Angular Momentum (warm-up for H-atom)
Classically, angular momentum defined as (for a 1-particle system)

\[ \vec{L} = \vec{r} \times \vec{p} \]

\[ = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \]

Note: \( \vec{L} \) defined w.r.t. an origin of coords.

\[ \vec{L} = \hat{x}(yp_z - zp_y) + \hat{y}(zp_x - xp_z) + \hat{z}(xp_y - yp_z) \]

(In QM, the operator corresponding to \( L_\theta \) is \( \vec{L}_x = \hat{y} \hat{p}_x - \hat{z} \hat{p}_y, \quad p_x = \frac{\hbar}{i} \frac{\partial}{\partial z} \), etc. according to prescription of Postulate 2, part 3.)

Classically, torque defined as \( \vec{\tau} = \vec{r} \times \vec{F} \), and \( \vec{\tau} = \frac{d\vec{L}}{dt} \) (rotational version of \( \vec{F} = m\vec{a} \))

If the force is radial (central force), then \( \vec{\tau} = \vec{r} \times \vec{F} = 0 \Rightarrow \vec{L} = \text{const.} \)

H-atom:

In a multi-particle system, total average momentum:

\[ \vec{L}_{tot} = \sum \vec{L}_i \text{ is conserved for system isolated from external torques.} \]

sum over particles

Internal torques can cause exchange of average momentum among particles, but \( \vec{L}_{tot} \) remains constant.

In classical and quantum mechanics, only 4 things are conserved:

- energy
- linear momentum
- angular momentum
- electric charge
Back to QM. Define vector operator \( \hat{\mathbf{L}} \)

\[
\hat{\mathbf{L}} = \hat{L}_x \hat{x} + \hat{L}_y \hat{y} + \hat{L}_z \hat{z}
\]

Recall \( \frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar} \left\langle \left[ \hat{H}, \hat{Q} \right] \right\rangle \)

\[
\Rightarrow \quad \frac{d\langle \hat{L} \rangle}{dt} = \frac{i}{\hbar} \left\langle \left[ \hat{H}, \hat{L} \right] \right\rangle
\]

\[
\frac{d}{dt} < \hat{L}_x > \hat{x} + \frac{d}{dt} < \hat{L}_y > \hat{y} + \ldots
\]

Claim: for a central force such as in H-atom

\[
V = V(r) = -\frac{ke^2}{r}, \text{ then } \left[ \hat{H}, \hat{L} \right] = 0 \quad \text{(will show this later)}
\]

This implies \( \frac{d\hat{L}}{dt} = 0 \) (just like in classical mechanics)

Angular momentum of electron is H-atom is constant, so long as it does not absorb or emit photon. Throughout present discussion, we ignore interaction of H-atom w/photons.

Will show that for H-atom or for any atom, molecule, solid – any collection of atoms – the angular momentum is quantized in units of \( \hbar \). \( |\vec{L}| \) can only change by integer number of \( \hbar \)'s.

Units of \( L = [L] = [h] \)

Note \( [L] = [rp][p] = \left[ \frac{\hbar}{r} \right] \) (since \( p = \hbar k \))

\[
\Rightarrow \left[ L \right] = \left[ r \right] \left[ \frac{\hbar}{r} \right] = [h]
\]

Claim: \( \left[ \hat{L}_x, \hat{L}_y \right] = i\hbar \hat{L}_z \)

and \( \left[ \hat{L}_x, \hat{L}_z \right] = i\hbar \hat{L}_y \quad (i, j, k \text{ cyclic: } \begin{array}{ccc} x & y & z \end{array} \text{ or } \begin{array}{ccc} y & z & x \end{array} \text{ or } \begin{array}{ccc} z & x & y \end{array} )\)
To prove, need two very useful identities: 

\[
[A + B, C] = [A, C] + [B, C] \\
\]

Proof: 

\[
\left[L_x, L_y\right] = \left[yp_z - zp_y, zp_x - xp_z\right] = \left[yp_z, zp_x\right] - \left[zp_y, xp_z\right] = \left[yp_z, xp_z\right] + \left[zp_y, zp_x\right] - i\hbar (xp_y - yp_z) = i\hbar L_z
\]

(Have used \([x, p_x] = i\hbar, [x, y] = 0, [x, p_y] = 0, [p_x, p_y] = 0\), etc.)

I’m dropping the ^ over operators when no danger of confusion.

Since \([L_x, L_y] \neq 0\), cannot have simultaneous eigenstates of \(\hat{L}_x\) and \(\hat{L}_y\).

\[
\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left( \frac{1}{2i} \left\langle \left[\hat{L}_x, \hat{L}_y\right] \right\rangle \right)^2 = \left( \frac{\hbar}{2} \right)^2 \langle L_z \rangle^2
\]

However, \(L_z^2 = \hat{L}_z \cdot \hat{L}_x = L_x^2 + L_y^2 + L_z^2\) does commute with \(L_z\).

Claim: 

\[
\left[\hat{L}_x^2, \hat{L}_z\right] = 0\\n\left[\hat{L}_y^2, \hat{L}_z\right] = 0, i = x, y, or z
\]

Proof: 

\[
\left[\hat{L}_x^2, \hat{L}_z\right] = \left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right] - i\hbar L_y - i\hbar L_y + i\hbar L_x + i\hbar L_x = 0
\]

\([\hat{L}_x^2, \hat{L}_z] = 0 \implies \text{can have simultaneous eigenstates of } \hat{L}_x^2, \hat{L}_z (\text{or } \hat{L}_y^2, \hat{L}_z, \text{any } i)\)
Looking forward to H-atom:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \cdot (\ )$$

We will show that $[\hat{H}, \hat{L}^2] = 0$, $[\hat{H}, \hat{L}_z] = 0$

$\Rightarrow$ simultaneous eigenstates of $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$

energy q-nbr

$$\psi = \psi_{n \ell m} \quad \text{L}_z \text{q-nbr}$$

$$\psi = \psi_{n \ell m} \quad \text{L}^2 \text{q-nbr}$$

When we solve the TISE $\psi = E \psi$ for the H-atom, the natural coordinates to use will be spherical coordinates: $r, \theta, \varphi$ (not $x, y, z$)

$$x = r \sin \theta \cos \varphi$$
$$y = r \sin \theta \sin \varphi$$
$$z = r \cos \theta$$

Just rewriting $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in spherical coordinates is gawd-awful. But separation of variables will give special solutions, energy eigenstates, of form

$$\psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi)$$

The angular part of the solution $Y(\theta, \varphi)$ will turn out to be eigenstates of $L^2$, $L_z$ and will have form completely independent of the potential $V(r)$. 

* * *
Given only \([L^2, L_z] = 0\) and \(\hat{L}^2, \hat{L}_z\) hermitean we know there must exist simultaneous eigenstates \(f\) (which will turn out to be the \(Y(\theta, \varphi)\) mentioned above) such that

\[
\hat{L}^2 f = \lambda \cdot f, \quad \hat{L}_z f = \mu \cdot f
\]

(\(\lambda\) will be related to \(l\), and \(\mu\) will be related to \(m\))

We will show that \(f\) will depend on quantum-numbers \(l, m\), so we write it as \(f_{lm}\), and that

\[
\begin{align*}
L^2 f_{lm} &= \hbar^2 l(l + 1) \cdot f_{lm} \\
L_z f_{lm} &= \hbar m \cdot f_{lm}
\end{align*}
\]

where \(l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots\) \(m = -l, -l + 1, \ldots l - 1, l\)

\(f_{lm} = Y_{lm}^m(\theta, \varphi)\) will be determined later.

Notice max eigenvalue of \(L_z\) \((= l\hbar)\) is smaller than square root of eigenvalue of \(L^2 = \hbar \sqrt{l(l + 1)}\)

So, in QM, \(L_z < |L|\) Odd!

