The eigenstates of $L_x$ or $L_y$.

Since $L_x = \frac{1}{2} (L_+ + L_-)$ can not change the value of $l$ one might expect that some linear combination of eigenstates of $L_z$ with the same $l$ value would be an eigenstate of $L_x$.

Alternatively one can see from the matrix form of $L_x$. The matrix has a block diagonal form and therefore it is sufficient to diagonalize only the submatrices.

Consider the $l=1$ submatrix ($l=0$ is trivial).

$$L_x = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

Setting $\det [ L_x - \lambda I] = 0$

$$\begin{vmatrix} -\lambda & \frac{1}{2} & 0 \\ \frac{1}{2} & -\lambda & \frac{1}{2} \\ 0 & \frac{1}{2} & -\lambda \end{vmatrix} = -\lambda^3 + \frac{1}{2} \lambda^2 + \frac{1}{4} \lambda = 0$$

or $\lambda (\lambda^2 - \frac{1}{2}) = 0$  \(\lambda = 0\)  \(\lambda = \pm \sqrt{\frac{1}{2}}\)

So the $m_l$ values are the same $-l \leq m_l \leq l$ or $-1 \leq m_l \leq 1$.

To find the eigen vectors substitute in for $\lambda$

$\lambda = \pm \sqrt{\frac{1}{2}}$

$$\begin{pmatrix} \pm \sqrt{\frac{1}{2}} & \frac{1}{2} & 0 \\ \frac{1}{2} & \pm \sqrt{\frac{1}{2}} & \frac{1}{2} \\ 0 & \frac{1}{2} & \pm \sqrt{\frac{1}{2}} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = 0$$

$$\begin{align*}
\pm a + \frac{1}{2} b &= 0 \\
\frac{1}{2} a + \frac{1}{2} b + \frac{1}{2} c &= 0 \\
\frac{1}{2} b + c &= 0
\end{align*}$$

$$\begin{align*}
\lambda = + \sqrt{\frac{1}{2}} \\
\lambda &= - \sqrt{\frac{1}{2}}
\end{align*}$$
\[ \lambda = 0 \]
\[
\begin{pmatrix}
0 & \frac{1}{\sqrt{2}} & 0 \\
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & \frac{1}{\sqrt{2}} & 0
\end{pmatrix}
\begin{pmatrix}
q \\
b \\
c
\end{pmatrix}
= 0
\]
\[
\begin{align*}
b &= 0 \\
a + c &= 0 \\
a &= -c
\end{align*}
\]
\[
\lambda = 0 \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}
\]

So the eigenstates of \( L_x \) are
\[
\begin{align*}
\lambda &= k & 14_{11}^x &= \frac{1}{2} \left\{ |111\rangle + \sqrt{2} |10\rangle + |11-1\rangle \right\} \\
\lambda &= 0 & 14_{10}^x &= \frac{1}{\sqrt{2}} \left\{ |111\rangle - |11-1\rangle \right\} \\
\lambda &= -k & 14_{1-1}^x &= \frac{1}{2} \left\{ |111\rangle - \sqrt{2} |10\rangle + |11-1\rangle \right\}
\end{align*}
\]
Special representations of $L^2$ elements.

Convenient to work in spherical coordinates.

\[ x = r \sin \theta \cos \phi, \]
\[ y = r \sin \theta \sin \phi, \]
\[ z = r \cos \theta. \]

\[
\frac{\partial}{\partial \phi} |_{r, \theta} = (\frac{\partial}{\partial \phi} \frac{\partial}{\partial x}) \frac{\partial x}{\partial \phi} + (\frac{\partial}{\partial \phi} \frac{\partial}{\partial y}) \frac{\partial y}{\partial \phi} + (\frac{\partial}{\partial \phi} \frac{\partial}{\partial z}) \frac{\partial z}{\partial \phi}.
\]

But \[ \frac{\partial x}{\partial \phi} = -r \sin \phi \sin \theta, \quad \frac{\partial y}{\partial \phi} = r \cos \phi \cos \theta, \quad \frac{\partial z}{\partial \phi} = 0. \]

\[
\frac{\partial}{\partial \phi} |_{r, \theta} = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y}.
\]

And so \[ L_{z} = -i h (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) = -i h \frac{\partial}{\partial \phi}. \]

Similarly,

\[
\frac{\partial}{\partial \theta} |_{r, \phi} = \cos \phi \cos \theta \frac{\partial}{\partial x} + \cos \phi \sin \theta \frac{\partial}{\partial y} - \sin \phi \frac{\partial}{\partial z}.
\]

So \[ \sin \frac{\partial}{\partial \theta} = \cos \frac{\partial}{\partial \phi} \frac{\partial}{\partial \theta} \cos \cos \theta \frac{\partial}{\partial \phi} \cos \sin \theta \frac{\partial}{\partial \phi} = \cos \theta \frac{\partial}{\partial \phi}, \]

\[ \sin \frac{\partial}{\partial \phi} = \cos \theta \cos \phi \frac{\partial}{\partial x} + \cos \theta \sin \phi \frac{\partial}{\partial y} - \sin \theta \sin \phi \frac{\partial}{\partial z}. \]

But \[ \sin^2 \theta = 1 - \cos^2 \phi, \]

\[ \sin \frac{\partial}{\partial \phi} = \cos \phi \cos \theta \frac{\partial}{\partial x} - \cos \phi \cos \theta \frac{\partial}{\partial y} + z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z}. \]

\[ \sin \frac{\partial}{\partial \theta} = \frac{\cos \phi}{\sin \theta} (\cos \phi) \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) + z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z}. \]
\[ y \frac{\partial z}{\partial y} - 2 \frac{\partial y}{\partial y} = - \sin \theta \frac{\partial \theta}{\partial y} = \cot \theta \cos \theta \frac{\partial y}{\partial y} \]

and so

\[ L_x = -i k (y \frac{\partial z}{\partial y} - 2 \frac{\partial y}{\partial y}) = ik \left\{ \sin \theta \frac{\partial \theta}{\partial y} + \cot \theta \cos \theta \frac{\partial y}{\partial y} \right\} \]

Similarly

\[ L_y = -i k (z \frac{\partial x}{\partial y} - x \frac{\partial z}{\partial y}) = -ik \left\{ \cos \theta \frac{\partial \theta}{\partial y} - \cot \theta \sin \theta \frac{\partial y}{\partial y} \right\} \]

\[ L = L_x \pm i L_y \]

\[ = ik \left\{ \sin \theta \frac{\partial \theta}{\partial y} + i \cos \theta \frac{\partial \theta}{\partial y} + \cot \theta \frac{\partial y}{\partial y} (\cos \theta \pm isin \theta) \partial \phi \right\} \]

\[ = ik \left\{ i e^{\pm i \phi} \frac{\partial \phi}{\partial y} + \cot \theta \ln \frac{\partial y}{\partial \phi} \right\} \]

\[ L = -ik e^{\pm i \phi} \left\{ \pm i \frac{\partial \phi}{\partial y} - \cot \theta \frac{\partial y}{\partial \phi} \right\} \]

To solve for the form of \( |l, m> \) we can use the fact that

\[ L^+ |l, m> = 0 \]

Call \( |l, m> = Y_l^m (\theta, \phi) \) then.

\[ L^+ Y_l^m (\theta, \phi) = -i k e^{\pm i \phi} \left\{ \pm i \frac{\partial \phi}{\partial y} - \cot \theta \frac{\partial y}{\partial \phi} \right\} Y_l^m (\theta, \phi) = 0 \]

Assume \( Y_l^m (\theta, \phi) = \Theta (\theta) \Xi (\phi) \)

\[ \frac{i \frac{\partial \Phi}{\partial \Phi}}{\cot \theta (\Phi)} - \frac{\cot \theta \frac{\partial \Phi}{\partial \Phi}}{\Xi} = 0 \]

so \( \frac{\partial \Phi}{\partial \Xi} = \frac{i \frac{\partial \Phi}{\partial \Phi}}{\cot \theta (\Phi)} = \text{constant} \)
since \( \frac{\partial}{\partial \varphi} \psi (\varphi, \theta, \phi) = -i \hbar \frac{\partial}{\partial \phi} \psi (\varphi, \theta, \phi) = i \hbar \frac{\partial}{\partial \theta} \psi (\varphi, \theta, \phi) \)

this constant must be \( i \hbar \) and so \( \overline{\psi}(\varphi) = e^{i \frac{\theta}{\hbar}} \)

and

\[
\frac{\partial}{\partial \theta} \overline{\psi} = \frac{\partial}{\partial \theta} (\overline{\psi} \cos \theta) = \frac{\partial}{\partial \theta} \overline{\psi} \cos \theta
\]

\[
\frac{\partial}{\partial \theta} \overline{\psi} \sin \theta = \ln \overline{\psi} = \ln (\sin \theta) + \ln A
\]

or \( \overline{\psi}(\varphi) = A \left[ \sin \varphi \right]^{l} \)

Together then

\[
\psi (\varphi, \theta, \phi) = A (\sin \varphi)^{l} e^{i \frac{\theta}{\hbar}} \quad \text{where } A \text{ is chosen for normalization.}
\]

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz \rightarrow \int_{0}^{2\pi} \int_{0}^{\pi} r^2 dr d\theta d\varphi
\]

Require

\[
\int_{0}^{\pi} \int_{0}^{2\pi} \left| \psi (\varphi, \theta, \phi) \right|^2 = 1
\]

\[
\int_{0}^{\pi} \int_{0}^{2\pi} \left| A \right|^2 (\sin \varphi)^{2l+1} = 1
\]

The \( \varphi \) integral is easy.

\[
2\pi \left| A \right|^2 \int_{0}^{\pi} (\sin \varphi)^{2l+1} d\varphi = 1
\]

