3-Dimensional Quantum Mechanics

In 3-D, we have $\psi(\vec{r},t)$ and $\hat{H} = -\hbar^2 \nabla^2 + V(\vec{r})$.
and $\hat{A} \psi(\vec{r},t) = i\hbar \partial \psi(\vec{r},t)/\partial t$.

We will concentrate on stationary states:

$\psi(\vec{r},t) = \psi(\vec{r}) e^{-iEt/\hbar}$, $\hat{A} \psi(\vec{r}) = E \psi(\vec{r})$.

As in classical mechanics, the 3-D problem can be expressed in different coordinate systems, notably cartesian $(x,y,z)$ and spherical $(r,\theta,\phi)$ with the best choice dictated by the symmetry of the problem.

For example, if $V(\vec{r}) = V_x(x) + V_y(y) + V_z(z)$ (eg, for a rectangular crystal),

the we write $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

and $\hat{A} = \hat{A}_x + \hat{A}_y + \hat{A}_z$, with $\hat{A}_x = -\frac{i\hbar}{\partial x} - V_x(x)$, etc.

Then the Schrödinger Eqn is separable. Write $\psi(\vec{r}) = \psi_x(x) \psi_y(y) \psi_z(z)$

and we get, in the usual way, 3 independent Schrödinger Eqns:

$\left\{ \begin{array}{ll}
\hat{H}_x \psi_x(x) = E_x \psi_x(x) \\
\hat{H}_y \psi_y(y) = E_y \psi_y(y) \\
\hat{H}_z \psi_z(z) = E_z \psi_z(z)
\end{array} \right\}$

In classical mechanics, we have independent coordinates $x(t), y(t), z(t)$.

InQM, we have one wavefunction $\psi(x,y,z)$,

and 3 operators $\hat{A} = (\hat{A}_x, \hat{A}_y, \hat{A}_z)$, which all commute with one another:

$[\hat{A}_x, \hat{A}_y] = 0 = [\hat{A}_y, \hat{A}_z] = 0 = [\hat{A}_z, \hat{A}_x] = 0$.

If $\psi(\vec{r})$ is separable, as above, then there are no correlations between $x, y, z$.

Examples are: 3-D "box" potential, 3D QHO, etc. - we have already solved these problems.
Symmetry and degeneracies

If there is some symmetry in the problem, e.g., in 3D QHD, if
\[ V(\vec{r}) = V(r) = \frac{1}{2} m \omega^2 r^2 = \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2) \]  
"spherically symmetric", then \( H = \hbar \omega \vec{x} \cdot \vec{H} \) is along, and \( E = \hbar \omega (\vec{Q} + \vec{r}) \), etc., so \( E = \hbar \omega (\vec{Q} + \vec{r}) \). There is degeneracy: more than one set of quantum numbers \( \vec{Q} = (n_x, n_y, n_z) \) give the same \( E \) (e.g., \( 1, 2, 2 \), \( 2, 1, 2 \), and \( 2, 1, 2 \); all give \( E = \hbar \omega - \frac{1}{2} \hbar \omega \)).

If there is no spherical symmetry, e.g., \( V = \frac{1}{2} m \left( \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2 \right) \)
with \( \omega_x \neq \omega_y \neq \omega_z \), there are no degeneracies. Thus, Symmetry \( \Rightarrow \) Degeneracy.

Spherically symmetrical potentials - "Central force" Problem

When \( V(\vec{r}) = V(r) \), the problem is simpler and more separable, using polar coordinates \((r, \theta, \phi)\) rather than \((x, y, z)\).

\[ r = \sqrt{x^2 + y^2 + z^2} \]
\[ \cos \theta = \frac{z}{r} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \]
\[ \tan \phi = y/x \]
\[ z = r \cos \theta \]
\[ \hat{r} = \sin \theta \sin \phi \]
\[ \hat{\phi} = \cos \theta \sin \phi \]
\[ \hat{\theta} = \cos \phi \]
\[ \vec{\hat{r}} \times \vec{\hat{\phi}} = \vec{\hat{r}} \cdot \vec{\hat{\phi}} \]

And \( \vec{p}^2 = p_r^2 + \vec{p}_\theta^2 = p_r^2 + \frac{\vec{p}_\phi^2}{\sin^2 \theta} \)

So the kinetic energy part of \( \hat{H} \) is \( \frac{\vec{p}^2}{2m} = \frac{p_r^2}{2m} + \frac{\vec{p}_\phi^2}{2m \sin^2 \theta} \)

Tempting to write \( p_r = \vec{p} \cdot \vec{r} / r \), but \( \vec{r} \) and \( \vec{p} \) don't commute!

That means \( \vec{p} \) won't be Hermitian, which is a problem.

Instead, symmetrize: \( \vec{p} = \left( \vec{r} / r \right) \cdot \vec{p} + \vec{p} \cdot \left( \vec{r} / r \right) \)
Thus, using \( \hat{\rho} = \frac{\hbar}{i} \hat{\theta} = \frac{\hbar}{i} \left( \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \theta} \sin \theta \right) \) and unit vectors, not operators!

the \( \hat{\theta} \) is the operator!

\[
\frac{\partial}{\partial x} = \frac{\partial}{\partial \xi} \frac{\partial}{\partial \eta} + \frac{\partial}{\partial \zeta} \frac{\partial}{\partial \bar{\eta}} + \frac{\partial}{\partial \zeta} \frac{\partial}{\partial \bar{\eta}}
\]

and similarly for \( \frac{\partial}{\partial \eta} \) and \( \frac{\partial}{\partial \zeta} \).

We get \( \hat{\rho} = \frac{\hbar}{i} \left( \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \theta} \sin \theta \right) \) which operates on \( \psi \).

\[
\psi \rightarrow \frac{\hbar}{i} \left( \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \theta} \sin \theta \right) \psi
\]

which is Hermitian. And \( [\hat{\rho}, \hat{\phi}] = 0 \) (easy to prove).

Now \( \hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z) \), \( \hat{L}_x = y \hat{p}_z - z \hat{p}_y \), etc.

\[
\hat{L}_x = y \hat{\frac{\partial}{\partial z}} - z \hat{\frac{\partial}{\partial y}}
\]

Convenient shorthand: \( \mathbf{L} = (x, y, z) \) for \( \hat{L} \), etc.

\[
\Rightarrow \quad \mathbf{L} = \sum_{jk} E_{jk} \hat{\gamma}_j \hat{\gamma}_k
\]

where \( E_{jk} = 1 \) for \( 1, 2, 3 \), \( 2, 3, 1 \), \( 3, 1, 2 \) (cyclic permutations),

\( -i \) for \( 1, 3, 2 \), \( 2, 1, 3 \), \( 3, 2, 1 \) (anti-cyclic permutations),

0 otherwise (any \( jk \) or \( jk \) or \( ijk \)).