Also notice \(l = 0, m = 0\) state has zero angular momentum \((L^2 = 0, L_z = 0)\) so, unlike Bohr model, can have electron in state that is "just sitting there" rather than revolving about proton in H-atom.

---

Proof of boxed \(\star\) formulae: (This proof takes 2 \(\frac{1}{2}\) pages!)

Define \(L_+ = L_x + i L_y = \) "raising operator"
\(L_- = L_x - i L_y = \) "lowering operator"

(Note \(L_+^\dagger = L_-, \quad L_-^\dagger = L_+\), \(A^\dagger =\) hermitean adjoint of \(A\))

Neither \(L_+\) or \(L_-\) are hermitean (self-adjoint).

Note

\[
\begin{bmatrix}
L^2, L_z\end{bmatrix} = 0
\]

\[
\begin{bmatrix}
L^2, L_+\end{bmatrix} = \begin{bmatrix}
L^2, L_z
\end{bmatrix} + i \begin{bmatrix}
L^2, L_y
\end{bmatrix} = 0
\]

\(\Rightarrow\) Consider \(f\):

\[
L^2 f = \lambda \cdot f, \quad L_z f = \mu \cdot f
\]
Claim: \( g = L_+ f \) is an eigenfunction of \( L_z \) with eigenvalue \( = (\mu + \hbar) \). So \( L_+ \) operator raises eigenvalue of \( L_z \) by \( 1 \hbar \).

Proof: 
\[
L^2 g = L^2 (L_+ f) = L_+ (L^2 f) = \lambda \cdot L_+ f = \lambda \cdot g
\]

To prove \( L_+ g = (\mu + \hbar) g \), need to show that \([L_z, L_+] = \hbar L_+\)

\[
\left[ L_z, L_+ + iL_y \right] = \left[ L_z, L_+ \right] + \frac{i}{\hbar} \left[ L_z, L_y \right] = \hbar \left( L_z + iL_y \right)
\]

Now \( L_+ g = \frac{L_z(L_+ f)}{\mu f} = L_+ L_z f + \hbar L_+ f = (\mu + \hbar) L_+ f \)

So, operating on \( f \) with raising operator \( L_+ \) raises eigenvalues of \( L_z \) by \( \hbar \) but keeps eigenvalue of \( L^2 \) unchanged.

(Similarly, \( L_- \) lowers eigenvalue of \( L_z \) by \( \hbar \).)

Operating repeatedly with \( L_+ \), raises eigenvalue of \( L_z \) by \( \hbar \) each time: \( L_+ (L_+ f) \) has \( (\mu + 2\hbar) \) etc.

But eigenvalue of \( L_z \) cannot increase without limit since \( \langle L_z \rangle \) cannot exceed \( \sqrt{\langle L^2 \rangle} \)

\[
\frac{\langle L^2 \rangle}{\lambda} = \frac{\langle L_z^2 \rangle}{\mu^2} + \frac{\langle L_y^2 \rangle}{\geq 0} \implies \lambda > \mu^2,
\]

\[
\lambda > |\mu|
\]

There is only one way out. There must be for a given \( \lambda \) a "top state" \( f_t \) for which \( L_+ f_t = 0 \).
Likewise, there must be for a given \( \lambda \) a "bottom state" \( f_b \) for which \( L_- f_b = 0 \).

\[
\begin{align*}
L_+ f_t & = 0 \\
L_- f_b & = 0
\end{align*}
\]

all with same \( \lambda = \text{eigenvalue of} \ L^2 \)
Write \( L_z f = m \hbar \cdot f \), \( m \) changes by integers only

\[
L_z f_{\ell} = \ell \hbar \cdot f_{\ell}, \quad \ell = \max\ \text{value of} \ m
\]

\( L^2 f_{\ell} = ? \) Want to write \( L^2 \) in terms of \( L_x, L_z \):

\[
L_x L_z = (L_x - iL_y)(L_x + iL_y) = L_x^2 + L_y^2 + i[L_x, L_y] = \frac{L^2 - L_z^2}{\ell \hbar L_z} = \hbar L_z
\]

\[
\Rightarrow L^2 = L_x L_z + L_z^2 + \hbar L_z
\]

(Also, \( L^2 = L_x L_z + L_z^2 - \hbar L_z \))

\[
\Rightarrow L^2 f_{\ell} = L_x L_z f_{\ell} + L_z^2 f_{\ell} + \hbar L_z f_{\ell} = \hbar^2 \ell (\ell + 1) f_{\ell}
\]

So, \( L^2 f = \hbar^2 \ell (\ell + 1) f \) where \( \ell = \max m \), same \( \lambda \) for all \( m \)'s.

Repeat for \( f_b : L_z f_b = \hbar \overline{\ell} f_b \), \( \overline{\ell} = \min \text{value of} \ m \).

\[
L^2 f_b = L_x L_z f_b + L_z^2 f_b + \hbar L_z f_b = \hbar^2 \overline{\ell} (\overline{\ell} - 1) f_b
\]

\[
\lambda = \overline{\lambda} \Rightarrow \ell(\ell + 1) = \overline{\ell}(\overline{\ell} - 1) \Rightarrow \overline{\ell} = -\ell \ (\text{try it!})
\]

So \( m_{\min} = -m_{\max} \) and \( m \) changes only in units of 1.

\[
\Rightarrow m = -\ell, -\ell + 1, \ldots \ell - 2, \ell - 1, \ell
\]

\( N \) integer steps

\[
\Rightarrow 2 \ell = N, \ \ell = N / 2 \Rightarrow \ell = 0, 1/2, 1, 3/2, 2, 5/2, \ldots
\]

End of proof of \( \star \)
We'll see later that there are 2 flavors of angular momentum:

1. Orbital
   Ang. Mom.
   (integer $\ell$ only)

2. Spin
   Ang. Mom.
   (integer or $\frac{1}{2}$ integer OK)
The H- atom

\[ m_p \gg m_e \implies \text{proton (nearly) stationary} \]

Hamiltonian of electron = \( \hat{H} = \frac{\hat{p}^2}{2m} + V(r) \)

\[ V(r) = -\frac{ke^2}{r}, \quad k = \frac{1}{4\pi\varepsilon_0} \quad \text{(or} \quad V(r) = -\frac{kZe^2}{r} \text{)} \]

\[ \frac{\hat{p}^2}{2m} = \frac{\hat{p}^2 \cdot \hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 (\ ) \]

TISE: \( \hat{H} \psi_n = E_n \psi_n \implies \text{special solutions (stationary states).} \)

\[ \psi_n (x) = \psi_n (x, t) = \psi_n (x) e^{-iE_n t / \hbar} \]

General Solution to TDSE: \( \Psi(x, t) = \sum_n c_n e^{-iE_n t / \hbar} \psi_n (x) \)

Spherical Coordinate System:

\[ \psi = \psi (r, \theta, \varphi) \]

Normalization:

\[ \int dV |\psi|^2 = 1 \]

\[ \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi r^2 \sin \theta |\psi|^2 = 1 \]

Need \( \nabla^2 \) in spherical coordinates

Hard Way: \( \nabla^2 f = \nabla \cdot \nabla f = \frac{\partial^2 f}{\partial x^2} + \ldots \)
Also need 9 derivatives: \( \frac{\partial r}{\partial x}, \frac{\partial r}{\partial y}, \ldots, \frac{\partial \theta}{\partial x} \ldots \)

Easier Way: Curvilinear coordinates (See Boas)

path element:
\[
d\vec{s} = \hat{x} dx + \hat{y} dy + \hat{z} dz
\]
\[
= \hat{r} dr + \hat{\theta} \ r \ d\theta + \hat{\phi} \ r \sin \theta \ d\phi
\]
\[
= \hat{e}_r \ r \ dx + \hat{e}_\theta \ \ r \ \sin \theta \ dx + \hat{e}_\phi \ \ dx
\]
\[
= \sum_{i=1}^{3} \hat{e}_i \ h_i \ dx_i \quad (h_i = "scale \ factor")
\]
\[
\nabla f = \sum_{i=1}^{3} \hat{e}_i \ \frac{1}{h_i} \ \frac{\partial f}{\partial x_i}
\]
\[
\nabla^2 f = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial x_1} \left( h_2 h_3 \frac{\partial f}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( h_1 h_3 \frac{\partial f}{\partial x_2} \right) + \ldots \right]
\]

