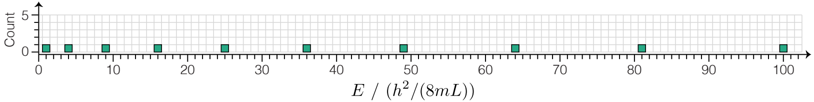
We can readily find states with identical energy

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

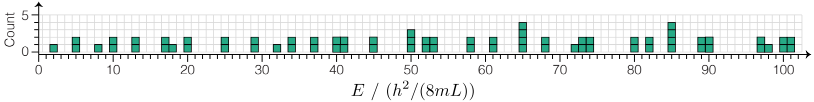
Degeneracy and density of states

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

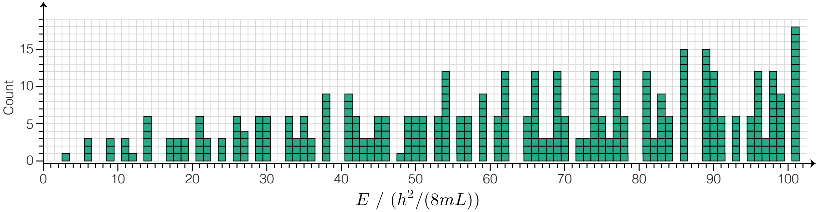
- 1D



- 2D



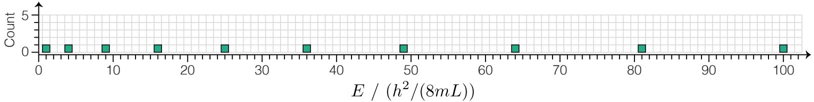
- 3D



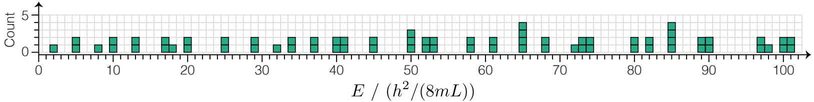
Degeneracy and density of states

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

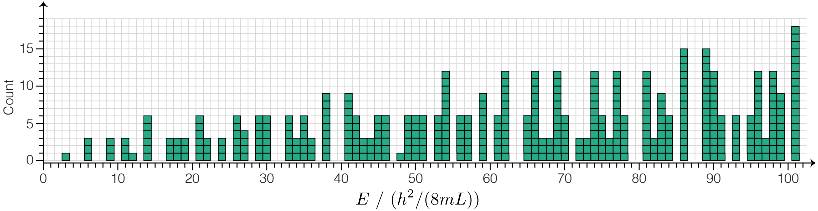
- Density of states in 1D in given dE decreases with increasing E



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

For particle in 1D infinite well the energy is

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

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

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

Rearranging energy

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

and calculate

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

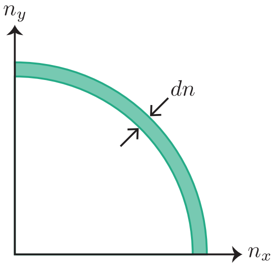
Consistent with 1D energy histogram plot – density of states decreases with inverse square root of energy.

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

For particle in 2D infinite well the energy is

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

- Defines circle passing through positive n_1 and n_2 quadrant of 2D space.
- Taking $1/4$ of circle circumference 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

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

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

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

In 3D 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 $E + dE$.

Taking $1/8$ of surface area of this sphere times dn as number of states that lie in n to $n + dn$ we write number of states associated with a given dE in 3D as

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

Substituting expressions for n and dn/dE gives

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

Consistent with 3D energy histogram plot – density of states increase with the square root of energy.

Quantum Theory of Angular Momentum

Quantum Theory of Angular Momentum

Angular momentum of particle with respect to origin is

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

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.

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

and we find

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

Quantum Theory of Angular Momentum

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

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 $\hat{L}_z$.

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

Notice cyclic permutation of subscripts, $x \to y \to z \to x \cdots$.

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 $\hat{L}_z$

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

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

Angular momentum eigenvalues

To determine eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ start with

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

where λ and μ represent the yet-to-be-determined eigenvalues.
Convenient to introduce related raising and lowering operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \text{and} \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Similar approach taken for harmonic oscillator

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

Recalling that $[\hat{L}_z, \hat{L}_+] = \hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z = \hbar\hat{L}_+$ then we have

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

and obtain

$$\hat{L}_z\psi' = \hbar\hat{L}_+\psi + \hat{L}_+\mu\psi = \underbrace{(\hbar + \mu)}_{\text{eigenalue of } \psi'}\hat{L}_+\psi,$$

Effect of $\hat{L}_+$ is to increase eigenvalue of $\hat{L}_z$ by $\hbar$.

Angular momentum eigenvalues

Similarly show that $\hat{L}_-$ is a lowering operator—operates on eigenstate of $\hat{L}_z$ to make new eigenstate with eigenvalue lower by $\hbar$.

- $\hat{L}_z$ corresponds to z component of angular momentum,
- $\hat{L}^2$ corresponds to square of total angular momentum.
- $\hat{L}_+$ cannot create new $\hat{L}_z$ eigenstate with eigenvalue greater than total angular momentum.
- one component of vector cannot exceed total length of vector.

So there is an eigenstate of $\hat{L}_z$ with highest possible eigenvalue, ψ_{max}, and we require

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

where ℓ is value to be determined.