"Completely anti-symmetric Levi-Civita Tensor".

More shorthand: \( \mathbf{L} = E_{ijk} \hat{\gamma}_j \hat{\gamma}_k \) (4-vectors: \( \mathbf{E} = \mathbf{L} \))

"Summation convention" - sum over repeated indices.

Handy identity:

\[
E_{ijk} E_{km} = \delta_{jm} \delta_{kl} - \delta_{ik} \delta_{jl}
\]

Converting \( \mathbf{L}^2 = (\mathbf{L} \times \mathbf{p}) \cdot (\mathbf{L} \times \mathbf{p}) \) into spherical coordinates:

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

Note that \( \mathbf{L} \) has units of \( \hbar \):

\[ L \sim \frac{\hbar}{\hbar} \sim 1 \] (for)

Note that \( \hat{\rho} \) depends on \( r \), not \( \theta \) or \( \phi \).

\( \hat{L} \) depends on \( \theta \) or \( \phi \), not \( r \).

\( \Rightarrow \) Schrödinger equation is separable! Try \( \psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \).
\[ L_z = E \gamma k \gamma \beta \]

\[ L_x = y p_z - z p_y = i \hbar \left( \sin \varphi \frac{2}{\hbar} + \cot \theta \cos \varphi \frac{2}{\hbar} \right) \]

\[ L_y = z p_x - x p_z = i \hbar \left( -\cos \varphi \frac{2}{\hbar} + \cot \theta \sin \varphi \frac{2}{\hbar} \right) \]

\[ L_z = x p_y - y p_x = -i \hbar \frac{2}{\hbar} \frac{d}{d\varphi} \]

- Note that \( L \) has units of \( \text{J} \cdot \text{m} \):

\[ L \sim r p \sim r \hbar k \sim \hbar (kr) \quad \text{units, phase} \]

- Hence,

\[ L^2 = L_x^2 + L_y^2 + L_z^2 = \hbar^2 \frac{1}{\sin^2 \theta} \left[ \sin \theta \frac{2}{\hbar} \left( \sin \theta \frac{2}{\hbar} \right) + \frac{2}{\hbar^2} \right] \]

- Can easily show \( [L_x, L_y] = i \hbar L_z \), etc. (cyclic permutation)

\[ [L_y, L_z] = i \hbar E \gamma k \gamma \beta \]
Then $H\psi = \frac{1}{2m} \left( \frac{\hat{p}^2}{m} (\gamma) \right) + \frac{e^2}{2\varepsilon_0 m} \left( \gamma \right) = E\gamma - V(\gamma)\gamma$

$\gamma \left( \frac{\hat{p}^2}{2m} \gamma \right) + \frac{e^2}{2\varepsilon_0 m} \left( \gamma \right) = E\gamma - V(\gamma)\gamma$

$\left( \frac{\hat{p}^2}{2m} \gamma \right) + \frac{1}{2m} \left( \frac{\gamma^2}{\gamma} \right) = \frac{E}{\gamma} - V(\gamma)\gamma$

$\gamma \propto \text{constant}$

$\gamma^2 \propto \text{dependent on } \gamma$

$\text{dependent on } \theta, \phi$

$\frac{2m\gamma^2}{\gamma} \left[ \frac{\hat{p}^2}{2m} \gamma + (\gamma - E)\gamma \right] = \frac{\gamma^2}{\gamma} = \ell^2 \gamma = \text{const. independent of } \gamma, \theta, \phi.$

Both sides of the eqn must equal a constant, since the left-hand side depends only on $\gamma$, and the right-hand side depends on $\theta, \phi.$

First, the angular part: $\Delta^2 \gamma(\theta, \phi) = \ell^2 \gamma(\theta, \phi)$, an eigenvalue eqn.

Or: $\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\gamma}{d\theta} \right) + \sin \theta \frac{d^2 \gamma}{d\theta^2} + \gamma = 0$

Separate again: $\gamma(\theta, \phi) = \Theta(\theta) \Phi(\phi)$, so that

$\frac{\Phi''}{\Phi} = -\frac{\sin \theta}{\theta} \left[ \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) + \ell \Theta \right] = -m^2$

So $\Theta = e^{im\phi} \Rightarrow e^{i\ell \phi} = R(\ell) \Theta(\theta) \Phi(\phi)$

Now, $\langle L^2 \rangle = \langle \Psi | \frac{\hat{L}^2}{\ell^2} \gamma | \Psi \rangle = \langle \gamma | \frac{\hat{\Phi}^2}{\ell^2} \gamma | \Phi \rangle = m^2$

since $L^2$ is Hermitian, $m^2$ real.

$\Psi$ must be single valued (boundary condition)

$\Psi(r, \theta, \phi + 2\pi) = \Psi(r, \theta, \phi) \Rightarrow \Phi(\phi + 2\pi) = \Phi(\phi) \Rightarrow e^{i2\pi n} = 1$

so $n$ must be integer (called the magnetic quantum number).

Now the $\Theta$ eqn:

$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( 1 - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0$

Use $x = \cos \theta$, $dx = -\sin \theta d\theta$,

$\Rightarrow \frac{d}{dy} (1-x^2) \frac{d\Theta}{dx} + (1 - \frac{m^2}{1-x^2}) \Theta(x) = 0$.
This is a Legendre eqn. The solutions are obtained using the polynoimal method, as we did with Hermite polynomials.

The series converges only for values of \( l = l(l+1), \ l = 0, 1, 2, \ldots \).

And we get the Associated Legendre Polynomials

\[
\ell^m(\theta) = \frac{2l+1}{(2\ell)!} \ell^m(\cos \theta),
\]

\[
\ell^0(\theta) = 1, \ \ell^{2m}(\theta) = \frac{\ell(2\ell-1)(2\ell-3)\cdots(2\ell-2m+1)}{(2\ell)!} \sin^m \theta,
\]

\[
\ell^{2m+1}(\theta) = \frac{\ell(2\ell-1)(2\ell-3)\cdots(2\ell-2m-1)}{(2\ell-1)!(2\ell)!} \cos^m \theta.
\]

The complete angular functions \( Y_{\ell m}(\theta, \phi) \times \ell^m(\theta) \) e^{im\phi}

are called "spherical harmonics." They are the standing waves in angular space \( \cos \theta \in [-1, 1], \ \phi \in [0, 2\pi] \), analogous to \( \sin \phi \cos \theta \) for the square well.