Spherical coordinates:
\[
\{r\} = \{r, \ \theta, \ \phi\}
\]
\[
\{\vec{e}\} = \{\hat{r}, \ \hat{\theta}, \ r \ \sin \theta \ \hat{\phi}\}
\]
\[
\Rightarrow \nabla^2 f = \frac{1}{r^2} \ \frac{\partial}{\partial r} \left( r^2 \ \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \ \sin \theta} \ \frac{\partial}{\partial \theta} \left( \sin \theta \ \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \ \sin^2 \theta} \ \frac{\partial^2 f}{\partial \phi^2}
\]
\[
= (\text{radial}) \ + \frac{1}{r^2} \ (\text{angular})
\]

In Classical Mechanics (CM), KE = \( p^2 / 2m = KE = \)|m\vec{v}| (radial motion KE) + (angular, axial motion KE)

\[
\Rightarrow \vec{v}_\perp = \frac{L}{mr}
\]

\[
KE = \frac{1}{2} m v^2 = \frac{m}{2} (v_r^2 + v_\perp^2) = \frac{p_r^2}{2m} \ (\text{radial)} + \frac{L^2}{2mr^2} \ (\text{angular)}
\]

\[
\vec{L} = |\vec{r} \times \vec{mv}| = mrv_\perp
\]
Same splitting in QM:

\[ \hat{L}^2 = \left( \frac{\hbar}{i} \hat{r} \times \nabla \right)^2 = -\hbar^2 \left[ \frac{1}{s} \frac{\partial}{\partial \theta} \left( s \frac{\partial}{\partial \theta} \right) + \frac{1}{s^2} \frac{\partial^2}{\partial \phi^2} \right] \]

(Notice \( \hat{L}^2 \) depends only on \( \theta, \phi \) and not \( r \).)

\[ \hat{H}\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(r)\psi = E\psi \]

\[ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} \psi + V(r)\psi = E\psi \]

Separation of Variables! (as usual)
Seek special solution of form:

\[ \psi(r,\theta,\phi) = R(r) \cdot Y(\theta,\phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi) \]

Normalization: \( \int dV \mid \psi \mid^2 = \int_0^\infty r^2 |R|^2 \cdot \int_0^\pi \int_0^{2\pi} \sin \theta |Y|^2 = 1 \)

(Convention: normalize radial, angular parts individually)

Plug \( \psi = R \cdot Y \) into TISE =>

\[ -\frac{\hbar^2}{2m} \frac{Y}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{R}{2mr^2} \hat{L}^2 Y + V \cdot R \cdot Y = E \cdot R \cdot Y \]

Multiply thru by \( \frac{-2mr^2}{\hbar^2} \frac{1}{R \cdot Y} \):

\[ \left\{ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} (V - E) \right\} f(r) \]

\[ \Rightarrow f(r) = g(\theta, \phi) = \text{constant } C = \ell(\ell + 1) \]

\[ \hat{L}^2 Y = \hbar^2 C \cdot Y = \hbar^2 \ell(\ell + 1) Y \] (Page H-5)
Have separated TISE into radial part \( f(\mathbf{r}) = \ell(\ell + 1) \), involving \( V(\mathbf{r}) \), and angular part \( g(\theta, \phi) = \ell(\ell + 1) \) which is independent of \( V(\mathbf{r}) \).

\[ \Rightarrow \] All problems with spherically symmetric potential \( (V = V(\mathbf{r})) \) have exactly same angular part of solution: \( Y = Y(\theta, \phi) \) called "spherical harmonics".

We'll look at angular part later. Now, let's examine

Radial SE: \( \left( x - \frac{\hbar^2}{2mr} \cdot \mathbf{R} \right) \)

\[ \frac{-\hbar^2}{2mr} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + r \cdot R(V - E) = \frac{-\hbar^2 \cdot rR}{2mr^2} \ell(\ell + 1) \]

Change of variable: \( u(r) = r \cdot R(r) \)

\[ \int_0^\infty dr |u|^2 = 1 \]

Can show that \( \frac{1}{r} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = \frac{d^2u}{dr^2} : \)

\[
\frac{du}{dr} = R + r \frac{dR}{dr}, \quad \frac{d^2u}{dr^2} = \frac{dR}{dr} + \frac{dR}{dr} + r \frac{d^2R}{dr^2}
\]

\[ \frac{1}{r} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = \frac{1}{r} \left( 2r \frac{dR}{dr} + r^2 \frac{d^2R}{dr^2} \right) = 2 \frac{dR}{dr} + r \frac{d^2R}{dr^2} \]

\[ \frac{-\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[ V + \frac{\hbar^2 \ell(\ell + 1)}{2mr^2} \right] u = Eu \]

Notice: identical to 1D TISE:

\[ \frac{-\hbar^2}{2m} \frac{d^2\psi}{dr^2} + V \cdot \psi = E \psi \quad \text{except} \]

\( r: 0 \to \infty \) instead of \( x: -\infty \to +\infty \) and

\( V(x) \) replaced with \( \frac{\hbar^2}{2mr^2} \ell(\ell + 1) \)

\( V_{\text{eff}} = \text{"effective potential"} \)

Boundary conditions:
Seek bound state solutions $E < 0$

$E > 0$ solutions are unbound states, scattering solutions

Full solution of radial SE is very messy, even though it is effectively a 1D problem (different problem for each $\ell$)

Power series solution (see text for details). Solutions depend on 2 quantum numbers: $n$ and $\ell$ (for each effective potential $\ell = 0, 1, 2, \ldots$ have a set of solutions labeled by index $n$.)

Solutions:  

\[
\ell = 0, 1, \ldots (n - 1) \quad \ell_{\text{max}} = (n - 1)
\]

$n =$ "principal quantum number"

energy eigenvalues depend on $n$ only (it turns out)

\[
E_n = \frac{E_1}{n^2}, \quad E_1 = -\frac{m(ke^2)^2}{2\hbar^2} \quad \text{(independent of $\ell$)}
\]

• same as Bohr model, agrees with experiment!
First few solutions: $R_{n\ell}(r)$

\[ R_{10} = A_{10} e^{-r/a_0}, \quad a_0 = \frac{\hbar^2}{kme^2} = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} \]
\[ R_{20} = A_{20} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \]
\[ R_{21} = A_{21} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \]

**NOTE:**

- for $\ell = 0$ (s states), $R(r = 0) \neq 0 \Rightarrow$ wavefunction $\psi$ "touches" nucleus.
- for $\ell \neq 0$, $R(r = 0) = 0 \Rightarrow \psi$ does not touch nucleus.