Note

\[
\int_{0}^{\pi} (\sin \varphi)^{2l+1} d\varphi = \int_{0}^{\pi} (\sin \varphi)^{2l-1} (1 - \cos^2 \varphi) d\varphi
\]

\[
= \int_{0}^{\pi} (\sin \varphi)^{2l-1} d\varphi - \int_{0}^{\pi} (\sin \varphi)^{2l-1} \cos^2 \varphi d\varphi
\]
Integrating the second term by parts,

\[ \int_{0}^{\pi} (\sin \phi)^{2l-1} d\phi = \left[ \cos \phi \cdot (\sin \phi)^{2l} \right]_{0}^{\pi} - \int_{0}^{\pi} \frac{2l}{2l} \cdot (\sin \phi)^{2l} \cdot \cos \phi \cdot \sin \phi \ d\phi \]

\[= \int_{0}^{\pi} (\sin \phi)^{2l-1} d\phi + \int_{0}^{\pi} (\sin \phi)^{2l+1} d\phi \]

and so

\[\left(\frac{2l+1}{2l}\right) \int_{0}^{\pi} (\sin \phi)^{2l+1} d\phi = \int_{0}^{\pi} (\sin \phi)^{2l-1} d\phi \quad \text{PROGRESS!} \]

\[\int_{0}^{\pi} (\sin \phi)^{2l+1} d\phi = \left(\frac{2l}{2l+1}\right) \int_{0}^{\pi} (\sin \phi)^{2l} d\phi \]

\[= \left(\frac{2l}{2l+1}\right) \left(\frac{2l-2}{2l-1}\right) \left(\frac{2l-4}{2l-3}\right) \left(\frac{2l-6}{2l-5}\right) \cdots 2 \int_{0}^{\pi} (\sin \phi)^{2l-5} d\phi \]

\[= \frac{(2l)(2l-2)(2l-4) \cdots 4 \cdot 2}{(2l+1)(2l-1)(2l-3) \cdots 5 \cdot 3} \int_{0}^{\pi} (\sin \phi)^{2l-1} d\phi \]

\[\int_{0}^{\pi} (\sin \phi)^{2l+1} d\phi = \frac{(l!)}{(2l+1)!} \frac{2^{2l} \cdot 2}{(l!)^{2}} \\
\frac{(l!)}{(2l+1)!} \cdot \frac{2^{2l+1}}{(2l+1)!} \]

**Therefore**

\[\frac{2\pi A_1 (l!)}{(2l+1)!} \frac{(2l+1)!}{(l!)^{2} 2^{2l+1}} = 1 \quad \text{or} \quad 1A_1 = \left[ \frac{(2l+1)!}{(l!)^{2} 2^{2l+1} 2\pi} \right]^{\frac{1}{2}} \]
By convention \( A = (-1)^l |A| \)

\[
Y^l_0 (\theta, \phi) = \frac{(-1)^l}{l!} \left( \frac{(2l+1)!}{\pi} \right)^{\frac{1}{2}} (\sin \theta)^l e^{i \phi}.
\]

[Result in Anderson 7.53 seems wrong.]

To find other \( Y^m \)'s use \( L \).

\( l = 0 \quad Y^0_0 (\theta, \phi) = \frac{1}{4\pi} \).

\( l = 1 \quad Y^1_0 (\theta, \phi) = -\left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \sin \theta e^{i \phi} \).

\[
L \cdot \left| 1 \ 1 \right> = \frac{k}{\sqrt{2}} \left| 1 \ 0 \right> \quad \text{or}
\]

\[ -ik e^{-i \phi} \left\{ -i \frac{\partial}{\partial \theta} - \cot \theta \frac{\partial}{\partial \phi} \right\} \left[ -\left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \sin \theta e^{i \phi} \right] = \frac{k}{\sqrt{2}} Y^0_0
\]

\[
Y^0_1 (\theta, \phi) = \frac{i}{12} e^{-i \phi} \left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \left\{ -i \cos \theta e^{i \phi} - \cot \theta \sin \theta e^{i \phi} \right\}
\]

\[ = 2 \left( \frac{3}{16\pi} \right)^{\frac{1}{2}} \cos \theta = \left( \frac{3}{4\pi} \right)^{\frac{1}{2}} \cos \theta
\]

Similarly

\[
L \cdot \left| 1 \ 1 \right> = \frac{k}{\sqrt{2}} \left| 1 \ 1 \right> = -ik e^{-i \phi} \left\{ -i \frac{\partial}{\partial \theta} - \cot \theta \frac{\partial}{\partial \phi} \right\} \left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \cos \theta
\]

\[
Y^1_1 (\theta, \phi) = \frac{-i}{12} e^{-i \phi} \left\{ +i \left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \sin \theta \right\}
\]

\[ = \left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \sin \theta e^{-i \phi}.
\]
Spherical Harmonics:

\[ l = 0 \]
\[ Y_0^0 (\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad \text{Spherical Symmetric (constant).} \]

\[ l = 1 \]
\[ Y_1^1 (\theta, \phi) = -\frac{\sqrt{3}}{2\sqrt{\pi}} \sin \theta e^{i\phi} \quad \frac{-\sqrt{3}i}{2\sqrt{\pi}} \frac{1}{r} (x+iy) \]
\[ Y_1^0 (\theta, \phi) = \frac{\sqrt{3}}{2\sqrt{\pi}} \cos \theta \quad \frac{\sqrt{3}i}{2\sqrt{\pi}} \frac{z}{r} \]
\[ Y_1^{-1} (\theta, \phi) = \frac{\sqrt{3}}{2\sqrt{\pi}} \sin \theta e^{-i\phi} \quad \frac{-\sqrt{3}i}{2\sqrt{\pi}} \frac{(x-iy)}{r} \]

\[ l = 2 \]
\[ Y_2^2 (\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{2\pi}} \sin^2 \theta e^{2i\phi} \quad Y_2^0 (\frac{15\pi}{2\pi})^2 \frac{1}{2} \frac{((x^2-y^2)+2ixy)}{r^2} \]
\[ Y_2^1 (\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{2\pi}} \sin \theta \cos \theta e^{i\phi} \quad Y_2^{-1} (\frac{15\pi}{2\pi})^2 \frac{1}{2} \frac{2(x+iy)}{r^2} \frac{1}{r^2} \]
\[ Y_2^0 (\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{2\pi}} (3\cos^2 \theta - 1) \quad Y_2^0 (\frac{5\pi}{2\pi})^2 \frac{3y^2}{r^2} \]
\[ Y_2^{-1} (\theta, \phi) = \frac{1}{2} \sqrt{\frac{5}{2\pi}} \sin \theta \cos \theta e^{-i\phi} \quad Y_2^{-1} (\frac{15\pi}{2\pi})^2 \frac{2(x-iy)}{r^2} \frac{1}{r^2} \]
\[ Y_2^2 (\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{2\pi}} \sin^2 \theta e^{-i\phi} \quad Y_2^2 (\frac{15\pi}{2\pi})^2 \frac{1}{2} \frac{((x^2-y^2)-2ixy)}{r^2} \]

\[ [l = 2 \text{ looks like a 2nd RANK TENSOR}] \]

Remark: For \( l = 1 \) the eigenstates of \( L_x \) were:
\[ \lambda = \pm k \quad \frac{1}{2} \left[ 11 \hat{r}_x \pm i2 \ 10 \hat{r}_x \pm 11-1 \hat{r}_x \right] \]
\[ \lambda = 0 \quad \sqrt{1} \left[ 11 \hat{r}_x - 11-1 \hat{r}_x \right] \]

Expressing these in terms of \( x, y, z \) we have:
\[ \lambda = \pm k \quad |1\pm1\rangle_x = -i \sqrt{\frac{3}{2\pi}} (y \pm iz) \quad -i \sqrt{\frac{3}{2\pi}} (y \pm iz) \]
\[ \lambda = 0 \quad |10\rangle_x = \sqrt{\frac{3}{2\pi}} \frac{x}{r} \]

(Same form as eigenstates of \( L_x \) as it should be since there is nothing to tell you orientation of area.)
In[5]:=
SphericalPlot3D[
Abs[SphericalHarmonicY[2, 2, theta, phi] - SphericalHarmonicY[2, -2, theta, phi]]
{theta, 0, Pi, Pi/30}, {phi, 0, 2 Pi, Pi/15}]

Out[5]=
-Graphics3D-

\[
\left| \begin{array}{c}
Y_2^2 - Y_2^{-2} \\
\frac{1}{4} \frac{\sqrt{15}}{2\pi} \sin^2 \theta \sin 2\phi
\end{array} \right|
\]
SphericalHarmonics

SphericalPlot3D[Abs[SphericalHarmonicY[3, 2, theta, phi]],
{theta, 0, Pi, Pi/30}, {phi, 0, 2Pi, Pi/15}]

\[ Y_3^2 = \frac{1}{4} \sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \phi e^{+2i\phi}. \]
SphericalHarmonics

\[ \text{SphericalPlot3D}[\text{Abs}[\text{SphericalHarmonicY}[3, 1, \theta, \phi]], \{\theta, 0, \pi, \pi/30\}, \{\phi, 0, 2\pi, \pi/15\}] \]

\[ Y_3^1(\theta, \phi) = -\frac{1}{\sqrt{5}} \sin \theta (5 \cos^2 \theta - 1) e^{i \phi} \]
\[ Y_3^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{7}{\pi}} \left( 5 \cos^2 \theta - 3 \cos \phi \right). \]
SphericalHarmonics

SphericalPlot3D[Abs[SphericalHarmonicY[4, 4, theta, phi]],
{theta, 0, Pi, Pi/30}, {phi, 0, 2Pi, Pi/15}]

- Graphics3D -

\[ Y_4^4 (\theta, \phi) = \]
SphericalHarmonics

SphericalPlot3D[Abs[SphericalHarmonicY[4, 3, theta, phi]],
{theta, 0, Pi, Pi/30}, {phi, 0, 2Pi, Pi/15}]
SphericalHarmonics

SphericalPlot3D[Abs[SphericalHarmonicY[4, 2, theta, phi]],
{theta, 0, Pi, Pi/30}, {phi, 0, 2Pi, Pi/15}]
In[9]:=
SphericalPlot3D[Abs[SphericalHarmonicY[4, 0, theta, phi]],
{theta, 0, Pi, Pi/30}, {phi, 0, 2Pi, Pi/15}]

Out[9]=
-Graphics3D-
Rotating Operators.