They are simultaneous eigenfunctions of \( \hat{L}^2 \) and \( \hat{L}^2 \):

\[
\ell^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1) \ell^m(\cos \theta), \quad \ell = 0, 1, 2, \ldots
\]

\[
\ell^2 Y_{\ell m}(\theta, \phi) = m^2 Y_{\ell m}(\theta, \phi)
\]

\( m = 0, \pm 1, \pm 2, \ldots, \pm \ell \).

The \( Y_{\ell m} \) are orthonormal over the surface of a sphere:

\[
\int_{\text{sphere}} Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) \, dS = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \ Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) \sin \theta \, d\theta
\]

where \( dS = d\Omega = d\phi \int_0^\pi \sin \theta d\theta \) and

\[
SdS = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta = 4\pi
\]

Under parity, \( \theta \to \pi - \theta, \ \cos \theta \to -\cos \theta, \ \phi \to \phi + \pi \),

\[
\ell Y_{\ell m}(\theta, \phi) = (-1)^\ell Y_{\ell m}(\theta, \phi)
\]

even, odd, even, odd, etc.

Completeness: \( f(\theta, \phi) \equiv \sum_{\ell m} a_{\ell m} Y_{\ell m}(\theta, \phi) \Rightarrow a_{\ell m} = \int dS \ Y_{\ell m}^*(\theta, \phi) f(\theta, \phi) \)
The Rigid Rotor:

Consider a dumbbell: \( M_1 = M_2 = M \)
separated by a massless rigid rod.
(Eg, a diatomic molecule, \( \text{O}_2 \), whose oscillatory motion is neglected).
(Ps - In perturbation theory, we will learn how to combine 2 different types of motion, eg oscillatory \( \rightarrow \) rotational).

\[ E = E_{\text{rot}} + E_{\text{osc}} + E_{\text{ext}}. \]

The dumbbell system (mass \( 2M \)) moves through space with \( v = \frac{\hbar}{2I} \), \( E_{\text{ext}} = \frac{\hbar^2}{2I} \).

The motion in space, the dumbbell rotates, with \( \text{Ext} = \frac{\hbar}{2I} \).

\[ I = \text{moment of inertia} = \sum M_i d_i^2 = 2Ma^2. \]

QM: \( \hat{H}_{\text{rot}} = \frac{\hat{p}^2}{2I} \rightarrow \hat{H}_{\text{rot}} \psi = E_{\text{rot}} \psi \)

solution:

\[ L^2 \psi_m = L(l+1) \hbar^2 \psi_m, \quad \psi_m = Y_m(r, \theta, \phi). \]

\[ E_{\text{rot}} = \frac{L(L+1)\hbar^2}{2I}. \]

Energy depends on \( L^2 \), not on orientation of \( \hat{L} \).

degeneracy \( \text{in } m \in [-l, l] \) = \( 2l + 1 \)

The orbital angular momentum quantum number \( l \)
is referred to in atomic spectroscopy as the term:

\[ \begin{array}{ll}
  l & \text{Term rotation} \\
  0 & \text{S state} \\
  1 & \text{P state ("sharp") or ("principal")}
  \text{state)} \\
  2 & \text{D state ("doublet") or ("doublet")}
  \text{state) or ("doublet")}
  \text{state)} \\
  3 & \text{F state ("triplet") or ("triplet")}
  \text{or ("triplet") states)} \\
  & \text{or ("triplet") states)}
\end{array} \]
The result of all this is that for any spherically symmetric potential $V(r) = V(r)$, we can write $\Psi(r) = R(r) \Phi(r, \theta, \phi)$ and we need only solve the radial equation

$$-\frac{\hbar^2}{2m} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\hbar^2 (l+1)^2}{2m r^2} R = ER$$

For each $l$, there is a different eqn, so we label the eigenfunction $R_l(r)$, taking $R_l(0) = \frac{U_l(0)}{r}$ and get

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 (l+1)^2}{2m r^2} + V(r) \right] \Phi_l(r) = E \Phi_l(r)$$

which looks just like a 1-D Schrödinger eqn with effective potential $V_{\text{eff}}(r) = \frac{\hbar^2 (l+1)^2}{2m r^2} + V(r)$, and $r \geq 0$ only.

Careful at the origin: to keep $R = \frac{U}{r}$ finite at $r=0$, $U(\infty) = 0$

E.g.: Coulomb:

$$V_{\text{eff}}(r) = -\frac{(l+1)^2 \hbar^2}{2mr^2}$$

Normalise:

$$\int V_{\text{eff}}(r) dr = 1 = \int 1 \frac{1}{r} dr = 1 = \int 4\pi r^2 dr = 1$$

as in 1-D case, steady waves which match smoothly to exp. dying solutions beyond classical turning points are quantized, with principle quantum number $n$, and with $n-1$ nodes $(0$ and $\infty)$

so we have $R_n(r)$, $\Phi_n(r)$.

Note that $E_n$ does not depend on $n$, so we already have degeneracy:

$$n = 0, 1, 2, \ldots, 2l + 1$$

so $2l + 1$ -fold degeneracy.

E.g.: O.H.O.
The Hydrogen Atom

\[ T = \frac{\hbar^2}{2m_N^2} + \frac{\hbar^2}{2m_e} - \frac{Ze^2}{r_{NN}} \]

Move to CMS coordinates.

\[ \tilde{R} = \frac{m_e \tilde{r} + m_N \tilde{r}_{NN}}{m_e + m_N} , \quad \tilde{r} = \tilde{r}_{NN} - \tilde{r} \]

\[ \tilde{H} = \frac{\hbar^2}{2(m_e + m_N)^2} \frac{\nabla_{\tilde{r}}^2}{m_e + m_N} + \frac{\hbar^2}{2m_e} \frac{\nabla_{\tilde{r}}^2}{m_e} - \frac{Ze^2}{r} \]

\[ \text{Separation of variables: } \Psi(R, \tilde{r}) = R(R) \phi(\tilde{r}) \]

and

\[ \mu = m_e + m_N \]

\[ \tilde{C}(\tilde{r}) = \frac{\hbar^2 \nabla_{\tilde{r}}^2}{2(\mu m_e m_N)} C_R(\tilde{r}) \]

\[ \Psi(\tilde{r}) = \frac{\hbar^2 \nabla_{\tilde{r}}^2}{2\mu} - \frac{Ze^2}{r} \]

with

\[ E = E_N + E_r \]

The relative motion - a spherically symmetric potential,

\[ \Psi(\tilde{r}) = \frac{\hbar^2}{2\mu} \frac{\partial^2 \Phi(\tilde{r})}{\partial \tilde{r}^2} - \frac{Ze^2}{r} = \frac{\hbar^2 k^2}{2m_e m_N} \]