$\ell \neq 0 \Rightarrow$ electron has angular momentum. Same as classical behavior, particle with non-zero $L$ cannot pass thru origin ($\hat{L} = \vec{r} \times \vec{p} : r = 0 \Rightarrow p = \infty$)

Can also see this in QM: for $\ell \neq 0$, $V_{\text{eff}}$ has infinite barrier at origin $\Rightarrow u(r)$ must decay to zero at $r=0$ **exponentially**.

\[ V_{\text{eff}} \]
\[ r \]
\[ \Rightarrow \text{exponential decay in} \]
\[ R(r) = \frac{u(r)}{r} \] as well.
Back to angular equation: \( \hat{L}^2 Y^m_\ell = \hbar^2 \ell (\ell + 1) Y^m_\ell \) Want to solve for the \( Y^m_\ell \)'s - "spherical harmonics". Before, started with commutation relations,
\[
[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, \quad [\hat{L}^2, \hat{L}_z] = 0
\]
and, using operator algebra, solved for the eigenvalues of \( L^2, L_z \). We found
\[
\begin{align*}
L^2 Y^m_\ell &= \hbar^2 \ell (\ell + 1) Y^m_\ell \\
L_z Y^m_\ell &= m \hbar Y^m_\ell
\end{align*}
\]
where \( \ell = 0, \frac{1}{2}, 1, 3/2, \ldots \)
\( m = -\ell, -\ell + 1, \ldots + \ell \)

In the process, we defined raising and lowering operators:
\[
\begin{align*}
\hat{L}_+ Y^m_\ell &= c_m Y^{m+1}_\ell \quad \text{(for } m < m_{max} = \ell) \\
\hat{L}_- Y^m_\ell &= c_m Y^{m-1}_\ell \quad \text{(for } m > m_{min} = \ell)
\end{align*}
\]
(c\(_m\) is some constant)
\[
\hat{L}_+ \psi_{\text{top}} = \hat{L}_- Y^\ell_\ell = 0 \quad \text{and} \quad \hat{L}_- Y^{-\ell}_\ell = 0
\]
So, if we can find (for a given \( \ell \)) a single eigenstate \( Y^m_\ell \), then we can generate all the others (other \( m \)'s) by repeated application of \( \hat{L}_+ \) or \( \hat{L}_- \).

\( Y^m_\ell = Y^m_\ell (\theta, \varphi) \).

It’s easy to find the \( \varphi \)-dependence; don’t need the \( \hat{L}_z \) business yet.
\[
\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi} \quad \text{(showed in HW)}
\]
\[
\hat{L}_z Y = \frac{\hbar}{i} \frac{\partial Y}{\partial \varphi} = \hbar m Y \quad \text{(and you can cancel the } \hbar \text{)}
\]
Assume \( Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi) \)

\[
\frac{d\Phi}{d\varphi} = im \Phi \quad \Rightarrow \quad \Phi(\varphi) = e^{im\varphi}
\]

If we assume (postulate) that \( \psi \) is single-valued than
\[
\Phi(\varphi + 2m) = \Phi(\varphi) \Rightarrow e^{im2\pi} = 1
\]
\( \Rightarrow m = 0, \pm 1, \pm 2, \ldots \text{ But } m = -\ell, \ldots + \ell \)

So for orbital angular momentum, \( \ell \) must be integer only: \( \ell = 0, 1, 2, \ldots \) (throw out \( \frac{1}{2} \) integer values)
(algebra!)

\[ L_+ = L_x + iL_y = \hbar e^{i\phi} \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \]

\[ L_- = L_x - iL_y = \hbar e^{-i\phi} \left( -\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \]

\[ (L_- L_+)^\dagger \rightarrow \text{adjoint} \quad \langle f | A^\dagger g \rangle = \langle Af | g \rangle \]

Can deduce \( Y_\ell^m \) from \( \hat{L}_- Y_\ell^\ell = 0 \)

\[ \Rightarrow \quad \frac{\partial Y_\ell^\ell}{\partial \theta} + i \cot \theta \frac{\partial Y_\ell^\ell}{\partial \varphi} = 0 \]

\[ Y_\ell^\ell (\theta, \varphi) = (\sin \theta)^\ell e^{i\ell \varphi} \quad \text{Solution: (un-normalized)} \]

Checks: Plug back in.

\[ \ell (\sin \theta)^{-1} \cos \theta e^{i\varphi} + i \cot \theta (\sin \theta)^\ell (i \ell \theta) e^{i\varphi} = 0 \]

\[ \ell (\sin \theta)^{\ell - 1} \frac{\cos \theta}{\sin \theta} e^{i\varphi} - \cot \theta (\sin \theta)^\ell \frac{\ell}{\cot \theta} = 0 \quad \checkmark \]

Now, can get other \( Y_\ell^m \)'s by repeated application of \( \hat{L}_- \). Somewhat messy (HW!)

Normalization from \( \int d\theta \int d\varphi \sin \theta \left| Y_\ell^m \right|^2 \)

Notice case \( \ell = 0 \)

\[ Y_0^0 = \text{const} = \frac{1}{\sqrt{4\pi}} \]

(since \( \int_0^\varphi \int_0^{2\varphi} \sin \theta = \int d\varphi = 4\pi \))

Example:

\[ Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi} \]

\[ Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta \]

\[ Y_1^{-1} = +\sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi} \]

Convention on \( \pm \) sign: \( Y_\ell^{-m} = (-1)^m \left( Y_\ell^m \right) \)
The spherical harmonics form a complete, orthonormal set (since eigenfunctions of hermitean operators)

\[ \int d\Omega \ (Y^m_\ell)^* Y^{m'}_{\ell'} = \delta_{\ell\ell'} \delta_{mm'} \]

Any function of angles \( f = f(\theta, \varphi) \) can be written as linear combo of \( Y^m_\ell \)s :

\[ f(\theta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell m} Y^m_\ell \]

Likewise:

\[ \int_0^\infty dr \ r^2 (R_{nl})^* R_{n'l'} = \delta_{nn'} \delta_{\ell\ell'} \]

=> H-atom **energy eigenstates** are

\[ \psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) Y^m_\ell(\theta, \varphi) = R_{n\ell} \Theta_{\ell m} e^{im\varphi} \]

\( n = 1, 2, \ldots \); \( \ell = 0, 1 \ldots (n-1) \); \( m = -\ell \ldots + \ell \)

Arbitrary (bound) state is

\[ \psi = \sum_{n,\ell,m} c_{n\ell m} \psi_{n\ell m} \quad (c's \text{ are any complex constants}) \]

energy of state \( (n, \ell, m) \) depends only on \( n \).

\[ E_n = - \text{constant}/n^2 \quad (\text{states } \ell, m \text{ with same } n \text{ are degenerate}) \]

\[
\begin{array}{c|cccc}
\ell = & 0 & 1 & 2 & 3 \\
\hline
n = 4 & 4 (1) & 4p (3) & 4d (5) & 4f (7) \\
3 & 3 & 3p & 3d \\
2 & 2p \\
1 & 1 \\
\end{array}
\]

Degeneracy of \( n^{\text{th}} \) level is \( n^2 \)

\( 2 \cdot n^2 \) if you include spin
Radial Probability Density

\[ \int dV |\psi|^2 = 1 \]

Prob (find particle in dV about \( \vec{r} \)) = \( |\psi(\vec{r})|^2 \) dV

If \( \ell = 0 \), \( \psi = \psi(r) \) then \( \int dV |\psi|^2 = \int dr 4\pi r^2 |\psi(r)|^2 \)

Prob (find in \( r \leq r + dr \)) = \[ P(r)dr = 4\pi r^2 |\psi(r)|^2 \] dr

\( P(r) \) = radial probability density

Ground state: \( \psi_{100} = A e^{-r/a_0} \)

\( P(r) = |A|^2 4\pi r^2 e^{-2r/a_0} \)

Notice \( P(r) \) very different from \( \psi(r) \):

If \( \ell \neq 0 \), \( \psi = \psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \), then

\[ \int dV |\psi|^2 = \int dr \frac{r^2 |R|^2}{1} \int d\Omega |Y|^2 = 1 \]

"solid angle"

Prob (find in \( r \leq r + dr \)) = \( r^2 |R|^2 \) dr

\[ P(r) = r^2 |R|^2 \] even if \( \ell \neq 0 \)

Note: \( \psi = \psi(r) = R \cdot Y = R \cdot \frac{1}{\sqrt{4\pi}} \Rightarrow |R|^2 = 4\pi |\psi|^2 \) if

so \( P(r) = r^2 |R|^2 = 4\pi r^2 |\psi|^2 \)

H-atom and emission/absorption of radiation:

If H-atom is in excited state (\( n = 2, \ell = 1, m = 0 \)) then it is in energy eigenstate = stationary state. If atom is isolated, then atom should remain in state \( \psi_{210} \) forever, since stationary state has simple time dependence:

\[ \Psi(\vec{r}, t) = \psi_{210}(r) \cdot e^{-\epsilon_2 t/\hbar} \]
But, experimentally, we find that H-atom emits photon and de-excites: $\psi_{210} \rightarrow \psi_{100}$ in $\approx 10^{-7} \text{ s} \rightarrow 10^{-9} \text{ s}$

The reason that the atom does not remain in stationary state is that it is not truly isolated. The atom feels a fluctuating EM field due to "vacuum fluctuations". Quantum Electrodynamics is a relativistic theory of the QM interaction of matter and light. It predicts that the "vacuum" is not "empty" or "nothing" as previously supposed, but is instead a seething foam of virtual photons and other particles. These vacuum fluctuations interact with the electron in the H-atom and slightly alter the potential $V(r)$. So eigenstates of the coulomb potential are not eigenstates of the actual potential: $V_{\text{coulomb}} + V_{\text{vacuum}}$

Photons possess an intrinsic angular momentum (spin) of $1 \hbar$, meaning

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

and $L_{z_{\text{max}}} = \hbar$

So when an atom absorbs or emits a single photon, its angular momentum must change by $1 \hbar$, by Conservation of Angular Momentum, so the orbital angular momentum quantum number $\ell$ must change by 1.

"Selection Rule": $\Delta \ell = \pm 1$ in any process involving emission or absorption of 1 photon $\Rightarrow$ allowed transitions are:

If an H-atom is in state 2s ($n = 2, \ell = 0$) then it cannot de-excite to ground state by emission of a photon. (since this would violate the selection rule). It can only lose its energy (de-excite) by collision with another atom or via a rare 2-photon process.
Matrix Formulation of QM

complete orthonormal set

\[ |\psi\rangle = \sum_n c_n |n\rangle, \quad |\psi\rangle \rightarrow \{ c_n \} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{pmatrix} \]

\[ |u_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \quad |u_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \]

\[ |\psi\rangle = \sum_n c_n |u_n\rangle \rightarrow \langle \psi | = \sum_n c_n^\ast \langle u_n | \]

\[ \langle \psi | = (c_1^\ast \quad c_2^\ast \quad c_3^\ast \quad \ldots) \]

\[ \langle \psi | \psi \rangle = \begin{pmatrix} c_1^\ast & c_2^\ast & c_3^\ast & \ldots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = |c_1|^2 + |c_2|^2 + \ldots = \sum_n |c_n|^2 \]

Operators can be represented by matrices:

\[ \hat{A} \rightarrow \{ A_{mn} \} = \{ m | \hat{A} n \} = \begin{pmatrix} A_{11} & A_{12} & \ldots \\ A_{21} & A_{22} & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix} \]

where \{ | n \rangle \} is some complete orthonormal set.
Why is that? Where does that matrix come from?

Consider the operator $\hat{A}$ and 2 state vectors $|\psi\rangle, |\varphi\rangle$ related by

$$|\varphi\rangle = \hat{A} |\psi\rangle \quad (\star)$$

In basis $\{|n\rangle\}$,

$$|\psi\rangle = \sum_n c_n |n\rangle = \sum_n \langle n|n\rangle |\psi\rangle$$

$$|\varphi\rangle = \sum_n d_n |n\rangle = \sum_n \langle n|n\rangle |\varphi\rangle$$

Now project equation $\star$ onto $|m\rangle$ by acting with bra:

$$\langle m|\varphi\rangle = \langle m|\hat{A}|\psi\rangle = \sum_n c_n \langle m|\hat{A}|n\rangle$$

$$d_n = \sum_n A_{mn} c_n$$

But, this is simply the rule for multiplication of matrix $\times$ column.

$$\begin{pmatrix} d_1 \\ d_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

So there you have it, that's why the operator is defined as this matrix, in this basis!

Now, suppose $\hat{A} = \hat{H}$ and $\{|n\rangle\}$ are energy eigenstates, then

$$\hat{H}|n\rangle = E_n |n\rangle, \quad \hat{H}_{mn} = \langle m|\hat{H}|n\rangle = E_n \delta_{mn}$$

$$\hat{H}|2\rangle = E_2 |2\rangle \Rightarrow \begin{pmatrix} E_1 & 0 & \cdots \\ 0 & E_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix} = E_2 \begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix}$$

A matrix operator $\langle m|\hat{A}|n\rangle$ is diagonal when represented in the basis of its own eigenstates, and the diagonal elements are the eigenvalues.

Notice that in general operators don't commute $\hat{A} \hat{B} \neq \hat{B} \hat{A}$. Same goes for Matrix Multiplication: $A B \neq B A$. 

Claim: The matrix of a hermitian operator is equal to its transpose conjugate:

\[ \hat{A} \text{ hermitian} \Leftrightarrow A_{mn} = A_{nm}^* \]

Proof:
\[ \langle m | \hat{A} n \rangle = \langle \hat{A} m | n \rangle = \langle n | \hat{A}^* m \rangle \]
\[ \Rightarrow A_{mn} = A_{nm}^* \]

Similarly, adjoint (or "Hermitian conjugate") \( \hat{A}' : A_{mn}^* = A_{nm} \)

Proof:
\[ \langle \hat{A} m | n \rangle = \langle m | \hat{A}' n \rangle = \langle n | \hat{A}^* m \rangle \]

Of course, it’s difficult to do calculations if the matrices and columns are infinite dimensional. But there are Hilbert subspaces that are finite dimensional. For instance, in the H-atom, the full space of bound states is spanned by the full set \( \{ n, \ell, m \} \) (\( = | n\ell m \rangle \)). The sub-set \( \{ n=2, \ell=1, m = +1, 0, -1 \} \) forms a vector space called a subspace.

Subspace? In ordinary Euclidean space, any plane is a subspace of the full volume. If we consider just the xy components of a vector \( \vec{R}_{xy} = \hat{x} R_x + \hat{y} R_y \), then we have a perfectly valid 2D vector space, even though the "true" vector is 3D.

Likewise, in Hilbert space, we can restrict our attention to a subspace spanned by a small number of basis states.

Example: H-atom subspace \( \{ n=2, \ell=1, m = +1, 0, -1 \} \)

Basis states are \( \{ | m \rangle \} = \{ +1 \}, \{ 0 \}, \{ -1 \} \) (can drop \( n=2, \ell=1 \) in label since they are fixed.)

\[ \hat{L}_z | m \rangle = \hbar m | m \rangle \]
\[ (\ell = 1) \]
\[ \hat{L}_z | m \rangle = \hbar^2 \ell (\ell + 1) | m \rangle = 2\hbar^2 | m \rangle \] (for all m)

\[ \Rightarrow (L_z)_{mn} = \langle m | \hat{L}_z | n \rangle = \hbar \begin{pmatrix} +1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \]
\[ L_{mn} = \langle m | \hat{L}^2 | n \rangle = 2\hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

(What about \( L_\alpha \)? \( L_\beta \)?)

Before seeing what all this matrix stuff is good for, let's examine spin because it's very important physically and because it will lead to 2D Hilbert space with simple 2x2 matrices.

**Review of Dirac Bra - Ket Notation**

Bracket or inner-product:

\[ \langle f | g \rangle = \int dx f^*(x)g(x) \text{ or } \int dV f^*(\vec{r})g(\vec{r}) \text{ or } d\Omega (\theta, \phi) \ldots \]

Which integral you do depends on the configuration space of problem.