In our initial description of the angular momentum operators we found that the unitary operator which describes a rotation about an arbitrary axes \( \hat{n} \) by the angle \( \theta \) is just

\[
R(\hat{n}, \theta) = e^{i \theta \mathbf{L} \cdot \hat{n}}/k
\]

Therefore, let's try rotating a state of \( L_z \) by an angle \( \pi/2 \) about the \( \hat{x} \)-axis.

Try

\[
R(\hat{x}, \pi/2) = e^{i \pi/2 L_x / k} \quad \text{on the state } 110 \rangle_2
\]

\[
e^{i \pi/2 L_x / k} 110 \rangle_2 = \left[ 1 + \frac{i \pi}{2k} L_x + \frac{(i \pi)^2}{2k} L_x^2 + \frac{(i \pi)^3}{3k} L_x^3 \ldots \right] 110 \rangle_2
\]

but since \( L_x = \frac{L_+ + L_-}{2} \)

\[
R(\hat{x}, \pi/2) 110 \rangle_2 = \left[ 1 + \frac{i \pi}{2k} \frac{L_+ + L_-}{2} + \frac{(i \pi)^2}{2k} \frac{(L_+ + L_-)^2}{2^2 2!} \ldots \right] 110 \rangle_2
\]

Clearly it can be done but let us try a trick. If we could write the state \( 110 \rangle_2 \) in terms of eigenstates of \( L_x \) then the evaluation of \( e^{i \pi L_x / 2k} \) would be simple. Looking at the definitions of the eigenstates of \( L_x \)

\[
m_{L_x} = \pm \hbar \quad 11 \pm \rangle_{L_x} = \frac{1}{2} \left[ 111 \rangle_2 \pm \sqrt{2} 110 \rangle_2 + 11- \rangle_2 \right]
\]

\[
m_{L_x} = 0 \hbar \quad 110 \rangle_{L_x} = \frac{1}{\sqrt{2}} \left[ 111 \rangle_2 - 11- \rangle_2 \right]
\]

we can write

\[
\frac{\sqrt{2}}{2} \ 110 \rangle_2 = 11+ \rangle_{L_x} - 11- \rangle_{L_x} \quad \text{or}
\]

\[
110 \rangle_2 = -\frac{1}{\sqrt{2}} \left[ 111 \rangle_{L_x} - 11- \rangle_{L_x} \right]
\]
Now
\[ e^{i \pi x^2} |10\rangle_z = e^{i \pi x^2} \left\{ \frac{1}{\sqrt{2}} \left( |111\rangle_x - |1-1\rangle_x \right) \right\} \]
\[ = \frac{1}{\sqrt{2}} \left[ e^{i \pi x^2} |111\rangle_x - e^{-i \pi x^2} |1-1\rangle_x \right] \]
\[ = \frac{i}{\sqrt{2}} \left[ |111\rangle_x + |1-1\rangle_x \right] \]

Transforming back to z - basis,
\[ e^{i \pi x^2} |10\rangle_z = \frac{i}{\sqrt{2}} \left\{ |111\rangle_z + |1-1\rangle_z \right\} = \frac{i}{\sqrt{2}} (-2i) \left( \frac{3}{2\pi} \right)^{\frac{1}{2}} \frac{\chi}{\tau} \]
\[ = \left( \frac{3}{4\pi} \right)^{\frac{1}{2}} \sin \theta \sin \phi \]

Physically we have taken a state which looks oriented along the \( z \)-axis to one oriented along the \( y \)-axis is

\[ \begin{array}{c}
\text{\( x \)} \\
\text{\( y \)} \\
\text{\( z \)}
\end{array} \quad \Rightarrow \quad \begin{array}{c}
\text{\( x \)} \\
\text{\( y \)} \\
\text{\( z \)}
\end{array} \]

Note: One could have done the entire calculations in the \( z \)-basis but one would need to consider the effect of \( (L^+ + L^-) \) on \( |110\rangle_z \). Then higher powers of \( (L^+ + L^-) \)
\[ (L^+ + L^-)|110\rangle_z = \sqrt{2} \left( |111\rangle_z + |1-1\rangle_z \right) \]
\[ = 2 \left( |110\rangle_z + |10\rangle_z \right) \]
\[ = 4 |10\rangle_z \]
so sequence is cyclic.
Example

Rotating dumbbell

\[ \begin{align*}
\text{Moment of inertia} & : \ 2ma^2 \\
\text{Kinetic energy} & : \ \frac{1}{2} I \omega^2 \\
\text{Angular momentum} & : \ I\omega
\end{align*} \]

If there are no forces then the total energy will just be

kinetic energy \[ E = \frac{1}{2} I \omega^2 = \frac{1}{2} \frac{p^2}{I} \]

To quantize this classical problem we need only make \( I^2 \)
the quantum mechanical operator. So

\[ H = \frac{1}{2} \frac{I^2}{I} \]

The eigenstates of this system can be read off immediately

\[ \psi_{l,m} (\theta, \phi) = \chi_{l}^{m} (\theta, \phi) \text{ with } E_{l} = \frac{1}{2} \frac{l(l+1)\hbar^2}{I} \text{ (does not depend on } m) \]

which are \( 2l+1 \) degenerate.

<table>
<thead>
<tr>
<th>( l )</th>
<th>( 3/\hbar^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l=2 )</td>
<td>5 fold degenerate</td>
</tr>
<tr>
<td>( l=1 )</td>
<td>3 fold degenerate</td>
</tr>
<tr>
<td>( l=0 )</td>
<td>1 fold degenerate</td>
</tr>
</tbody>
</table>

These states can be seen by looking for characteristic radiation given off by atoms going from 1 level to the next.

\[ k\omega = \Delta E = E_{l=1} - E_{l=0} = \frac{\hbar^2 l}{I} = \frac{(hc)^2}{2\hbar \omega^2} \]

\( hc \approx 197 \text{MeV} \times 10^{-15} \text{m} \)

\( 2\pi \approx 6.93 \times 10^{-5} \text{eV} \)

\( \lambda \sim 1.99 \text{mm} \)

\( \omega \sim 2 \times 10^{10} \text{cm}^{-1} \)
Consider the classical angular momentum:

\[ L^2 = (r \times p)^2 = (r \times p) \cdot (r \times p) \]

\[ = \sum_i (r \times p)_i (r \times p)_i \]

but \((r \times p)_i = \sum_{ijk} \epsilon_{ijk} r_j p_k \)

\[ L^2 = \sum_{ijk} \epsilon_{ijk} \epsilon_{ilm} r_j p_k r_l p_m \]

but \(\sum_i \epsilon_{ijk} \epsilon_{ilm} = \delta_{jel}\delta_{km} - \delta_{jml}\delta_{kl} \) so that

\[ L^2 = \sum_{jkl} (\delta_{jel}\delta_{km} - \delta_{jml}\delta_{kl}) r_j p_k r_l p_m \]

\[ = \sum_{lml} (r_l p_m r_l p_m - r_m p_l r_l p_m) \]

If we allow the order of the operators to change.

\[ L^2 = \sum_r r_r r_r \sum_m p_m p_m - \sum_r r_r p_r \sum_m r_m p_m \]

or

\[ L^2 = r^2 p^2 - (r \cdot p)^2 \]

In quantum mechanics we cannot arbitrarily change the order of the \(v_i \) \(p_i \) operators since some do not commute.

In particular

\[ [r_i , p_j] = r_i p_j - p_j r_i = i k \delta_{ik}.\]
Taking this into account we now have for the quantum operator $L^2$

$$L^2 = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})(\mathbf{r} \cdot \mathbf{p}) + ik (\mathbf{r} \cdot \mathbf{p})$$

(see homework)

which is very close to the classical expression.

---

Solving for $p^2$ in the above expression we find

$$p^2 = \frac{1}{r^2} \left\{ L^2 + (\mathbf{r} \cdot \mathbf{p})(\mathbf{r} \cdot \mathbf{p}) - ik (\mathbf{r} \cdot \mathbf{p}) \right\}$$

But what is $\mathbf{r} \cdot \mathbf{p}$? In spherical coordinates $\mathbf{p} = r \hat{\mathbf{r}}$

and $p = -ik \left[ \hat{\mathbf{i}} \frac{\partial}{\partial x} + \hat{\mathbf{j}} \frac{\partial}{\partial y} + \hat{\mathbf{k}} \frac{\partial}{\partial z} \right] = -ik \nabla$

and $\hat{\mathbf{r}} = \sin \theta \cos \phi \hat{\mathbf{i}} + \sin \theta \sin \phi \hat{\mathbf{j}} + \cos \theta \hat{\mathbf{k}}$ so that

$$\mathbf{r} \cdot \mathbf{p} = -ik \left[ r \sin \theta \cos \phi \frac{\partial}{\partial x} + r \sin \theta \sin \phi \frac{\partial}{\partial y} + r \cos \theta \frac{\partial}{\partial z} \right]$$

but this is just $\mathbf{r} \cdot \mathbf{p} = -ik r \frac{\partial}{\partial r}$.

We therefore can write

$$p^2 = \frac{1}{r^2} \left\{ L^2 + (-ik r \frac{\partial}{\partial r}) (-ik r \frac{\partial}{\partial r}) - ik (-ik r \frac{\partial}{\partial r}) \right\}$$

$$= \frac{1}{r^2} \left\{ L^2 - k^2 \left[ r^2 \frac{\partial^2}{\partial r^2} + r \frac{\partial}{\partial r} \right] - k^2 r \frac{\partial}{\partial r} \right\}$$

$$= \frac{1}{r^2} \left\{ L^2 - k^2 \left[ r^2 \frac{\partial^2}{\partial r^2} + 2 \frac{\partial}{\partial r} \right] \right\}$$

$$p^2 = \frac{1}{r^2} \left\{ L^2 - k^2 \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \right] \right\}$$
What is the significance of $p^2$. Given a Hamiltonian of the form

$$\hat{H} = \frac{p^2}{2m} + V(x, y, z)$$

we can rewrite it as

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} (r^2 \frac{\partial}{\partial r}) + \frac{L^2}{2mr^2} + V(x, y, z).$$

Alternatively, one could have expressed $-\frac{\hbar^2}{2m} \nabla^2$ in spherical coordinates to obtain the above result. (Of course you would need to be able to recognize $L^2$ in terms of $\Omega$ and $\Theta$.)