The relative motion is separable into bound states:

\[ \Psi_N(\tilde{r}) = \frac{\hbar^2}{2\mu} \frac{\partial^2 \Phi_N(r)}{\partial r^2} - \frac{Ze^2}{r} = \frac{\hbar^2 k^2}{2m_e m_N} \]

Change to dimensionless coordinates, \( r^* = kr \), \( k = \sqrt{\frac{2m_e (-E_N)}{\hbar^2}} \)

\[ \Phi'' - \frac{(2l+1)}{r^*} \Phi' + \frac{l(l+1)}{r^*} \Phi = 0 \]

Asymptotic behavior:

\[ \Phi \sim r^l e^{-r^*}, \quad r^* \to \infty \]

Try \( \Phi = A r^l e^{-r^*} \), solve by polynomial method.
Polynomial method:

\[ \left[ -\frac{\hbar^2}{2}\frac{d^2}{dr^2} - \frac{Ze^2}{r} + \frac{\ell(\ell+1)}{2}\right] U_{n\ell}(r) = E_{n\ell}(r) U_{n\ell}(r) \]

Full solution:

\[ U_{n\ell}(r) = \frac{U_{n\ell}(r)}{r} Y_{n\ell}(\theta, \phi) e^{-\kappa r/L} \]

\[ \kappa = \sqrt{n \lambda \hbar} \]

\( n \approx \text{radial quantization (only integer \( n \))} \cdot \hbar^2 \)

\( L \approx \text{angular quantization} \cdot \hbar \)

\( M = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell \approx \text{quantization} \)

Chap variates:

\[ k = \sqrt{\frac{Ze^2}{\hbar^2}} = \sqrt{\frac{2 \lambda \hbar}{\kappa}} \]

\[ \rho = k r \]

\[ \Rightarrow \frac{d^2 U}{dr^2} - \frac{\ell(\ell+1)}{\rho^2} U + \left( \frac{\rho_0}{\rho} - 1 \right) U = 0, \quad \rho_0 \approx \frac{Ze^2}{1.6 \times 10^{-21}} \]

\[ \rho \to \infty \Rightarrow U'' - U = 0 \Rightarrow U = Ae^{-\rho} + Be^{+\rho} \]

\[ \rho \to 0 \Rightarrow U'' - \ell(\ell+1) U = 0 \Rightarrow U = A r^{\ell+1} + B r^{-\ell} \]

\[ \Rightarrow U = A r^{\ell+1} e^{-\rho} U(\rho) \text{ separates out all the asymptotic behavior} \]

Assume:

\[ U(\rho) = \text{polynomial} = \sum_{j=0}^{\infty} \alpha_j \rho^j \]

\[ \Rightarrow \rho U'' + 2(\ell+1 - \rho) U' + [\rho_0 - 2(\ell+1)] U = 0 \]

\[ U' = \sum_{j=0}^{\infty} \alpha_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) \alpha_{j+1} \rho^j \]

\[ U'' = \sum_{j=0}^{\infty} (j+1)(j+2) \alpha_{j+2} \rho^j \]

\[ (\text{in reality} \ j \to j+1, \text{and lower limit of summation} \ j \text{really} -1, \but \text{that term is zero}) \]

Limit into different:

\[ \sum_{j=0}^{\infty} \left[ -2(j+2)(j+3) \alpha_{j+3} \rho^{j+1} + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) \alpha_{j+1} \rho^{j+1} - 2 \sum_{j=0}^{\infty} (j+1) \alpha_{j+1} \rho^{j+1} \right] \]

\[ + [\rho_0 - 2(\ell+1)] \sum_{j=0}^{\infty} \alpha_j \rho^j = 0 \]

\[ \Rightarrow \alpha_{j+1} = \left[ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2)(j+3)} \right] \alpha_j \]

\[ \Rightarrow \alpha_{j+1} = \left[ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2)(j+3)} \right] \alpha_j \]
This is a recursion relation. Start with $a_0$ as arbitrary,
and generate $a_1$, $a_2$, $a_3$, ...

But this series will not converge to a finite value $\rho \to \infty$
either under certain (quantum) conditions!
To see this, consult the $\rho \to \infty$ limit of $V(\rho) = \sum a_j / \rho^j$.
In this case, only large $j$ terms contribute.
In the large $j$ limit 
\[ a_j \to \frac{2^j}{j!} \frac{2}{j+1} a_o \]
and so
\[ a_j \to \frac{2^j}{j!} a_o \]
\[ V(\rho) \to a_o \sum \frac{2^j \rho^j}{j!} = e^{2\rho} \]
and so
\[ \rho = \frac{V}{e^\rho} = \rho e^\rho e^{-\rho} \to \rho e^\rho e^{-\rho} = \rho e^\rho \to \infty \]
How to prevent this? Cut off the sum, so that for some $j = j_{\text{max}},$
\[ a_{j_{\text{max}} + 1} = 0, a_{j_{\text{max}}} \to 2(j_{\text{max}} + 1) - \rho_o = 0 \]
define $n = j_{\text{max}} + 1 = l + 1$ as principal quantum number
( $n_r = j_{\text{max}}$ as radial quantum number, $n = n_r + l + 1$)
\[ \rho_o = 2n = \frac{2me^2}{\hbar^2} \Rightarrow E = \frac{\hbar^2 k^2}{2m} = -\frac{me^4}{2\hbar^2 n^2} \]
\[ E_n = E_{\text{me}} = -\frac{Z^2 R_y}{n^2} \]
\[ R_y = \frac{-me^4}{2\hbar^2} = -\frac{1}{2}(\frac{e^2}{hc}) \left( \frac{\hbar}{m} \right)^2 \]
\[ = -\frac{1}{2} \left( 0.511 \text{ MeV} \right) \left( \frac{1}{\text{137}} \right)^2 = 13.6 \text{ eV} \]
And $k = \frac{Z^2 me^4}{\hbar^2 n^2} = \frac{Z^2 \alpha \hbar}{n^2}, \quad a_0 = \frac{\hbar}{\mu e} = \left( \frac{\hbar c}{2e^2 \alpha \hbar c} \right) = 1973 \text{ eV} \cdot \text{A}^2 = 0.529 \text{ Å, Bohr radius}.$
\[ \psi(r) = (2\pi r / a_0 n)^{1/2} e^{-r/2a_0} \cdot \text{Normalization} \cdot Y_\ell m(\theta, \phi) \]
\[ \psi_{2n_00}(r) = \frac{1}{\sqrt{4a_0^3}} e^{r/2a_0}, \quad \psi_{2n_00}(r) = \frac{1}{4a_0^3} \left( 1 - \frac{r}{2a_0} \right) e^{-r/2a_0} Y_{200} \]
\[ \psi_{2n} = \frac{1}{\sqrt{4a_0^3}} \frac{r}{a_0} e^{-r/2a_0} Y_{2m} \]
The \( W_n(p) \) finite polynomials are the
"associated Legendre polynomials" \( \psi_n(p) = L_n^m(p) \)
tabulated in the math books:

\[
L_0^0 = 1 \quad L_1^0 = 1 \quad L_2^0 = 2
\]

\[
L_1^1 = 1 - x \quad L_2^1 = 4 - 2x \quad L_1^1 = 18 - 6x
\]

\[
L_2^1 = x^2 - 4x + 2 \quad L_2^1 = 3x^2 - 18x + 18 \quad L_2^0 = 12x^2 - 36x + 14
\]

And they are orthogonal to one another. They have \( n \) nodes: \( \psi_n(p) \) has \( n \) nodes if \( \theta \neq (2k\pi) \) and \( \infty \).

The eigenstates, \( \psi_{nlm}(\theta) = (\theta \mid nlm) \) are orthonormal:

\[
(\psi_{nlm} \mid \psi_{n'l'm'}) = \delta_{nn'} \delta_{ll'} \delta_{mm'}
\]

And their discrete energy spectrum gives rise to the terms

Hydrogen spectrum

from transitions

\[
-\frac{\alpha}{n^2} \quad \frac{\alpha}{n^3} \quad \frac{\alpha}{n^4} \quad \cdots
\]

amongst the

\( n \)th eigenstates

(Stationary states)

\( l = n - 1, n - 2 \)

with emission or absorption

\( (s \downarrow n) \quad (p \uparrow n) \quad (d \downarrow n) \)

of photons = Lyman, Balmer, Paschen, etc. series.

The existence of transitions means these are not truly stationary states!
We have ignored the coupl. of electron to EM field (and more, bands!)

Time-dependent Perturbation Theory (TDPT, Phys125) treats these as
quasi-stationary, determines correction to the levels \( \Delta \varepsilon \), and
transition rates between 4th levels.
Take \( \psi(r) = R(r) Y_n(\theta) \).

The relative motion, etc., then reads:

\[
\left( -\frac{\hbar^2}{2\mu} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\beta^2 r l(l+1)}{2\mu r^2} \right) R = E R
\]

Use \( R(r) = u(r)/r \Rightarrow \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\beta^2 r l(l+1)}{2\mu r^2} - \frac{\beta^2}{r} \right) u(r) = E u(r) \)

Then convert to dimensionless variable \( \rho = \frac{\sqrt{2\mu l(l+1)}}{\beta} r \Rightarrow 2K \rho = -E = |\lambda| \)

\[
\Rightarrow \left( \frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{3}{\rho} - \frac{1}{2} \right) u(\rho) = 0
\]

When \( I = \frac{\mu e^2}{2K} \)

so \( I_0 = \int_{2\mu l(l+1)}^{\beta} \rho^2 e^{-\rho} d\rho \Rightarrow E = -|\lambda| = -\frac{\mu e^2}{2K} = -\frac{(\lambda\alpha)^2}{(2\mu l(l+1))} = \frac{\lambda^2}{\alpha^2} \)

Look at asymptotic regimes:

\( U'' - \left[ \frac{l(l+1)}{\rho^2} - \frac{l(l+1)}{\rho} + \frac{3}{2} \right] U = 0 \)

\( \rho \to \infty : \ U'' + \frac{3}{2} U = 0 \Rightarrow U \propto e^{\frac{3}{2} \rho} \Rightarrow \psi \propto \rho^{\frac{3}{2} \rho^2} \)

\( \rho \to 0 : \ U'' - \frac{l(l+1)}{\rho^2} U = 0 \Rightarrow U \propto \rho^a \)

\( \Rightarrow a(a-1) \rho^{a-2} - l(l+1) \rho^{a-2} = 0 \Rightarrow a = 1 \text{ or } (l+1) \)

but \( U \propto \rho^a \) is not integrable \( \rho \to 0 \)

so choose \( U \propto \rho^{-1/2} \)

Then the solution to the full equation is

\[
U = \rho^{-1/2} L_\lambda(\rho) e^{-\rho^2/4}
\]

Substitute into, collect coefficients of powers of \( \rho \), set \( \lambda = 0 \),

get recursion relation:

\[
\frac{\partial L_n}{\partial n} = \frac{L_{n-1}(n+1)}{(n+1)(n+2)}
\]

As \( n \to \infty \), this atop \( \frac{1}{n^2} \), so series behaves asymptotically like \( L_n(\rho) \to e^{\frac{\rho^2}{4}} \).

No good - series must terminate \( \Rightarrow \lambda = (n+1+l+1) \to \lambda n \)

When \( n = \text{integer } > 1 \), The \( L_n(\rho) \), multiplied by \( n \) and \( l \), are Laguerre polys.

Then:

\[
E = -\frac{\hbar^2}{2\mu} (\alpha^2 + \frac{\beta^2}{\alpha^2}) \Rightarrow \frac{\beta^2}{\alpha^2} = -(\omega_0^2 \alpha^2)^2 \Rightarrow \frac{\beta^2}{\alpha^2} = -(\omega_0^2 \alpha^2)^2
\]
The total wave function is:

$$\psi_{nm} = \frac{\psi}{\rho} = \frac{\rho^{l+1}}{\rho} \cdot \psi_{nl}(\rho) \cdot e^{-\varphi_n(\rho)} = \rho^l \psi_{nl}(\rho) \cdot e^{-\varphi_n(\rho)}$$

where

- $n = \text{integer} \geq 1$
- $l = \text{integer} \quad [n, -n-1]$
- $m = \text{integer} \quad [l, -l]$

Quantum numbers

- $\lambda$ labels energy eigenstates

Degeneracy: for each $\lambda_i$, $m$ can have $(2l+1)$ values,

$$\Delta_{\text{deg}} = \sum_{l=0}^{n} (2l+1) = n^2$$

But: electrons have spin: can be up ($\uparrow$) or down ($\downarrow$). $\Rightarrow \text{magnetic}$

Two spin states for each $\psi_{nm} \Rightarrow \text{Degeneracy} = [2n^2]$.