Key defining properties of bracket:

- \( \langle f | g \rangle^* = \langle g | f \rangle \)
- \( \langle f | c \cdot g \rangle = c \langle f | g \rangle \), \( \langle c \cdot f | g \rangle = c^* \langle f | g \rangle \)
- \( \langle \alpha | (b | \beta \rangle + c | \gamma \rangle \rangle = b \langle \alpha | \beta \rangle + c \langle \alpha | \gamma \rangle \)

Dirac proclaims: \( \langle g | f \rangle = \langle g | \text{ next to } | f \rangle \)

Bracket = "bra" and "ket"

Ket \( | f \rangle \) represents vector in H-space (Hilbert Space)

\( | \psi \rangle \) is to \( \psi(x) \) as \( \vec{R} \) is to \((R_x, R_y, R_z)\)

Both \( \psi \) and \( \psi(x) \) describe same state, but \( | \psi \rangle \) is more general:
position-representation, momentum-rep, energy-rep.
What is a "bra"? < g | is a new kind of mathematical object, called a "functional".

\[ \langle g | = \int dx g^* (x) \] 

< g | wants to bind with | f > to produce inner product < g | f >

For every ket | f > there is a corresponding bra < f |. Like the kets, the bra's form a vector space.

- | c f > \( \equiv \) c | f > = c^* < f |
- | \alpha f + \beta g > \( \equiv \) < \alpha f + \beta g | = \alpha^* f + \beta^* g |
- < \alpha f + \beta g | h > = \alpha^* f | h > + \beta^* g | h >

Complex number \( \times \) bra = another bra  
any linear combo of bra's = another bra  
\( \Rightarrow \) bra's form a vector space

The vector space of bras is called a "dual space". It's the dual of the ket vector space.

\( \hat{A} | f > = | \hat{A} f > \) is a ket. What is the corresponding bra? | \( \hat{A} f > \rangle \rightarrow \langle \hat{A} f | = \langle f | \hat{A} \rangle \]  

Definition: hermitean conjugate or adjoint \( \hat{A}' \) of operator \( \hat{A} \) (\( \hat{A}' = \text{"A - dagger"} \))

\( \langle \hat{A} f | g \rangle = \langle f | \hat{A}' g \rangle \) for all f, g.

(If \( \hat{A} = A' \), then \( \hat{A} \) is hermitean or self-adjoint.)

Some properties:

- \( (\hat{A} \hat{B})' = \hat{B}' \hat{A}' \)
- \( (\hat{A}')' = \hat{A} \)

\[ \begin{align*}
\text{Proof:} & \quad \langle f | (\hat{A}')' g \rangle = \langle \hat{A}' f | g \rangle \\
& \quad \langle g | \hat{A}' f \rangle^* = \langle \hat{A} g | f \rangle^* = \langle f | \hat{A} f \rangle
\end{align*} \]
The adjoint of an operator is analogous to complex conjugate of a complex number:
\[ c^{**} = c, \quad \hat{A}^{**} = \hat{A} \]
\[ c^* = c \implies c \text{ real}, \quad \hat{A}^* = \hat{A} \implies \hat{A} \text{ hermitean}. \]

The "ket-bra" \( |f \rangle \langle g| \) is an operator. It turns a ket (function) into another ket (function):
\[
( |f \rangle \langle g| ) |h\rangle = |f\rangle \langle g| h\rangle
\]

**Projection Operators**
\[
\hat{H} u_n(x) = E_n u_n(x) \rightarrow \hat{H} |n\rangle = E_n |n\rangle
\]
\[
\psi(x) = \sum_n c_n u_n(x) = \sum_n \langle u_n |\psi\rangle u_n(x) \rightarrow
\]
\[
|\psi\rangle = \sum_n c_n |n\rangle = \sum_n \langle n|\psi\rangle |n\rangle = \sum_n \langle n|\psi\rangle
\]

\[
\sum_n |n\rangle\langle n| = \hat{1} \quad \Rightarrow \quad \text{"Completeness relation"}
\]
(discrete spectrum case)

\[
\hat{P}_n = |n\rangle\langle n| = \text{"projection operator"}
\]
\[
\hat{P}_n \text{ picks out portion of vector } |\psi\rangle \text{ that lies along } |n\rangle
\]
\[
\hat{P}_n |\psi\rangle = |n\rangle \langle n|\psi\rangle = c_n |n\rangle
\]

\[ u_2 = |2\rangle \]

\[
|n\rangle\langle n| \text{ is like } \hat{x} (\hat{x} \cdot \_)
\]
\[
\hat{x} (\hat{x} \cdot \hat{R}) = \hat{x} R_x
\]
\[ |\psi\rangle = \sum_{n} |n\rangle \langle n| \psi\] like \( \vec{R} = \hat{x}(\vec{x} \cdot \vec{R}) + \hat{y}(\vec{y} \cdot \vec{R}) \)

\[ \hat{1} = \sum_{n} |n\rangle \langle n| \] like \( \hat{1} = \hat{x}(\vec{x} \cdot \vec{1}) + \hat{y}(\vec{y} \cdot \vec{1}) \)

Anywhere there is a vertical bar in the bracket, or a ket or a bra, we can replace the bar with \( 1 = \sum_{n} |n\rangle \langle n| \)

Example: \( \langle \psi | \psi \rangle = 1 \)

\[ = \sum_{n} \langle \psi | n \rangle \langle n| \psi\rangle = 1 \Rightarrow \sum_{n} c_{n}^{*} c_{n} = \sum_{n} |c_{n}|^{2} = 1 \]

If eigenvalue spectrum is continuous (as for \( \hat{x} \) or \( \hat{p} \)) then must use integral, rather than sum, over states.

\[ \int dx |x\rangle \langle x| = \hat{1} \] Completeness Relation
(continuous spectrum)

Example: \( \Phi(p) = \langle f_{p} | \psi \rangle = \int dx \langle f_{p} | x \rangle \langle x| \psi\rangle = \frac{1}{2\pi\hbar} \int dx e^{-ipx/\hbar} \psi(x) \)

The Measurement Postulates 3 and 4 can be restated in terms of the projection operator:

Starting with state \( |\psi\rangle = \sum_{n} c_{n} |n\rangle = \sum_{n} |n\rangle \langle n| \psi\rangle \),

where sum \( \{n\} \) is over any complete set of states, if we measure observable associated with \( n \), then we will find value \( n_{0} \) with probability

\[ P(n_{0}) = |c_{n_{0}}|^{2} = \langle \psi | n_{0} \rangle \langle n_{0} | \psi\rangle = \langle \psi | \hat{P}_{n_{0}} | \psi\rangle \]

\[ P(n_{0}) = \langle \hat{P}_{n_{0}} | \psi\rangle = \langle \psi | \hat{P}_{n_{0}} | \psi\rangle \]

Probability of finding eigenvalue \( n_{0} = \) expectation value of projection operator \( \hat{P}_{n_{0}} \).

And as result of measurement state \( | \psi \rangle \) collapses to state \( | n_{0} \rangle = \hat{P}_{n_{0}} | \psi\rangle \).

(apart from normalization)
We can now generalize to case of states described by more than one eigenvalue, such as H-atom.

\[ \Psi = \sum_{n\ell m} c_{n\ell m} \Psi_{n\ell m} \rightarrow |\Psi\rangle = \sum_{n\ell m} |n\ell m\rangle \langle n\ell m|\psi\rangle \]

If we measure energy (but not also \(\vec{L}_1, L_z\)), find \(n_0\), then we are projecting onto subspace spanned by \(\{\ell, m\}\) with some \(n_0\).

\[
\hat{P}_{n_0} = \sum_{\ell m} |n_0\ell m\rangle \langle n_0\ell m| \quad \ell = 0, 1 \ldots (n_0 - 1) \\
P(n_0) = \langle \psi | \hat{P}_{n_0} |\psi\rangle = \sum_{\ell m} |c_{n_0\ell m}|^2 \\
m = -\ell \ldots + \ell
\]

State collapses to \(\hat{P}_{n_0} |\psi\rangle = \sum_{\ell m} |n_0\ell m\rangle \langle n_0\ell m|\psi\rangle\)

must renormalize
Spin $\frac{1}{2}$
Recall that in the H-atom solution, we showed that the fact that the wavefunction $\Psi(r)$ is single-valued requires that the angular momentum quantum number $l$ be integer: $l = 0, 1, 2, \ldots$. However, operator algebra allowed solutions $l = 0, 1/2, 1, 3/2, 2, \ldots$

Experiment shows that the electron possesses an intrinsic angular momentum called spin with $l = \frac{1}{2}$. By convention, we use the letter $s$ instead of $l$ for the spin angular momentum quantum number: $s = \frac{1}{2}$.