If $V(x, y, z)$ depends only on $r$ (not $\Omega$ or $\Theta$) then the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} (r^2 \frac{\partial}{\partial r}) + \frac{L^2}{2mr^2} + V(r)$$

commutes with $L_x$, $L_y$, and $L_z$.

$L_i$ involves derivatives with respect to angles and $L^2$ commutes with all $L_i$ operators.

We conclude then that for spherical symmetric potentials, angular momentum will be conserved.

1. States of $\hat{H}$ can be found to be eigenstates of $L^2$ and $L_z$.
2. Both $L$ and $m$ are good quantum numbers.

One expects solutions

$$\psi(r, \Omega, \Theta) = R(r) Y^m_{\ell}(\Omega, \Theta).$$
Probability Interpretation.

\[ \psi(r, \theta, \phi) = \sum_{l, m} R_{lm}(r) Y_{l}^{m}(\theta, \phi). \]

\[
\text{Normalize } \int_{0}^{\infty} r^2 \, dr \int_{0}^{\pi} \sin \theta \, d\theta \int_{0}^{2\pi} \, d\phi \left| Y_{l}^{m}(\theta, \phi) \right|^2 = 1
\]

So \[ \int_{0}^{\infty} r^2 \, dr \left| R(r) \right|^2 = 1 \]

\[ |R(r)|^2 r^2 \, dr \] is the probability that the particle can be found within a spherical shell of radii \( r \) and \( r + dr \).

One can ask what is the probability that the particle has a specific angular momentum. If the state is described by

\[ \psi(r, \theta, \phi) = \sum_{l, m} R_{lm}(r) Y_{l}^{m}(\theta, \phi) = \sum_{l, m} C_{lm} Y_{l}^{m}(\theta, \phi) \]

then the probability that the particle is in a \( l, m \) state is just the coeff. \( C_{lm} \) (absolute value squared) is

\[ |C_{lm}|^2 \equiv |R_{lm}(r)|^2 \]

So the interpretation is that \( |C_{lm}|^2 \) is the probability that the particle has angular momentum \( l, m \) and can be found within a region of \( r \)-space.

If one wants the prob. that the particle has ang. mom. \( l, m \) anywhere in space then one can integrate the above result over \( r \).
\[ \mathcal{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} (r^2 \frac{d}{dr} r) + \frac{p^2}{2m} + V(r) \]

has solutions of the form
\[ \psi(r, \theta, \phi) = R(r) Y^m_l(\theta, \phi) . \]

where \( R(r) \) satisfies
\[ \left[ -\frac{\hbar^2}{2m} \frac{d}{dr} (r^2 \frac{d}{dr} r) + \frac{\ell(\ell + 1) \hbar^2}{2m} + V(r) \right] R(r) = \text{ER} \]

What restrictions are there on \( R(r) \)?

- Clearly for bound states we want \( R(r) \to 0 \) as \( r \to \infty \)

  in particular \( \int_0^\infty r^2 |R(r)|^2 \) must converge.

- If one repeats the argument for small \( r \) you might require
\[ \int_0^\infty r^2 |R(r)|^2 \to \text{converge} \]

  which would imply
\[ R \sim r^{-1 + \xi/2} \]

  where \( \xi > 1 \)

However a more stringent requirement can be made by requiring \( \langle \mathcal{H} \rangle \)

to exist. i.e.
\[ \langle R(r) Y^m_l(\theta, \phi) \mid -\frac{\hbar^2}{2m} \frac{d}{dr} (r^2 \frac{d}{dr} r) + \frac{\ell(\ell + 1) \hbar^2}{2m} + V(r) \mid R(r) Y^m_l(\theta, \phi) \rangle . \]

\[ = \int_0^\infty r^2 dr \left[ \frac{\hbar^2}{2m} \frac{d}{dr} (r^2 \frac{d}{dr} r) + \frac{\ell(\ell + 1) \hbar^2}{2m} + V(r) \right] |R(r)|^2 \]

If \( R \sim r^{-1 + \xi/2} \) for \( r \to \infty \) then
\[ \int_0^{2\text{max}} r^2 dr \left[ \frac{\hbar^2}{2m} \left( \frac{d}{dr} - \frac{1}{2} \right) \right] r^{(\alpha - 1)} + \frac{\ell(\ell + 1) \hbar^2}{2m} r^{-1 - \xi/2} + V(r) r^{d - 2} \]
\[
\int_{\epsilon}^{R_{\text{max}}} dr \left\{ \left[ \frac{1}{2m} \left( \frac{m^2}{\hbar^2} - 1 \right)^{1/2} + \frac{e^{( \alpha + 1) \hbar^2}}{2m} \right] r^{\alpha - 2} + V(r) r^\alpha \right\}
\]

Therefore if \( V(r) \) diverges no faster than \( 1/r^2 \) as \( r \to 0 \), then \( \langle \hat{H} \rangle \) will exist for \( \alpha > 1 \).

Defining \( R(r) = g(r) \) then

\[
g(r) = r^\left( r^{-1+\frac{\alpha}{2}} \right) \sim r^{\frac{\alpha}{2}} \quad \text{and require}
\]

\( g(r) \) must vanish at small \( r \) no slower than \( r^{\frac{\alpha}{2} + \delta} \)

or \( R(r) \) must diverge no faster than \( r^{-\frac{\alpha}{2} + \delta} \).

---
Angular momentum in "effective potential"

\[ \mathbf{p} = -\frac{k^2}{2m} \frac{d}{dr} (r^2 \frac{d}{dr} \mathbf{r}) + \frac{l^2}{2mr^2} + V(r) \quad \mathbf{r} = R(r) \, \mathbf{e}_{\text{r}}(\theta, \phi). \]

or:

\[ -\frac{k^2}{2mr^2} \frac{d}{dr} (r^2 \frac{d}{dr} R) + \left[ V(r) + \frac{l(l+1)k^2}{2mr^2} \right] R = ER. \]

Do I understand this "potential"?

Centripetal Force \( F_c = \frac{mv^2}{r} \) but \( L^2 = (mv\mathbf{r})^2 \) so

\[ F_c = \frac{l^2}{mr^2} \]

But if you think this "force" is derivable from a potential then

since \( \mathbf{F} = -\nabla V \)

\[ \mathbf{F} = -\frac{1}{dr}(V(r)) = \frac{l^2}{mr^3} \quad \text{then} \quad V(r) = \frac{l^2}{2mr^2} \]

potential tries to keep particle away from origin

Now let \( g(r) = rR \)

\[ \frac{dg}{dr} = r \frac{dR}{dr} + R \]

\[ \frac{d^2g}{dr^2} = r \frac{d^2R}{dr^2} + 2 \frac{dR}{dr} - \frac{1}{r} \frac{d}{dr} (r^2 \frac{dR}{dr}) \]
\[
\frac{-k^2}{2m} (\frac{1}{r}) \frac{d^2 g}{dr^2} + \left[ V(r) + \frac{l(l+1)k^2}{2mr^2} \right] g = E \frac{g}{r}.
\]

\[
\frac{-k^2}{2m} \frac{d^2 g(r)}{dr^2} + \left[ V(r) + \frac{l(l+1)k^2}{2mr^2} \right] g = E g(r).
\]

which is exactly the 1D S.E. with an effective potential given by \( V(r) + \frac{l(l+1)k^2}{2mr^2} \).

Boundary Conditions on \( g(r) \):

\( g(r) \rightarrow 0 \) as \( r \rightarrow \infty \)

\( g(r) \rightarrow 0 \) as \( r \rightarrow 0 \). (looks like an infinite potential well at \( x = 0 \)).
Simple example.

V(r) = 0

\[-\frac{\hbar^2}{2m} \frac{\partial^2 g(r)}{\partial r^2} + \frac{l(l+1)\hbar^2}{2mr^2} g(r) = E g(r).\]

l = 0.

\[g'' = -\frac{2mE}{\hbar^2} g(r)\]

\[g = \begin{cases} \sin k & \text{when } k^2 = \frac{2mE}{\hbar^2} \\ \cos k & \text{constant} \end{cases}\]

Boundary Condition at r = 0 (i.e. \(g \to 0\)) forces you to choose \(\sin k\).

\[g = A \sin k \implies R(r) = \frac{A \sin k r}{r}\]

and

\[\Psi(r, \theta, \phi) = \frac{A \sin k \theta}{\sin \theta} Y^0_\ell(\theta, \phi)\]

The full time dependent solution becomes.

\[\Psi(r, \theta, \phi, t) = \frac{A \sin k \theta}{\sin \theta} Y^0_\ell e^{-iEt/\hbar}. \quad \omega = \frac{E}{\hbar}\]

\[= \frac{A}{2\pi r} Y^0_\ell \left[ e^{i(kr - \omega t)} - e^{-i(kr + \omega t)} \right]\]

spherical traveling wave moving outwards  
spherical traveling wave moving inwards
Analogous with 2D surface waves (circular) on water.

The upcoming wave passes through mano, and proceeds outwards. But because of the inversion through the origin it appears with the opposite phase! This produces the boundary condition at \( r = 0 \)

\[ g(r) \rightarrow 0 \]

The flux of particles is still given by the expression

\[ J = \frac{\varepsilon}{m} \text{Im} \left[ \frac{i}{r} \left( 4\pi \rho^2 + \frac{1}{r} \rho \hat{v} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \rho \sin \theta \hat{v} \right) \right) \right] \]

In this example \( \hat{v} \) is only a function of \( r \) and the current is only in the radial direction.

\[ J = \frac{\varepsilon}{m} \text{Im} \left\{ \frac{A \sin \kappa r}{r} \hat{x} e^{i \varepsilon \kappa r} \frac{\partial}{\partial r} \left[ \frac{A \sin \kappa r}{r} \hat{y} e^{-i \varepsilon \kappa r} \right] \right\} \]

\[ = 0 \text{ sence } \frac{\partial}{\partial r} \sin \kappa r = k \cos \kappa r \text{ and the entire term is real.} \]
This is not unreasonable since the wave function contains both incoming and outgoing waves.