Also, $\rho = 2 \sqrt{\frac{2m_e |\psi|}{\hbar^2}}$ re. Schrod. 1eV = $\frac{1}{2} m_e v^2 \cdot \frac{e^2}{\hbar^2}$

$$\Rightarrow \rho = 2 \frac{m_e^2 \cdot v}{\hbar^2} \cdot \frac{e^2}{\hbar^2} = \frac{2 \pi r}{\hbar^2}$$

$$\Rightarrow \psi_{nlm} = N_{nl} \cdot \frac{2 \pi r}{\hbar^2} \cdot \psi_{nl}(\rho) \cdot e^{-\varphi_n(\rho)} \cdot e^{\imath \frac{1}{2} l \theta}$$

SHORT HAND: $\langle nlm \rangle$.

The $L$'s have $n' = n-l-1$ nodes $\&$ in $r$

and $\psi \propto r^{l+1} L(r) e^{-\varphi_n(\rho)}$ has $l$ nodes at $\rho$ and $m$, as well.

A note on spin: Spin is "orbital" angular momentum, not orbital angular momentum.

In chemistry, $\vec{L} = \vec{r} \times \vec{p}$ - orbital

In QM, $\vec{L}$ is defined by $[\vec{L}, \psi] = i \hbar \vec{L} \psi$

which is satisfied by orbital angular momentum, eigenvectors $\psi_{nm}$, $\lambda = \text{integer} \geq 0$

but then an other eigenvectors, with $\lambda = \frac{1}{2}, \frac{1}{2}, \ldots$ (usual notation: $\frac{1}{2}$, $\frac{1}{2}$).

These are not orbital eigenvectors; they with $\lambda = \frac{1}{2}$ is not unique.

Can be represented by $f(\theta, \phi)$. They can only be represented abstractly: $|n, m\rangle$.

for an electron (or proton or neutron), $j = \frac{1}{2}$, $m = \pm \frac{1}{2}$: $|\frac{1}{2}, \frac{1}{2}\rangle = |\uparrow\rangle$, $|\frac{1}{2}, -\frac{1}{2}\rangle = |\downarrow\rangle$. 
Cut a neutron in half, which must terminate,
only for specific values of \( n \) \( T = 2(p + l + 1) \), \( p = \text{integer} \geq 0 \).

\[ T = 2n, \quad n = \text{integer} \geq l + 1 \]

\[ \Rightarrow n = \frac{2\mu^2 e^2}{k} = \frac{2\mu^2 e^2}{\sqrt{3\pi(\hbar c)^2} \cdot \hbar} \Rightarrow E_n = -\frac{\mu^2 e^2}{2\hbar^2 (p + l + 1)^2} \]

\[ = -\frac{\mu^2 e^2}{2\hbar^2 \cdot \hbar^2} \Rightarrow \frac{\mu^2 e^2}{\hbar^2} \]

where \( \hbar = \frac{\hbar e^2}{2\hbar} = \frac{1}{2} \left( \frac{e^2}{\hbar} \right)^2 = \frac{1}{2} \left( 51,000 \text{ eV} \right) \left( \frac{1}{\hbar^2} \right) = 13.6 \text{ eV} \)

And the \( R(r) = \frac{y(n)}{r}, \quad y = e^{-2r} / (2\pi \hbar) \cdot \text{Fermi}(p), \quad p = 2k \cdot \hbar = 2 \frac{n\hbar}{\hbar} \)

\[ \text{Fermi}(p) = \text{Associated Laguerre polynomial} \]

\[ P_{nm} (n) = \frac{\text{Laguerre polynomial}}{\text{hypergeometric}} \]

The spectrum, for \( Z = 1 \), will look like

\[ l = 0 \quad l = 1 \quad l = 2 \]

(5-wave) (P-wave) (D-wave) \( \in \) spectroscopic notation

Degeneracy - not only is each \( (n,l) \) level \( (2l+1) \)-fold degenerate

in \( m \), but for each \( n \), there are \( n-1 \) possible values of \( l \).

Since \( E_n = -\frac{\mu^2 e^2}{2\hbar^2} \cdot \text{index} \), \( l \)

degeneracy = \( \frac{n-1}{2} \cdot (2l+1) = n^2 \)  

(\( x2 \) for spin !)

\( n = 1 \):

\[ \begin{align*}
2^2 & = 4 \\
3^2 & = 9 \\
4^2 & = 16 \\
5^2 & = 25 \\
6^2 & = 36 \\
7^2 & = 49 \\
8^2 & = 64 \\
9^2 & = 81 \\
10^2 & = 100 \\
11^2 & = 121 \\
12^2 & = 144 \\
\end{align*} \]
The "real" Hydrogen atom:

- Velocity ~ \( \alpha c \), \( \alpha \approx 1/37 \) so there are relativistic corrections to the energy levels (fine structure).
- The electron has spin: \( \langle S_z \rangle = S_z (\pm \frac{1}{2}) \hbar \), \( S = \frac{1}{2} \Rightarrow \sqrt{\langle S_z^2 \rangle} = \frac{\sqrt{3}}{2} \hbar \)
  \( \langle S_z^2 \rangle = \pm \frac{1}{3} \hbar^2 \) - 2 states
  \( \Rightarrow \) for each \( l, m, m_s \) spatial state there are 2 spin states, so
  \( \langle \uparrow \downarrow \rangle = l, m, m_s \rangle \)
  \( \langle \uparrow \downarrow \rangle = l, m, m_s \rangle \)
- Thus, double the degeneracy

- Spin contribution to the relativistic corrections: spin-orbit interaction.

- The nucleus (proton) has finite size; the electron falls inside, lowering the energy level.
- The nucleus has spin, which interacts (electromagnetically) with the electron's spin: "spin-spin" or "hyperfine" interaction.

2. Multi-electron atoms -
- Pauli exclusion principle
- Electron-electron repulsion:

\[
H = \sum_{i} \left( \frac{p_i^2}{2m_i} + \frac{ze^2}{r_i} \right) + \sum_{i<j} \frac{e^2}{r_{ij}}
\]

Evaluate energies of electron orbitals, and total energy, using "Hartree-Fock method of self-consistent fields" approx.
The Periodic table

In the limit that the electrons don't interact with each other (a very poor approximation), we can understand the regularity in the periodic table from these degeneracies:

1. n=1, degeneracy 2, 1s, 1s
2. n=2, degeneracy 8, 2s, 2p

Well, then it gets a bit more complicated. The interaction between electrons lifts the degeneracy in l:

H, He: 1s, 1s
Li, Be: 2s, 2s, 2p, 2p
B, C, N, O, F, Ne: 2p, 2p, 2p (degeneracy $2 \times (2l+1) = 6$)
Ar, Mg: 3s, 3s
Al, Si, P, S, Cl, Ar: 3p, 3p, 3p
K, Ca: 4s, 4s
Sc→Zn: 3d, 3d
Ga→Kr: 4p, 4p

Lanthanides (Ce→Lu): 4f

This pattern of filling of the (nlm) states is understood, despite the complexity of the N-electron atom ($V = \sum_{M} \frac{ze}{r} + \sum_{M} \frac{e^2}{R-M}$), using approximation methods - Hartree Fock.
Physics 12b  3-Dimensional Quantum Physics  3/6/98

These plots were produced using the IQ program from the book “Quantum Mechanics on the Macintosh” by Siegmund Brandt and Hans Dieter Dahmen (Springer Verlag, 1991).