The existence of spin is not derivable from non-relativistic QM. It is not a form of orbital angular momentum; it cannot be derived from $\vec{L} = \vec{r} \times \vec{p}$.

(The electron is a point particle with radius $r = 0$.)

Electrons, protons, neutrons, and quarks all possess spin $s = \frac{1}{2}$. Electrons and quarks are elementary point particles (as far as we can tell) and have no internal structure. However, protons and neutrons are made of 3 quarks each. The 3 half-spins of the quarks add to produce a total spin of $\frac{1}{2}$ for the composite particle (in a sense, $\uparrow\uparrow\downarrow$ makes a single $\uparrow$). Photons have spin 1, mesons have spin 0, the delta-particle has spin $3/2$. The graviton has spin 2. (Gravitons have not been detected experimentally, so this last statement is a theoretical prediction.)
Spin and Magnetic Moment

We can detect and measure spin experimentally because the spin of a charged particle is always associated with a magnetic moment.

Classically, a magnetic moment is defined as a vector $\mu$ associated with a loop of current. The direction of $\mu$ is perpendicular to the plane of the current loop (right-hand-rule), and the magnitude is

$$\mu = i A = i \pi r^2.$$

The connection between orbital angular momentum (not spin) and magnetic moment can be seen in the following classical model: Consider a particle with mass $m$, charge $q$ in circular orbit of radius $r$, speed $v$, period $T$.

\[
i = \frac{q}{T}, \quad v = \frac{2\pi r}{T} \quad \Rightarrow \quad i = \frac{qv}{2\pi r} \quad \mu = i A = \left(\frac{qv}{2\pi r}\right) (\pi r^2) = \frac{qv r}{2}
\]

| angular momentum $| = L = p \cdot r = m v r$, so $v r = L/m$, and $\mu = \frac{qv r}{2} = \frac{q}{2m} L$.

So for a classical system, the magnetic moment is proportional to the orbital angular momentum:

$$\mu = \frac{q}{2m} L \quad \text{(orbital)}.$$

The same relation holds in a quantum system.

In a magnetic field $B$, the energy of a magnetic moment is given by

$$E = -\mu \cdot \vec{B} = -\mu_z B \quad \text{(assuming } \vec{B} = B \hat{z}). \quad \text{In QM, } L_z = h m.$$

Writing electron mass as $m_e$ (to avoid confusion with the magnetic quantum number $m$) and $q = -e$ we have \(\mu_z = -\frac{eB}{2m_e} m\), where $m = -\frac{1}{2} \to \frac{1}{2}$. The quantity
The possible energies of the magnetic moment in $\vec{B} = B \hat{z}$ is given by $E_{\text{orb}} = -\mu_z B = -\mu_B B m$.

For *spin* angular momentum, it is found experimentally that the associated magnetic moment is twice as big as for the orbital case: $\mu = \frac{e}{m} \hat{S}$ (spin)

(We use $S$ instead of $L$ when referring to spin angular momentum.)

This can be written $\mu_z = -\frac{e\hbar}{m} m = -2\mu_B m$.

The energy of a spin in a field is $E_{\text{spin}} = -2\mu_B B m$ ($m = \pm 1/2$) a fact which has been verified experimentally.

The existence of spin ($s = 1/2$) and the strange factor of 2 in the gyromagnetic ratio (ratio of $\mu$ to $\hat{S}$) was first deduced from spectrographic evidence by Goudsmit and Uhlenbeck in 1925.

Another, even more direct way to experimentally determine spin is with a Stern-Gerlach device, next page.
Stern-Gerlach Experiment (W. Gerlach & O. Stern, Z. Physik 9, 349-252 (1922)).

\[ \vec{F} = \nabla (\vec{\mu} \cdot \vec{B}) = (\vec{\mu} \cdot \nabla) \vec{B} \] (in current free regions), or here, \[ \vec{F} = \hat{z}(\mu_z \frac{\partial B_z}{\partial z}) \] (this is a little crude - see Griffiths Example 4.4 for a better treatment, but this gives the main idea)

Deflection of atoms in z-direction is proportional to z-component of magnetic moment \( \mu_z \), which in turn is proportional to \( L_z \). The fact that there are two beams is proof that \( s = \frac{1}{2} \). The two beams correspond to \( m = +1/2 \) and \( m = -1/2 \). If \( s = 1 \), then there would be three beams, corresponding to \( m = -1, 0, 1 \). The separation of the beams is a direct measure of \( \mu_z \), which provides proof that \( \mu_z = -2 \mu_n m \)

The extra factor of 2 in the expression for the magnetic moment of the electron is often called the "g-factor" and the magnetic moment is often written as

\[ \mu_z = -g \mu_n m \]. As mentioned before, this cannot be deduced from non-relativistic QM; it is known from experiment and is inserted "by hand" into the theory.
However, a relativistic version of QM due to Dirac (1928, the "Dirac Equation") predicts the existence of spin \( s = \frac{1}{2} \) and furthermore the theory predicts the value \( g = 2 \). A later, better version of relativistic QM, called Quantum Electrodynamics (QED) predicts that \( g \) is a little larger than 2. The \( g \)-factor has been carefully measured with fantastic precision and the latest experiments give \( g = 2.0023193043718(\pm 76 \) in the last two places). Computing \( g \) in QED requires computation of an infinite series of terms that involve progressively more messy integrals, that can only be solved with approximate numerical methods. The computed value of \( g \) is not known quite as precisely as experiment, nevertheless the agreement is good to about 12 places. QED is one of our most well-verified theories.

**Spin Math**

Recall that the angular momentum commutation relations

\[
[L^2, L_x] = 0, \quad [L_x, L_y] = i\hbar L_z, \quad (i j k \text{ cyclic})
\]

were derived from the definition of the orbital angular momentum operator:

\[
\vec{L} = \vec{r} \times \vec{p}.
\]

The spin operator \( \vec{S} \) does not exist in Euclidean space (it doesn't have a position or momentum vector associated with it), so we cannot derive its commutation relations in a similar way. Instead we boldly postulate that the same commutation relations hold for spin angular momentum:

\[
[S^2, S_z] = 0, \quad [S_x, S_y] = i\hbar S_z. \quad \text{From these, we derive, just as before, that}
\]
\[ S^2 |s m_s\rangle = \hbar^2 s (s+1) |s m_s\rangle = \frac{3}{4} \hbar^2 |s m_s\rangle \quad (\text{since } s = \frac{1}{2}) \]

\[ S_z |s m_s\rangle = \hbar m_s |s m_s\rangle = \pm \frac{1}{2} \hbar |s m_s\rangle \quad (\text{since } m_s = -s, +s = -1/2, +1/2) \]

Notation: since \( s = \frac{1}{2} \) always, we can drop this quantum number, and specify the eigenstates of \( L^2, L_z \) by giving only the \( m_s \) quantum number. There are various ways to write this:

\[ |s m_s\rangle = |m_s\rangle = |\uparrow\rangle, |\downarrow\rangle \]

These states exist in a 2D subset of the full Hilbert Space called \textit{spin space}. Since these two states are eigenstates of a hermitian operator, they form a complete orthonormal set (within their part of Hilbert space) and any, arbitrary state in spin space can always be written as \( |\chi\rangle = a |\uparrow\rangle + b |\downarrow\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \) (Griffiths' notation is \( \chi = a \chi_+ + b \chi_- \))

Matrix notation: \( |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \), \( |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \). Note that \( \langle \uparrow | \uparrow \rangle = \langle \downarrow | \downarrow \rangle = 1 \), \( \langle \uparrow | \downarrow \rangle = 0 \)

If we were working in the full Hilbert Space of, say, the H-atom problem, then our basis states would be \( |n \ell m, m_s\rangle \). Spin is another degree of freedom, so that the full specification of a basis state requires 4 quantum numbers. (More on the connection between spin and space parts of the state later.)