The flux from the individual term will not be zero.

\[ \Psi_{\text{outgoing}} = \frac{A e^{i(kr - \omega t)}}{2\pi r} \chi_0 \]

\[ J_{\text{out}} = \frac{k}{m} \text{Im} \left[ \frac{A^* e^{-i(kr - \omega t)}}{2\pi r} \chi_0 \frac{\partial}{\partial r} \left( \frac{A e^{i(kr - \omega t)}}{2\pi r} \chi_0 \right) \right] \]

\[ = \frac{k \varepsilon k}{m} \frac{1}{4} \frac{1}{r^2} \chi^2_0 = \frac{k \varepsilon k}{16\pi m} \frac{1}{r^2} \]

As before, \( |A|^2 \) is chosen to set the total flux.

Note the \( 1/r^2 \) dependence. This ensures that the number of particles is conserved as the wave moves out.

In particular, the total flux through a sphere of radius \( r \) is just

\[ \int J_{\text{out}} \cdot d\mathbf{S} = \int dS \cdot \frac{1}{r^2} J_{\text{out}} \cdot \hat{n} \]

\[ = \int dS \cdot \frac{k \varepsilon k}{m} \frac{1}{16\pi} \frac{1}{r^2} \]

\[ \text{Total Count} = \frac{k \varepsilon k}{m} \frac{1}{4}, \text{ independent of the size of the sphere.} \]
For \( l \neq 0 \) the equation is a bit more difficult to solve.

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

Letting \( V(r) = 0 \).

\[-\frac{\hbar^2}{2m} \frac{\partial^2 g}{\partial r^2} + \frac{k^2(\ell + 1)}{2mr^2} g(r) = E g(r)\]

Letting \( k^2 = \frac{2mE}{\hbar^2} \)

\[-\frac{\hbar^2}{2m} \frac{\partial^2 g}{\partial r^2} = \left[ -k^2 + \frac{\ell(\ell + 1)}{k^2} \right] g(r) \quad \text{let } x = kr.\]

\[-\frac{\hbar^2}{2m} \frac{\partial^2 g}{\partial x^2} = \left[ -1 + \frac{\ell(\ell + 1)}{x^2} \right] g(x) \quad \text{or}\]

\[-\frac{\partial^2 g}{\partial x^2} + \frac{\ell(\ell + 1)}{x^2} g(x) = g_e(x) \]

where \( g_e(x) \) is the solution for a specific value of \( \ell \).

\[(\frac{\partial}{\partial x} - \frac{1}{x} \frac{\partial}{\partial x})(\frac{\partial}{\partial x} + \frac{1}{x} \frac{\partial}{\partial x}) g_e(x) = g_e(x)\]

Rewriting \( \circ \) for \( \ell \to \ell - 1 \) solution then

\[-\frac{\partial^2 g_{\ell-1}}{\partial x^2} + \frac{(\ell-1)(\ell)}{x^2} g_{\ell-1}(x) = g_{\ell-1}(x) \quad \text{or}\]

\[(\frac{\partial}{\partial x} + \frac{1}{x} \frac{\partial}{\partial x})(\frac{\partial}{\partial x} - \frac{1}{x} \frac{\partial}{\partial x}) g_{\ell-1}(x) = g_{\ell-1}(x)\]
Taking \( \frac{\partial}{\partial x} \) on both sides
\[
(\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) (\frac{\partial}{\partial x} + \frac{\partial}{\partial x}) (\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) g_{e-1}(x) = (\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) g_{e-1}(x)
\]
\[
(\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) (\frac{\partial}{\partial x} + \frac{\partial}{\partial x}) \left[ (\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) g_{e-1}(x) \right] = \left[ (\frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2}) g_{e-1}(x) \right]
\]

But this implies:
\[ g_{e}(x) = \left( \frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2} \right) g_{e-1}(x) \]

So for \( e=0 \)
\[
\frac{\partial^2 g_0}{\partial x^2} = -g_0(x) \quad \left\{ \begin{array}{l}
  g_0^{(1)} = \sin x \\
  g_0^{(2)} = \cos x
\end{array} \right.
\]

Then
\[
g_1(x) = \left( \frac{\partial}{\partial x} - \frac{\partial^2}{\partial x^2} \right) g_0^{(1)}(x)
\]
\[
g_1^{(1)}(x) = \left( \frac{\sin x}{x} - \cos x \right)
\]
\[
g_1^{(2)}(x) = \left( \frac{\cos x}{x} + \sin x \right)
\]

True solution are \( R(r) = \frac{g(r)}{r} = g(x)/x \)

\[
\begin{align*}
  g_0(x) &= \frac{\sin x}{x} & \eta_0(x) &= -\frac{\cos x}{x} \\
  g_1(x) &= \frac{\sin x}{x^2} - \frac{\cos x}{x} & \eta_1(x) &= -\left[ \frac{\cos x}{x^2} + \frac{\sin x}{x} \right]
\end{align*}
\]

Regular at \( x=0 \) \quad Singula at \( x=0 \).
Second Example. (Finite spherical potential well).

\[ V(r) = -|V_0| \quad \text{for} \quad 0 \leq r < a \]
\[ V(r) = 0 \quad \text{for} \quad r > a \]

Solution of the form \( \Psi(r, \theta, \phi) = R(r) Y_l(m) \) when

\[
-\frac{k^2}{2m} \frac{d^2g_0(r)}{dr^2} + \left[ \frac{l(l+1)k^2}{2m} + V(r) \right] g_0(r) = E \ g_0(r)
\]

For \( l=0 \), the effective potential becomes simply \( V(r) \).

\[ \begin{array}{c}
\text{Region } 0 \\
-\frac{k^2}{2m} \frac{d^2g_0(r)}{dr^2} + -|V_0| g_0(r) = E \ g_0(r)
\end{array} \]

or

\[
\frac{d^2g_0(r)}{dr^2} = -\frac{2m}{k^2} \left( |V_0| + E \right) g_0(r)
\]

Two Cases \( E > 0 \); \( E < 0 \)

Unbound \quad Bound.

Unbound: \( E = |E| \) then solutions are of the form.

\[ g_0^e(r) = A \sin k_1 r \quad \text{where} \quad \frac{k_1^2}{2m} = |V_0| + |E| \]

Bound: \( E = -|E| \) then solutions have the form.

\[ g_0^e(r) = A \sin k_1 r \quad \text{where} \quad \frac{k_1^2}{2m} = |V_0| - |E| > 0 \]
Region II
\[-\frac{k^2}{2m} \frac{d^2 g_0^+(r)}{dr^2} = E g_0^+(r)\]

If \( E = |E| \) then
\[ g_0^+(r) = C \sin kr + D \cos kr \quad \text{for } \frac{k^2}{2m} = |E| \]

and
\[ E = -|E| \quad \text{then} \]
\[ g_0^+(r) = C e^{-kr} \quad \text{for } \frac{k^2}{2m} = |E| \]

The growing exponential is not allowed in order for \( U \) to be finite at \( \infty \).

To find relation between \( A, C, D \) require \( g(r) \) to be continuous and \( \frac{dg(r)}{dr} \) to be continuous.

unBound Solutions: \( E > 0 \)

1. \( A \sin k \alpha = C \sin k \alpha + D \cos k \alpha \)
2. \( A k \cos k \alpha = C k \cos k \alpha - D k \sin k \alpha \)

These two equations (+ normalization / flux determination) determine \( A, C \) and \( D \) with no constraint on \( |E| \). All possible \( |E| \) values are allow for \( E > 0 \).
Boundary solution: $E(x)$

1. $g(r)$ cont. $A \sin k_a a = c e^{-k_a a}$

2. $\frac{dg}{dr}$ cont. $A k_c \cos k_a = -k e^{-k_a a}$

$$\tan k_a a = -\frac{1}{k}$$

$$\tan k_a a = -\frac{k_i}{k}$$

$$\tan \left[ \frac{2ma^2}{k^2} \left[ \frac{IVo - IEI}{IEI} \right] \right]^{1/2} - \left[ \frac{IVo - IEI}{IEI} \right]^{1/2}$$

$$\tan \left[ \frac{2ma^2 IVo - IEI}{k^2} \left( 1 - \frac{IEI}{IVo} \right) \right]^{1/2} - \left[ \frac{1 - IEI/IVo}{IEI/IVo} \right]^{1/2}$$

Computer graph $a = \frac{2ma^2 IVo}{k^2}$

"no solution"

"one solution"
Form of solution

\[ g(r) = e^{-kr} \]

\[ R = \frac{g(r)}{r} \]

large "probability" of finding particle near origin.

What about higher \( l \)'s.

\[ \frac{(l+1)^2}{2\hbar^2} \]

effective potential

If \( l \) becomes too large.