All the relevant mathematics is in Liboff, sections 9.3, 10.2, 10.3. (These kind of figures are usually in introductory QM texts; Liboff is weak on figures). Here we set \( \hbar = 1 \), so we measure energy in units of sec\(^{-1}\). We also set \( m = 1 \), so distance is measured in units of energy\(^{-1/2}\) or sec\(^{1/2}\). Kinda funny, but perfectly consistent.

The figures are then made with the following parameters:

Page 2. The associated Legendre functions \( P_l^m(x) \) vs. \( x = \cos \theta \in [-1,1] \).

Page 3. The magnitude of the spherical harmonics \( |Y_{lm}| \) is plotted as the radial coordinate, as a function of \( \theta \).

Page 4. The radial eigenfunction for hydrogen \( R_{nl} \) vs. \( x = r/a, \ a = \) the Bohr radius. Note that \( R_{n0}(0) \) is non-zero for \( l = 0 \), else 0. The number of radial nodes is \( n - l - 1 \). The main peak shifts further out with \( l \) for fixed \( n \), and with \( n \) for fixed \( l \).

Page 5. The radial eigenfunction for the 3D isotropic QHO \( R_{nl,l} \) (not \( R_{nl} \)).

Page 6. The radial eigenfunction for hydrogen \( rR_{nl} \), “in” the potential, for \( l = 2 \).

Page 7. The radial eigenfunction for the 3D isotropic QHO \( R_{nl} \) “in” the potential, for \( l = 3 \).

Page 8. The radial eigenfunction for the 3D deep “square” (spherical) well, “in” the potential, for \( l = 0 \).

Page 9. The radial eigenfunction for the 3D finite “square” (spherical) well, “in” the potential, for \( l = 0 \).

Page 10. The eigenfunction squared for hydrogen \( \rho_{nll}(r, \theta) = |\psi_{nll}(r, \theta)|^2 \) vs. \( r/a \) and \( \theta \). Note that \( R_{nl0}(0) \) is non-zero for \( l = 0 \), else 0. The number of radial nodes is \( n - l - 1 \). The main peak shifts further out with \( l \) for fixed \( n \), and with \( n \) for fixed \( l \).

Page 11. The same, for the 3D deep “square” (spherical) well.

Come by if you want to play around with this program; it is quite interesting!
Three dimensional harmonic oscillator

\[ R_{n,l}(r), \quad l = 3 \]
Three dimensional square well potential with finite depth

\[ R_2^{(I)}(r) \]

\[ 0 = 1 \]
Angular momentum algebra \( \rightarrow \) spin

Just as we were able to establish the spectrum of the QHO
without solving a differential equation \((\hat{x}, \hat{p}) = i\hbar \Rightarrow [\hat{x}, \hat{p}] = i\hbar\),

\begin{align*}
[\hat{r}, \hat{p}] &= i\hbar \Rightarrow [\hat{r}, \hat{p}] = i\hbar \\
[\hat{\Theta}, \hat{p}] &= i\hbar \Rightarrow [\hat{\Theta}, \hat{p}] = i\hbar \\
[\hat{\Theta}, \hat{\Theta}] &= 0 \\
[\hat{\Theta}, \hat{\Theta}] &= 0 \\
[\hat{\Theta}, \hat{\Theta}] &= 0 \\
[\hat{\Theta}, \hat{\Theta}] &= 0
\end{align*}

we can do the same with the angular momentum algebra:

\[
[\hat{\Theta}, \hat{\Theta}] = 0 \\
[\hat{\Theta}, \hat{\Theta}] = 0 \\
[\hat{\Theta}, \hat{\Theta}] = 0 \\
[\hat{\Theta}, \hat{\Theta}] = 0
\]

Each of the \( \hat{\Theta} \) commutes with \( \hat{\Theta} \) : \([\hat{\Theta}, \hat{\Theta}] = 0\)
but not with each other ...

- One can find simultaneous eigenstates of \( \hat{\Theta} \) and one \( \hat{\Theta} \) (\( \hat{\Theta} \) is functions)

\[
\hat{\Theta}\ket{\pm}\ket{\pm} = \pm \sqrt{2} \ket{\pm}
\]

But not for \( \hat{\Theta}, \hat{\Theta} \) as well.

- There exist a Heisenberg uncertainty relation between the \( \hat{\Theta} \) 's,

\[
\sigma_{\hat{\Theta}} \sigma_{\hat{\Theta}} = \frac{\hbar}{2} \left| \bra{\Theta} \right| = \frac{\hbar}{2} \rho
\]

In QHO, we wrote \( \hat{h} \ket{\pm}\ket{\pm} = \pm \sqrt{2} \ket{\pm} \)

and used only the commutators to find \( \hat{h} \) of eigenstates \( \ket{\pm} \).

Here, we'll do the same:

Construct raising and lowering ops analogous to \( \hat{a}^\dagger, \hat{a} \):

\[
\hat{L} = \hat{L}_x + i \hat{L}_y
\]

\[
\Rightarrow [\hat{L}_x, \hat{L}_y] = \text{c.c.} \quad [\hat{L}_x, \hat{L}_y] = \text{c.c.} \quad [\hat{L}_x, \hat{L}_y] = \text{c.c.}
\]

Applying it to the (unknown) eigenstate \( \ket{\pm} \):

\[
\hat{L} \ket{\pm} = \pm \sqrt{2} \ket{\pm}
\]

Apply it to the (unknown) eigenstate \( \ket{-\pm} \):

\[
\hat{L} \ket{-\pm} = \pm \sqrt{2} \ket{-\pm}
\]

so \( \hat{L}^2 \) is an eigenstate of \( \hat{L}^2 \) with same eigenvalue as \( \hat{L} \).
\[
L_z \left( l \cdot \ell_n \right) = (L_x \cdot L_x) \cdot \ell_n \Rightarrow (L_z \cdot L_z) \cdot \ell_n \Rightarrow (L_x \cdot L_x + \ell^2) \cdot \ell_n = (m \pm 1) \frac{\hbar}{\ell} \left( l \cdot \ell_n \right)
\]

So \( L_z \ell_n \) is an eigenvector of \( L_z \) with eigenvalue \( m \pm 1 \hbar \) different from \( \ell \cdot \ell_n \); i.e., it is proportional to \( \ell \cdot \ell_n \).

\[
\left[ L_z \cdot \ell_n \right] \propto \left( \ell, m, \hbar \right)
\]

The states \( L_z \ell_n \propto \ell, m, \hbar \) form a ladder of states with same \( \ell^2 \) eigenvalue, and \( \ell \) eigenvalue differing by \( \hbar \) units, where \( \hbar \) is an integer.