Angular momentum eigenvalues

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

Use these equations to determine values of ℓ and λ.

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

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

Next we use identity

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

Proof of useful 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 as follows:

$$\begin{aligned}
\hat{L}_x^2 + \hat{L}_y^2 &= \left(\frac{\hat{L}_+ + \hat{L}_-}{2}\right)\left(\frac{\hat{L}_+ + \hat{L}_-}{2}\right) + \left(\frac{\hat{L}_+ - \hat{L}_-}{2i}\right)\left(\frac{\hat{L}_+ - \hat{L}_-}{2i}\right) \\
&= \frac{\left(\hat{L}_+^2 + \hat{L}_-\hat{L}_+ + \hat{L}_+\hat{L}_- + \hat{L}_-^2\right)}{4} + \frac{\left(\hat{L}_+^2 - \hat{L}_-\hat{L}_+ - \hat{L}_+\hat{L}_- + \hat{L}_-^2\right)}{-4} \\
&= \frac{1}{2}\left(\hat{L}_-\hat{L}_+ + \hat{L}_+\hat{L}_-\right).
\end{aligned}$$

Since $[\hat{L}_+, \hat{L}_-] = \hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+ = 2\hbar\hat{L}_z$ we can substitute for $\hat{L}_+\hat{L}_-$ and obtain first expression on the right.
One can similarly obtain second expression on the right.

Angular momentum eigenvalues

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

Use these equations to determine values of ℓ and λ.

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

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

Next we use identity

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

we can write

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

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

Angular momentum eigenvalues

Similarly, at the other end, the z component of the angular momentum vector can never be longer than the total angular momentum vector length so we have the analogous expressions:

$$\hat{L}_-\psi_{\text{min}} = 0,$$

and

$$\hat{L}_z\psi_{\text{min}} = \ell'\hbar\psi_{\text{min}}, \quad \text{and} \quad \hat{L}^2\psi_{\text{min}} = \ell(\ell+1)\hbar^2\psi_{\text{min}}.$$

As before we obtain

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

giving $\lambda = \ell'(\ell'+1)\hbar^2$.
Since $\hat{L}^2\psi = \lambda\psi$ for all ψ we must have

$$\ell(\ell+1) = \ell'(\ell'+1),$$

and so the only reasonable conclusion is that $\ell' = -\ell$.

Angular momentum eigenvalues

Bringing all this together we know that the eigenstates of $\hat{L}_z$ range from $-\ell$ for ψ_{min} to $+\ell$ for ψ_{max}, and increase in steps of $\hbar$ for wave functions in between. Thus we have

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

and

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

If there are N steps between $m = -\ell$ and $m = \ell$ then $\ell = -\ell + N$ and $\ell = N/2$.

That is, ℓ much have an integer or half-integer value,

$$\boxed{\ell = 0,\ 1/2,\ 1,\ 3/2,\ \dots.}$$

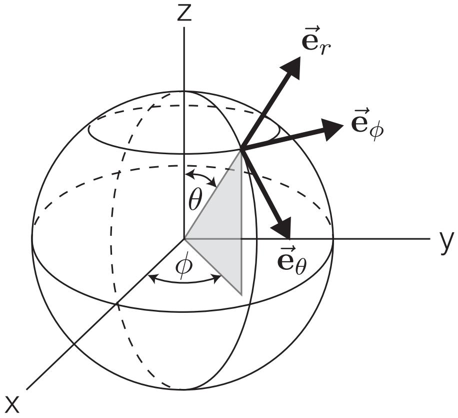
Notice that by using raising and lowering operators we could determine the behavior and values of the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ without actually having an explicit expression for ψ.

Angular momentum eigenstates

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

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

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



Angular momentum eigenstates

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

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

Angular momentum eigenstates

Using $\vec{\hat{r}} = \hat{r}\vec{e}_r$ we expand the angular momentum operator as

$$\vec{\hat{L}} = \frac{\hbar}{i}\left[\hat{r}(\vec{e}_r \times \vec{e}_r)\frac{\partial}{\partial r} + (\vec{e}_r \times \vec{e}_\theta)\frac{\partial}{\partial \theta} + (\vec{e}_r \times \vec{e}_\phi)\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right]$$

and since $\vec{e}_r \times \vec{e}_r = 0$, $\vec{e}_r \times \vec{e}_\theta = \vec{e}_\phi$, and $\vec{e}_r \times \vec{e}_\phi = -\vec{e}_\theta$ we obtain

$$\vec{\hat{L}} = \frac{\hbar}{i}\left[\vec{e}_\phi\frac{\partial}{\partial \theta} - \vec{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right]$$

Substituting the expressions for $\vec{e}_\phi$ and $\vec{e}_\theta$ on the previous page we obtain

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

Angular momentum eigenstates

Collecting the $\vec{e}_x$, $\vec{e}_y$, and $\vec{e}_z$ components gives

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

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

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

Similarly one can show that

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

Angular momentum eigenstates

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

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

Using separation of variables we can write $\psi(\theta, \phi)$ as

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

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

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

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

$$e^{im2\pi} = 1 \quad \text{requiring } m = 0, \pm 1, \pm 2, \dots$$

Angular momentum eigenstates

Next we consider

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

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

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

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.

We recognize this PDE as having the spherical harmonic wave solutions

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