No bound state possible in Q.M. problem!!
Coulomb Potential \( V(r) = -\frac{a}{r} \)

Thus for \( E < 0 \) one would expect solutions even for very large \( \ell \).
- What if we do not have a fixed center, but in fact two particles?

\[ V(r_1, r_2) \]

\[ H = -\frac{k^2}{2m_1} \nabla_1^2 - \frac{k^2}{2m_2} \nabla_2^2 + V(r_1, r_2) \]

Total kinetic energy

Usually \( V(r_1, r_2) \) depends only on the difference between \( r_1 \) and \( r_2 \) i.e. \( |r_2 - r_1| \). In such cases it is better to transform to the center of mass coordinates:

\[ \mathbf{r} = r_2 - r_1 \]

and

\[ R = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \]

Converting \( \nabla_1^2 \) to new coordinates we note that

\[ \frac{d}{dx_1} = \frac{dR_x}{dx_1} \frac{d}{dR_x} + \frac{dR_y}{dx_1} \frac{d}{dR_y} + \frac{dR_z}{dx_1} \frac{d}{dR_z} \]

\[ \frac{d}{dy_1} = \frac{dR_x}{dy_1} \frac{d}{dR_x} + \frac{dR_y}{dy_1} \frac{d}{dR_y} + \frac{dR_z}{dy_1} \frac{d}{dR_z} \]

\[ \frac{d}{dz_1} = \frac{dR_x}{dz_1} \frac{d}{dR_x} + \frac{dR_y}{dz_1} \frac{d}{dR_y} + \frac{dR_z}{dz_1} \frac{d}{dR_z} \]

or

\( \nabla_1 = \frac{m_1}{m_1 + m_2} \nabla_R - \nabla_r \)

Similarly

\( \nabla_2 = \frac{m_2}{m_1 + m_2} \nabla_R + \nabla_r \)
\[ \nabla_1^2 = \left( \frac{m_1}{m_1+m_2} \right) \nabla_R^2 + \nabla_R^2 - \frac{2m_1}{m_1+m_2} \nabla_R \cdot \nabla_R \]
\[ \nabla_2^2 = \left( \frac{m_2}{m_1+m_2} \right) \nabla_R^2 + \nabla_R^2 + \frac{2m_2}{m_1+m_2} \nabla_R \cdot \nabla_R \]

so that
\[ -\frac{k^2}{2m_1} \nabla_1^2 - \frac{k^2}{2m_2} \nabla_2^2 = -\frac{k^2}{2} \left[ \frac{m_1}{(m_1+m_2)^2} + \frac{m_2}{(m_1+m_2)^2} \right] \nabla_R^2 \\
+ \frac{k^2}{2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_R^2 \\
= -\frac{k^2}{2M} \nabla_R^2 - \frac{k^2}{2M} \nabla_R^2 \]

where \( M = (m_1+m_2) \) Total Mass
\( \mu = \frac{m_1 m_2}{m_1+m_2} \) Reduced Mass.

Then,
\[ H = -\frac{k^2}{2M} \nabla_R^2 - \frac{k^2}{2\mu} \nabla_R^2 + V(r) = H_{CM} + H_{REL} \]
\[ H_{CM} = -\frac{k^2}{2M} \nabla_R^2 \text{ Motion of "free" particle.} \]
\[ H_{REL} = \frac{k^2}{2\mu} \nabla_R^2 + V(r) \text{ Standard "fixed" potential at origin.} \]

Since \([H_{CM}, H_{REL}] = 0\)
\[ \psi_{TOTAL} = \psi_{CM}(\mathbf{r}) \psi_{REL}(\mathbf{\mathbf{r}}) \quad E_{TOTAL} = E_{CM} + E_{REL} \]
\[ \psi_{CM}(\mathbf{r}) = A e^{i \mathbf{K} \cdot \mathbf{r}} \quad \frac{k^2 \mathbf{K}^2}{2m} = E_{CM}. \]
Hydrogen Atom

\[ V(r) = \frac{-2e^2}{\pi \epsilon_0 r} \]

\[ p^2 = p_{\text{proton}}^2 - p_{\text{electron}}^2 \]

\[ H_{\text{eff}} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \]

\[ \mu = \frac{m_e m_p}{m_p + m_e} = m_e. \]

\[ \psi_{\text{rel}} = \frac{g(r)}{r} Y_l^m (\theta, \phi). \]

\[ \psi_{\text{rel}} = \frac{g(r)}{r} Y_l^m (\theta, \phi). \]

\[ \frac{-\hbar^2}{2m} \frac{d^2 g}{dr^2} + \left( \frac{-2e^2}{\pi \epsilon_0 r} + \frac{l(l+1)k^2}{2m r^2} \right) g(r) = E g. \]

1. Small \( r \):

\[ \frac{d^2 g}{dr^2} \sim \frac{2m}{\hbar^2} \left[ \frac{l(l+1)k^2}{2m r^2} \right] g(r) = \frac{l(l+1)}{r^2} g(r) \]

\[ g(r) \sim r^{l+1} \] then \( g' \sim (l+1) r^l \) and \( g'' \sim l(l+1) r^{l-2} \)

\[ g(r) \sim \frac{l(l+1)}{r^2} g(r) \]

2. Large \( r \):

\[ \frac{d^2 g}{dr^2} \sim -\frac{2mE}{\hbar^2} g(r) = \frac{2m|E|}{\hbar^2} g(r) \]

\[ g \sim e^{-\lambda r} \] where \( \lambda^2 = \frac{2m|E|}{\hbar^2}. \]
Variable subst.

\[ \rho = 2 \lambda r \quad \frac{\partial \rho}{\partial r} = \frac{1}{\rho} \frac{\partial \rho}{\partial \lambda} = 2 \lambda \frac{1}{\rho} \]

and

\[ 4 \lambda^2 \frac{d^2 g}{d \rho^2} = \frac{2m}{\rho^2} \left[ -\frac{2e^2}{4\pi \epsilon_0} \left( \frac{2\lambda}{\rho} \right) + \frac{k(l+1)k^2}{2m} \left( \frac{4\lambda^2}{\rho^2} \right) - E \right] g(\rho) \]

or

\[ \frac{d^2 g}{d \rho^2} = \left[ \frac{k(l+1)}{\rho^2} + \frac{1}{4} - \frac{s}{\rho} \right] g(\rho) \]

where

\[ S = \frac{2e^2}{4\pi \epsilon_0} \left( \frac{2m}{k^2} \right) \frac{1}{2\lambda} \]

For large \( \rho \):

\[ g(\rho) \sim e^{-\frac{1}{2} \rho} \]

Try a solution of the form

\[ g(\rho) \sim \rho^{l+1} e^{-\frac{1}{2} \rho} W(\rho) \]

Substituting:

\[ \rho W'(\rho) + \frac{dW}{d\rho} \left[ 2(l+1) - \rho \right] + \omega \rho \left[ S - (l+1) \right] = 0 \]

Try:

\[ W(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \]

\[ \sum_{k} \left[ a_k k(k-1)\rho^{k-1} + 2a_k k(l+1)\rho^{k-1} - a_k k\rho^k + a_k \rho^k (S-(l+1)) \right] = 0 \]

Equating all coefficients of \( \rho^n \) to zero:

\[ \left\{ \frac{a_{n+1} (n+1)n + (n+1)(l+1)}{a_n \left[ S - (l+1) - n \right]} \right\} = 0 \]

\[ a_{n+1} = \frac{-a_n \left[ S - (l+1) - n \right]}{(n+1)(l+1+n)} \]
For large $n$ then $a_{n+1} \approx \frac{a_n}{n+1}$. Therefore for $n > N$ (large)
we have $a_n \approx \frac{A_nN!}{n!}$.

Since $e^p \approx 1 + p + \frac{p^2}{2!} + \frac{p^3}{3!} + \cdots + \frac{p^n}{n!}$

This will eventually dominate the $e^{-kp}$ term in our original choice for $\psi$.

As before we must choose $S$ so that the series truncates.

By choose $S$ to be an integer we find that eventually $S = n + 1$ and $a_{n+1}$ and all subsequent $a$'s will be zero.

From the definition of $S = \frac{2e^2}{\pi \hbar c} \left(\frac{2m}{\hbar^2}\right) \frac{1}{2\lambda} = \frac{2e^2}{\pi \hbar c} \left(\frac{2m}{\hbar^2}\right) \left(\frac{t}{2m\hbar}\right)$
we have a condition on $|E|$:

$$|E| = \frac{\frac{2e^2}{\pi \hbar c} \left(\frac{m}{\hbar^2}\right) \frac{1}{S^2}}{S \text{ integer}}$$

$$= \frac{1}{2} \frac{Z^2 e^4}{(4\pi \epsilon_0)^2 k^2} \frac{1}{S^2} \approx \frac{1}{2} m \frac{v^2}{E} \text{ Energy}.$$ 

So $\frac{e^2}{(4\pi \epsilon_0) k}$ should have units of velocity. "v".

Taking the ratio of $\sqrt{\frac{v}{c}}$ with $c$ we have:

$$\sqrt{\frac{v}{c}} = \frac{e^2}{(4\pi \epsilon_0) k c} \approx 0.00729 = \frac{1}{137.036} \approx \text{ Fine Structure Constant}$$
\[ |E| = \frac{Z^2}{2} \frac{1}{m} \frac{e^2}{s^2} - \frac{Z^2}{2} \frac{1}{m} \frac{c^2}{s^2} \]

But \( \eta c^2 \approx 0.511 \text{ MeV} \) so.

\[ |E| = \frac{1}{S^2} \frac{Z^2}{2} \left( \frac{1}{137} \right)^2 \left( 0.511 \text{ MeV} \right) = (13.6 \text{ ev}) \frac{Z^2}{2} \left( \frac{1}{S^2} \right). \]

\[ \rho = 2 \lambda \Gamma = 2 \left( \frac{2m|E|}{k^2} \right)^{1/2} \Gamma = 2 \left( \frac{m^2 e^2}{4 \pi \varepsilon_0 k^2 c^2} \right)^{1/2} \]

\[ = \frac{2Z}{S} \left( \frac{\Gamma}{\lambda_0} \right) : \lambda_0 = \frac{4 \pi \varepsilon_0 k^2}{e^2 m} = \frac{4 \pi \varepsilon_0 k c}{e^2} \frac{k c}{\eta c^2} \]

\[ \lambda_0 = (0.386 \times 10^{-12} \text{ m})(137.03) = 0.52 \text{ Å} \]

\[ \rho = \left( \frac{2Z}{S} \right) \left( \frac{\Gamma}{\lambda_0} \right) \]