[Note on language: throughout this section I will use the symbol \( S_z \) (and \( S_x, \) etc) to refer to both the observable ("the measured value of \( S_z \) is \( +\hbar/2 \)) and its associated operator ("the eigenvalue of \( S_z \) is \( +\hbar/2 \)).]
The matrix form of $S^2$ and $S_z$ in the $|m^{(e)}\rangle$ basis can be worked out element by element. (Recall that for any operator $\hat{A}$, $A_{mn} = \langle m | \hat{A} | n \rangle$.)

$$\langle \uparrow | S^2 | \uparrow \rangle = \frac{3}{4} \hbar^2, \quad \langle \uparrow | S^2 | \downarrow \rangle = 0, \quad \text{etc.} \quad \langle \uparrow | S_z | \uparrow \rangle = +\frac{1}{2} \hbar, \quad \langle \uparrow | S_z | \downarrow \rangle = 0, \quad \text{etc.}$$

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Operator equations can be written in matrix form, for instance,

$$S_z | \uparrow \rangle = \frac{\hbar}{2} | \uparrow \rangle \quad \Rightarrow \quad \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

We are going ask what happens when we make measurements of $S_z$, as well as $S_x$ and $S_y$, (using a Stern-Gerlach apparatus). Will need to know: What are the matrices for the operators $S_x$ and $S_y$? These are derived from the raising and lowering operators:

$$S_+ = S_x + i S_y, \quad S_- = S_x - i S_y$$

To get the matrix forms of $S_+, S_-$, we need a result from the homework:

$$S_+ | s, m_s \rangle = \hbar \sqrt{s(s+1) - m(m+1)} | s, m_s + 1 \rangle$$
$$S_- | s, m_s \rangle = \hbar \sqrt{s(s+1) - m(m+1)} | s, m_s - 1 \rangle$$

For the case $s = \frac{1}{2}$, the square root factors are always 1 or 0. For instance, $s = \frac{1}{2}$,

$$m = -1/2 \quad \text{gives} \quad s(s+1) - m(m+1) = \frac{1}{4} \left( \tfrac{1}{2} \right) - \left( -\tfrac{1}{2} \right) \left( \tfrac{1}{2} \right) = 1.$$

Consequently,

$$S_+ | \downarrow \rangle = \hbar | \uparrow \rangle, \quad S_+ | \uparrow \rangle = 0 \quad \text{and} \quad S_- | \uparrow \rangle = \hbar | \downarrow \rangle, \quad S_- | \downarrow \rangle = 0,$$ leading to

$$\langle \uparrow | S_+ | \uparrow \rangle = 0, \quad \langle \uparrow | S_- | \downarrow \rangle = \hbar, \quad \text{etc. and}$$
Notice that $S_+, S_-$ are not hermitian.

Using $S_z = \frac{1}{2}(S_+ + S_-)$ and $S_y = \frac{i}{2}(S_+ - S_-)$ yields

\[
S_+ = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad S_- = \frac{\hbar}{2} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
\]

These are hermitian, of course.

Often written: $\vec{S} = \frac{\hbar}{2} \vec{\sigma}$, where $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$, $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ are called the Pauli spin matrices.

Now let’s make some measurements on the state $|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$.

Normalization: $\langle\chi|\chi\rangle = 1 \Rightarrow |a|^2 + |b|^2 = 1$.

Suppose we measure $S_z$ on a system in some state $|\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$.

Postulate 2 says that the possible results of this measurement are one of the $S_z$ eigenvalues: $+\hbar/2$ or $-\hbar/2$. Postulate 3 says the probability of finding, say $-\hbar/2$,

is $\text{Prob}(\text{find } -\hbar/2) = \left| \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \right|^2 = |a|^2$.

Postulate 4 says that, as a result of this measurement, which found $-\hbar/2$, the initial state $|\chi\rangle$ collapses to $|\downarrow\rangle$.

But suppose we measure $S_x$? (Which we can do by rotating the SG apparatus.)

What will we find? Answer: one of the eigenvalues of $S_x$, which we show below are the same as the eigenvalues of $S_z$: $+\hbar/2$ or $-\hbar/2$. (Not surprising, since there is
nothing special about the z-axis.) What is the probability that we find, say, \( S_x = +\hbar/2 \)? To answer this we need to know the eigenstates of the \( S_x \) operator. Let’s call these (so far unknown) eigenstates \( |\uparrow^{(x)}\rangle \) and \( |\downarrow^{(x)}\rangle \) (Griffiths calls them \( |\chi_+^{(x)}\rangle \) and \( |\chi_-^{(x)}\rangle \)). How do we find these? We must solve the eigenvalue equation:

\[
S_x |\chi\rangle = \lambda |\chi\rangle,
\]

where \( \lambda \) are the unknown eigenvalues. In matrix form this is,

\[
\begin{pmatrix}
0 & \hbar/2 \\
\hbar/2 & 0
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
= \lambda
\begin{pmatrix}
a \\
b
\end{pmatrix}
\]

which can be rewritten

\[
\begin{pmatrix}
-\lambda & \hbar/2 \\
\hbar/2 & -\lambda
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
= 0.
\]

In linear algebra, this last equation is called the characteristic equation.

This system of linear equations only has a solution if

\[
\det\left(\begin{pmatrix}
-\lambda & \hbar/2 \\
\hbar/2 & -\lambda
\end{pmatrix}\right) = \left|\begin{array}{cc}
-\lambda & \hbar/2 \\
\hbar/2 & -\lambda
\end{array}\right| = 0.
\]

As expected, the eigenvalues of \( S_x \) are the same as those of \( S_z \) (or \( S_y \)).

Now we can plug in each eigenvalue and solve for the eigenstates:

\[
\frac{\hbar}{2}\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}\begin{pmatrix}
a \\
b
\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}
a \\
b
\end{pmatrix} \Rightarrow a = b;
\frac{\hbar}{2}\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}\begin{pmatrix}
a \\
b
\end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix}
a \\
b
\end{pmatrix} \Rightarrow a = -b.
\]

So we have \( |\uparrow^{(x)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \) and \( |\downarrow^{(x)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \).

Now back to our question: Suppose the system in the state \( |\uparrow^{(x)}\rangle \), and we measure \( S_x \). What is the probability that we find, say, \( S_x = +\hbar/2 \)? Postulate 3 gives
the recipe for the answer:

\[
\text{Prob(find } S_x = +\hbar/2) = \left| \left\langle \uparrow^{(x)} \mid \uparrow^{(x)} \right\rangle \right|^2 = \left| \frac{i}{\sqrt{2}} (1 \quad 1) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right|^2 = \left| \frac{i}{\sqrt{2}} \right|^2 = 1/2
\]

Question for the student: Suppose the initial state is an arbitrary state \( |\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \)

and we measure \( S_x \). What are the probabilities that we find \( S_x = +\hbar/2 \) and \( -\hbar/2 \)?
Let's review the strangeness of Quantum Mechanics.

Suppose an electron is in the $S_x = +\hbar/2$ eigenstate $|S_x^{(+)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$. If we ask: What is the value of $S_x$? Then there is a definite answer: $+\hbar/2$. But if we ask: What is the value of $S_z$, then this is no answer. The system does not possess a value of $S_z$. If we measure $S_z$, then the act of measurement will produce a definite result and will force the state of the system to collapse into an eigenstate of $S_z$, but that very act of measurement will destroy the definiteness of the value of $S_x$. The system can be in an eigenstate of either $S_x$ or $S_z$, but not both.