But, \( \langle \ell_z \rangle \leq \langle \ell \rangle \), so for a given \( \ell \), \( \langle \ell_z \rangle = \ell (\ell + 1) \mu_0^2 \), there must be a top rung where \( (m_{top} \pm 1) \frac{\hbar}{\ell} \leq \ell (\ell + 1) \mu_0^2 \), so that \( L_z \cdot \ell_{m_{top}} = 0 \) annihilates the state.

\[
L_z \cdot \ell_{m_{top}} = m_{top} \frac{\hbar}{\ell} \ell_{m_{top}}
\]

Now:
\[
L \equiv L_x = (L_x \cdot L_y) \left( L_x \cdot L_y \right) = L_x^2 + L_y^2 = (L_x L_y - L_y L_x) \frac{\hbar}{\ell} (L_x L_y - L_y L_x)
\]

So:
\[
L_z = L_x^2 + \frac{\hbar}{\ell} L_x^2 \Rightarrow L_z = L_x + \frac{\hbar}{\ell} L_x
\]

\[
\Rightarrow \ell \cdot \ell_{m_{top}} = \ell (\ell + 1) \frac{\hbar}{\ell} \ell_{m_{top}}
\]

\[
= \left( L_x^2 + L_y^2 + \frac{\hbar}{\ell} L_x^2 \right) \cdot \ell_{m_{top}} = m_{top} (m_{top} + 1) \frac{\hbar}{\ell} \ell_{m_{top}}
\]

\[
\Rightarrow m_{top} = \ell \quad \text{or} \quad -\ell
\]

For the bottom rung, \( \ell \cdot 1 \cdot \ell_{m_{bot}} = 0 \)

\[
\Rightarrow m_{bot} = (l+1) \quad \text{or} \quad -l
\]

Since \( m_{bot} \leq m_{top} \), \( \Rightarrow m_{top} = +\ell \), \( m_{bot} = -\ell \).
\[ M_{\text{top}} - M_{\text{bot}} = \text{non-negative integer} = 2l \]

\[ \Rightarrow l = \text{non-negative integer or half-integer.} \]

\[ \Rightarrow m = -l, -l+1, \ldots, l \]

\[ \Rightarrow \text{We have solved the spectrum of the eigenstates of } L_z, L_\theta \]

\[ \text{without ever doing a differential eqn!} \]

- If you want to know \( \langle L_\theta L_\phi \rangle \), you can generate them starting from \( L_\theta L_\phi M_{\text{top}} = L_\theta L_\phi > 0 \)

and work down any \( l_-, l_0, l_+ \). \( \Rightarrow \) Problem set

- Note that \( \max \langle L_\theta^2 \rangle = \hbar^2 l^2 \leq \hbar^2 l(l+1) \)

so the angular momentum is \( \leq l \).

Can never be entirely in the \( + \theta \) direction

(or, by symmetry, in the \( +x \) or \( +y \) direction) \( \Rightarrow \) Uncertainly

- Note that \( l \) can be a half integer!

(all well as \( m = -l, -l+1 \)).

Not true for spherical harmonics - (classically related motion);

they must be single-valued:

\[ Y_\ell^\alpha(\theta, \phi) \propto \ell^\ell(\ell, 0) \\theta^\ell \phi^0 \]

\[ Y_\ell^0(\theta, \phi + 2\pi) = Y_\ell^\alpha(\theta, \phi) \Rightarrow m = \text{integer} \]

If \( m = \text{half-integer} \)

\[ \text{a rotation of } \frac{\pi}{2} \text{ brings it back.} \]

But that's not a spherical harmonic and it can't be written as a single-valued function in angular \( \phi \) space.

It's a new class of quantum states,

unique \( \ell \in \mathbb{Z} \) and such states are used to describe spin of a particle - its intrinsic angular momentum, not \( L = \vec{r} \times \dot{\vec{r}} \).
How do we represent the angular moment in space?

\[ \mathbf{\mathbf{L}} = r \times (m \mathbf{\hat{r}}) \] 
-Classically, \( \mathbf{L} \) has any magnitude or direction.

\[ |\mathbf{L}| = \sqrt{\mathbf{L} \cdot \mathbf{L}} = \sqrt{\sum_{i=1}^{3} (L_i) L_i} \]

Classically, \( |\mathbf{L}| \leq \sqrt{\sum_{i=1}^{3} (L_i) L_i} \)

What about \( L_x \), \( L_y \)?

\[ \langle \mathbf{L}_x \rangle = \langle \mathbf{L}_y \rangle = \frac{1}{2} (\langle \mathbf{L}_z \rangle + \langle -\mathbf{L}_z \rangle) \]

But

\[ \sqrt{\langle (L_x)^2 \rangle} = \sqrt{\langle (L_y)^2 \rangle} = \frac{\sqrt{\langle L_z \rangle} - m}{\sqrt{2}} \]

So \( L_x \) has a length, but is \( \pm \infty \) often \(-\infty \) Random.

Same for \( L_y \). But \( L_z = m \mathbf{\hat{z}} \) is well defined.

So the picture is:

\[ \hat{z} \rightarrow 0 \]

\[ \hat{z} \rightarrow \pm \infty \]

\[ S \text{ is not a vector, but a} \]

\[ \text{cone of vectors by } \mathbf{L} \text{ on} \]

\[ \text{a cone, with random } \hat{\Theta} \]

\[ \cos \Theta = \frac{|\mathbf{L}|}{|\mathbf{L}|} = \frac{m}{\sqrt{\sum_{i=1}^{3} (L_i) L_i}} \]

\[ \mathbf{L}_z \leftrightarrow \pm \infty \]

\[ \mathbf{L}_x \leftrightarrow \hat{z} \rightarrow 0 \]

\[ \mathbf{L}_y \leftrightarrow \hat{z} \rightarrow \pm \infty \]

We'll see how this works in more detail for spin.