From the Virial Theorem:

\[ \left\langle r \frac{\partial V}{\partial r} \right\rangle = 2 \left\langle T \right\rangle \]

\[ \Rightarrow r \frac{\partial V}{\partial r} \approx r \frac{\partial}{\partial r} \left( -\frac{2e^2}{4 \pi \varepsilon_0 r} \right) = -\sqrt{r} \]

so

\[ \left\langle T \right\rangle = -\frac{1}{2} \left\langle V \right\rangle \quad \text{but} \quad \left\langle T \right\rangle + \left\langle V \right\rangle = \left\langle E \right\rangle \]

\[ \left\langle E \right\rangle = \frac{1}{2} \left\langle V \right\rangle = -\frac{1}{2} \frac{Z^2}{2} \frac{1}{m} \frac{c^2}{s^2} \]

\[ \left\langle V \right\rangle = -\frac{Z e^2}{4 \pi \varepsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Z}{m} \frac{c^2}{s^2} \frac{1}{s^2} \]

or

\[ \left\langle \frac{1}{r} \right\rangle = \frac{Z}{S^2} \left( \frac{4 \pi \varepsilon_0}{e^2} \right) \frac{m c^2}{\lambda_0^2} \]

\[ \left\langle \frac{1}{r} \right\rangle = \left( \frac{Z}{S^2} \right)^{1/2} \lambda_0 \]
\[ \langle T \rangle = \langle \frac{p^2}{2m} \rangle = -\frac{1}{2} \langle V \rangle = -\langle E \rangle = \frac{Z}{2} \frac{1}{2} mc^2 \alpha^2 \]

\[ \langle V^2 \rangle = \langle \frac{p^2}{m} \rangle = \left( \frac{Z}{S^2} \right) \alpha^2 c^2 \]

\[ V_{\text{rms}} \sim \left( \frac{Z}{S} \alpha c \right) \quad \text{For} \quad Z \quad \text{large} \quad \text{small} \quad \text{speed of light.} \]

---

Form of wavefunction:

\[ S = n + (l+1) \quad \text{integer.} \quad \rightarrow \quad l + 1 \leq S \quad \text{or} \quad l + 1 \leq S - 1. \]

\[ g(p) = \left( \sum_{k=0}^{S-(l+1)} \alpha_k \beta^k \right) \beta^{l+1} e^{-\frac{1}{2} \rho} \]

\[ R(r) = g(r) \tau = \sum_{k=0}^{S-(l+1)} \alpha_k \left( \frac{Z}{S} \right)^{k+l} \left( \%_0 \right)^{k+l} e^{-\frac{Z^2}{S} \left( \%_0 \right)} \]

\[ R_s, l = A \left( c_0 + c_1 \left( \%_0 \right) \ldots \right) \left( \%_0 \right)^l e^{-\frac{Z^2}{S} \left( \%_0 \right)} \]

**Extreme Cases:**

\[ R_s, s-1 \sim \left( \%_0 \right)^l e^{-\frac{Z^2}{S} \left( \%_0 \right)} \]

\[ R_s, 0 \sim \left( c_0 + c_1 \left( \%_0 \right) \ldots \right) \left( \%_0 \right)^{s-1} e^{-\frac{Z^2}{S} \left( \%_0 \right)} \]
\[ \psi_{s l m}(r, \theta, \phi) = R_{s l} Y_{l}^{m} \]

\[ E = -\frac{13.6 \text{ eV} \frac{Z^2}{s^2}}{2} \quad l \leq s-1 \]

Energy does not depend on \( l \) or \( m \). 

**Multiple degeneracy.**

\( s=1 \)

\[ l=0, \quad \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{2r}{a_0} \right)^{3/2} e^{-2r/a_0} \]

\[ \text{Graph} \]

\( s=2 \)

\[ l=0,1, \quad \psi_{200} = \frac{1}{2\sqrt{2\pi}} \left( \frac{2r}{a_0} \right)^{3/2} \left( 1 - \frac{2r}{2a_0} \right) e^{-2r/2a_0} \]

\[ \text{Graph} \]

\[ \psi_{210} = \frac{1}{2\sqrt{2\pi}} \left( \frac{2r}{a_0} \right)^{3/2} \frac{2r}{2a_0} e^{-2r/2a} \cos \phi \]

\[ \psi_{211} = \frac{1}{\sqrt{\pi}} \left( \frac{2r}{a_0} \right)^{3/2} \frac{2r}{2a_0} e^{-2r/2a_0} \sin \phi \exp(i\phi) \]

\[ \text{Graph} \]

1. Large \( l \) states have smaller prob. density near origin \( R_{s, s-1} \sim (\frac{r}{a_0})^l \) near \( r=0 \)

2. \( l=0 \) states have higher prob. density near origin \( R_{s0} \sim e^{-\frac{2r}{a_0}} \)

3. Larger \( s \) states have extended wavefunction
Accidental Degeneracy of different $l$ states for the same value of $s$, due to another conserved quantity, Runge-Lenz Vector $M = p \times \ell - \frac{Ze^2}{\mu r^3}$. 

Lyman Series (Sharp)

Baloer Series (Principle)

Paschen Series (Diffuse)

Normalization 

$$\langle \psi_{sem} | \psi_{sem} \rangle$$

$$\langle R_{se} | R_{se} \rangle \quad \langle Y_{m}^{m} | Y_{m}^{m} \rangle$$

Some $\psi_{sem}$ and $\psi'_{s'e'm'}$ have different energy eigenvalues $E_s$ and $E_{s'}$, we have:

$$\langle s_{l} m | s'_{l'} m' \rangle = \delta_{ss'}$$

$$\langle s_{l} | s'_{l'} \rangle \langle l_{m} | l'_{m'} \rangle = \delta_{ss'}$$

Therefore $\langle s_{l} | s'_{l'} \rangle = \delta_{ss'}$ only when $l = l'$ and $m = m'$
Hydrogenic System:

1. Ionized Helium \( Z = 2 \):
\[
\mu = \frac{m_e m_n}{m_e + m_n}
\]
\[
E_n = -\frac{Z^2 (13.6 \text{ eV})}{n^2} = -\frac{54.4 \text{ eV}}{n^2}
\]

Characteristic length scale \( n a_0/2 \rightarrow n a_0/2 \).

Otherwise it is exactly a hydrogenic spectrum.

2. Lithium \( Z = 3 \):
\[
\mu = \frac{m_e m_n}{m_e + m_n}
\]

If last electron is in a highly excited state (large \( n \)) with angular momentum \( l \neq 0 \) then since it will have a small probability of being in the region of the nucleus it will see an apparent charge of only +1.

The spectrum will be exactly that of \( Z = 1 \) hydrogen. For smaller values of \( l \) the electron will spend more a more time near the nucleus and should see the true charge of the nucleus.

\[
l = 0 \quad l = 1 \quad l = 2 \quad l = 3
\]

---

... ---- --- --- degenerate for hydrogenic.

---

Lends an displaced by the amount electron spends within electron cloud of other 2 electrons.
3. Muonium: Replace an electron with a muon \( m_{\mu} = 206 m_e \)

\[
\mu = \frac{m_{\mu} m_p}{m_{\mu} + m_p}
\]

and

\[
\alpha_0 = \frac{\sqrt{\hbar e k^2}}{\mu e^2} \implies a_{\mu} = \frac{\alpha_0}{206} = 2.5 \times 10^{-13} \text{ m.}
\]

Effective radius of orbit means that muon will be much closer to nucleus than an electron. In fact for heavy nuclei, the muon will spend some time within the nucleus. By measuring the lifetime of these muonic atoms one can estimate the size of the nucleus.

4. Positronium: \( Z = 1 \) but instead of a proton we use a positron with \( m = m_e \) so that.

\[
\mu = \frac{m_e m_e}{m_e + m_e} = \frac{1}{2} m_e
\]

Effective radius of orbit is now twice that of hydrogen \( = 1 \text{ Å} \).
Other applications.

- Muonium / Positronium

Reduced mass \( \mu = \frac{m_1 m_2}{m_1 + m_2} \)

\( a_0 = \frac{4 \pi e^2}{\mu} \)

\( a_{\mu} = \frac{200}{m_1} \) for Muonium (larger mass \( m_1 = 200 \text{Me} \))

\( a_{\text{pos} + \text{tronium}} = \frac{1}{2} m_e \) for Positronium (smaller mass \( \mu_{\text{pos} + \text{tronium}} = \frac{1}{2} m_e \))

- Stripped ion \( ^3\text{Li}^+ \) and one electron. Only change is \( Z = 3 \) and reduced mass \( \mu \).

- Also possible to use these wavefunctions for \( \text{Li} \) atom if last electron does not probe true nuclear charge, i.e., it has a large value of \( s \) or \( \ell \), so that \( R_{2 \ell}^2 \) is small in the region of the two outer electrons.
Intrinsic Angular Momentum.

Spin

Integer.
"Bosons"
photons, pions, gluons,
W's, Z's, gravity
"mediators of forces"
S = 0, 1, 2, 3 ....

Half-Integer.
"Fermions"
electrons, neutrinos, quarks,
neutrinos.
"matter particles"
S = 1/2, 3/2, 5/2 ....

How do we know an electron has spin?

\[
\mu = (\text{Area}) I \\
\]

For any electron we do not know the charge distribution, so you might expect

\[
\mu = -\frac{g e}{m} S \\
\]

where the g-factor takes into account the internal structure of the electron.

As the electron orbits a proton in hydrogen, it sees a magnetic field associated with the orbiting proton. The interaction between this magnetic field and the magnetic moments of the electron causes shifts in the energy level of the electron, which can be measured spectroscopically.
Properties of Spin Angular Momentum.

Since our original derivation of the angular momentum operators did not depend on the angular momentum being an integer, all the operator properties are the same:

\[ S = S_x \hat{i} + S_y \hat{j} + S_z \hat{k} \quad S^2 = S_x^2 + S_y^2 + S_z^2 \quad [S^2, S_i] = 0 \]
\[ [S_i, S_j] = i \epsilon_{ijk} S_k \quad S \times S = i \hbar S \]

\[ S_+ = S_x + i S_y \quad S_+ S_- = S^2 - S_z^2 + \hbar S_z \quad [S_+, S_-] = 2 \hbar S_z \]
\[ S_- = S_x - i S_y \quad S_- S_+ = S^2 - S_z^2 - \hbar S_z \quad [S_-, S_z] = -\hbar S_+ \]

Eigenstates of \( S^2 \) and \( S_z \) have eigenvalues \( s(s+1)\hbar^2 \) and \( m \hbar \), with \( m = -s, -s+1, \ldots, s-1, s \). (or \( 2s+1 \) values).

Consider the simplest eigenstates of \( S^2 \) and \( S_z \) for \( s = \frac{1}{2} \). There are only two eigenstates with \( m = \frac{1}{2} \) and \( -\frac{1}{2} \). Call them respectively \( |\uparrow\rangle \) and \( |\downarrow\rangle \)

\[ S_z |\uparrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \quad \text{or} \quad S_z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle \]

\[ S^2 |\uparrow\rangle = \frac{3}{4} \hbar^2 |\uparrow\rangle \]

\[ S_+ |\uparrow\rangle = 0 \]
\[ S_- |\uparrow\rangle = \frac{\hbar}{2} \sqrt{(s+m)(s-m+1)} |\downarrow\rangle = t |\downarrow\rangle \]
\[ S_+ |\downarrow\rangle = \hbar \sqrt{s+1} |\uparrow\rangle \]
\[ S_- |\downarrow\rangle = 0 \]
Matrix elements of $S_2$.

\[
\langle \frac{1}{2} m_s | S_2 | \frac{1}{2} m_s' \rangle = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}.
\]

Similarly

\[
(S_+ = \frac{1}{2} (S_+ + S_-) \Rightarrow \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix},

S_y = \frac{1}{2} (S_+ - S_-) \Rightarrow \begin{pmatrix} 0 & i \frac{1}{2} \\ -i \frac{1}{2} & 0 \end{pmatrix},
\]

\[
(S^2)_{m_s m_s'} = \frac{3}{4} k^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

What is the total angular momentum of the electron in orbit about the proton in hydrogen?

Define $J = L + S$ to be the total angular momentum operator.

$L$ and $S$ commute since they operate on different spaces. $[L, S] = 0$

Thus I can find eigenfunctions of which are simultaneous eigenfunctions of $L$ and $S$.

\[
|l\phi \rangle = |l m_s \rangle |s m_s \rangle \quad \text{or} \quad \chi^m_s(\theta, \phi) \chi^m_s
\]

where

\[
L_z |l\phi \rangle = m_s |l\phi \rangle \quad \text{and} \quad L^2 |l\phi \rangle = \ell(\ell+1)\hbar^2 |l\phi \rangle
\]

and

\[
S_z |l\phi \rangle = m_s |l\phi \rangle \quad \text{and} \quad S^2 |l\phi \rangle = s(s+1)\hbar^2 |l\phi \rangle
\]
But is this an eigenfunction of $J^2 = L^2 + S^2$?

\[
J_2 1^4 > = (L_2 + S_2) 1^4 > = (L_2 + S_2) |l m_e > |s m_s >
\]
\[
J_2 1^4 > = (m_2 k + m_3 k) |l m_e > |s m_s > = (m_e + m_s) k 1^4 >
\]

YES!

But what about $J^2$? / do not need to worry about order $[L, S] = 0$

\[
J^2 = (L + S)^2 = L^2 + S^2 + 2 L \cdot S
\]
\[
= L^2 + S^2 + 2 L_2 S_2 + 2 L_x S_x + 2 L_y S_y
\]
\[
J^2 = L^2 + S^2 + 2 L_2 S_2 + L_+ S_+ + L_- S_-
\]

In general $1^4 >$ will not be an eigenfunction of $J^2$ because of the $L \pm S \mp$ terms!

Examples:

\[\ell = 0 \quad s = \frac{1}{2}\]

\[
J_2 |0, 0 > |\frac{1}{2} \pm \frac{1}{2} > = \pm \frac{1}{2} \hbar |0, 0 > |\frac{1}{2} \pm \frac{1}{2} >
\]
\[
J^2 |0, 0 > |\frac{1}{2} \pm \frac{1}{2} > = (L^2 + S^2 + 2 L_2 S_2 + L_+ S_+ + L_- S_-) |0, 0 > |\frac{1}{2} \pm \frac{1}{2} >
\]
\[
= (0 \quad 0 \quad 0 \quad 0 \quad 0) |0, 0 > |\frac{1}{2} \pm \frac{1}{2} >
\]
\[
J^2 |0, 0 > |\frac{1}{2} \pm \frac{1}{2} > = \frac{3}{4} \hbar^2 |0, 0 > |\frac{1}{2} \pm \frac{1}{2} >
\]

this is an eigenfunction of $J^2$ with eigenvalue $\frac{3}{4} \hbar^2$. 
\( l = 1 \) so \( 1/2 \). Since \( m_e = 1, 0, -1 \) and \( m_s = \pm 1/2 \) there are 6 distinct states of the form \( |1, m_e, m_s > \).

Each is an eigenfunction of \( J_z \) with eigenvalue \( m_e + m_s \).

\[
\begin{array}{ccc}
  m_e & m_s & m_j \\
  1 & \pm 1/2 & \pm 1, 1/2 \\
  0 & \pm 1/2 & \pm 1, -1/2 \\
 -1 & \pm 1/2 & \pm -1/2, 3/2 \\
\end{array}
\]

So it looks like \( j = 3/2 \) (has \( 2^{j+1} = 8 \) states) and \( j = 1/2 \) (which has \( 2^{j+1} = 4 \) states) for a total of 6 states.

But

\[
J_z^2 |11 > |\frac{1}{2}, -\frac{1}{2} > = (L^2 + S^2 + 2LzS_z + L+S_+ + L-S_+) |11 > |\frac{1}{2}, -\frac{1}{2} > = (1(1+1)k^2 + \frac{1}{2}(\frac{3}{2}+1)k^2 + 2(1k)(-\frac{1}{2}k)) |11 > |\frac{1}{2}, -\frac{1}{2} > + 0 + (\sqrt{2}k)(k) |10 > |\frac{1}{2}, \frac{1}{2} >
\]

and so \( |11 > |\frac{1}{2}, -\frac{1}{2} > \) is not an eigenstate of \( J_z^2 \). How about

\[
J_z^2 |11 > |\frac{1}{2}, \frac{1}{2} > = (L^2 + S^2 + 2LzS_z + L+S_+ + L-S_+) |11 > |\frac{1}{2}, \frac{1}{2} > = (1(1+1)k^2 + \frac{1}{2}(\frac{3}{2}+1)k^2 + 2(1k)(\frac{1}{2}k) + 0 + 0) |11 > |\frac{1}{2}, \frac{1}{2} >
\]

\textbf{YES!}

\[
J_z^2 |11 > |\frac{1}{2}, \frac{1}{2} > = \left( \frac{15}{4} \right) k^2 |11 > |\frac{1}{2}, \frac{1}{2} >
\]

or

\[
(\frac{3}{2})(\frac{3}{2}+1)k^2 |11 > |\frac{1}{2}, \frac{1}{2} >
\]

or \( j = \frac{3}{2} \) and \( m_j = \frac{3}{2} \).

\( |j = \frac{3}{2}, m_j = \frac{3}{2} > = |11 > |\frac{1}{2}, \frac{1}{2} > \)
We should be able to get the $j = \frac{3}{2}, m_j = \frac{1}{2}$ by using $J_-$ on $| j = \frac{3}{2}, \frac{3}{2} \rangle$

$$J_- | j = \frac{3}{2}, \frac{3}{2} \rangle = (L_- + S_-) | 11 \rangle | \frac{3}{2}, \frac{1}{2} \rangle$$

$$= \sqrt{2} (\sqrt{2} \right| 10 \rangle | \frac{3}{2}, \rac{1}{2} \rangle + \sqrt{1} | 11 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle$$

$$= \frac{1}{\sqrt{2}} \left\{ \sqrt{2} | 10 \rangle | \frac{3}{2}, \frac{1}{2} \rangle + \sqrt{1} | 11 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle \right\}$$

Normalising

$$\left[ \sqrt{2} | 10 \rangle | \frac{3}{2}, \frac{1}{2} \rangle + \sqrt{1} | 11 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle \right]$$

This state has $m_j = \frac{1}{2}$ as advertised but is it an eigenstate of $J^2$?

One could try calculating $J^2$ on this state but it is messy, so note that $[J^2, J_x] = [J^2, J_y] = 0$ so that $[J^2, J_z] = 0$.

Then $J^2 (J_- | j = \frac{3}{2}, \frac{3}{2} \rangle) = J_- (J^2 | j = \frac{3}{2}, \frac{3}{2} \rangle)$

$$= \frac{3}{2} (\frac{3}{2} + 1) \frac{1}{2} J_- | j = \frac{3}{2}, \frac{3}{2} \rangle$$

so $J_- | j = \frac{3}{2}, \frac{3}{2} \rangle$ is an eigenstate of $J^2$ with eigenvalue $j = \frac{3}{2}$. Thus,

$$| j = \frac{3}{2}, \frac{1}{2} \rangle = \sqrt{\frac{2}{3}} | 10 \rangle | \frac{3}{2}, \frac{1}{2} \rangle + \sqrt{\frac{1}{3}} | 11 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle$$

Using $J_-$ again we get

$$J_- | j = \frac{3}{2}, \frac{1}{2} \rangle = (L_- + S_-) \left( [\sqrt{2} | 10 \rangle | \frac{3}{2}, \frac{1}{2} \rangle + \sqrt{\frac{1}{3}} | 11 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle \right)$$

$$= \sqrt{\frac{2}{3}} \sqrt{12} | -1 \rangle | \frac{3}{2}, \frac{1}{2} \rangle + \sqrt{\frac{1}{3}} \sqrt{12} | 10 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle$$

$$+ \sqrt{\frac{2}{3}} \sqrt{12} | 10 \rangle | \frac{3}{2}, -\frac{1}{2} \rangle + 0$$
\[ J - |\frac{3}{2}, \frac{1}{2}\rangle = k \left[ \frac{2}{\sqrt{3}} |1-1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + 2\sqrt{\frac{2}{3}} |10\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \right] \]

Normalizing we get:
\[ |\frac{3}{2}, -\frac{1}{2}\rangle = \left[ \frac{1}{\sqrt{3}} |1-1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |10\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \right] \]

And lastly,
\[ J - |\frac{3}{2}, -\frac{1}{2}\rangle = (L^z + S^z) \left[ \frac{1}{\sqrt{3}} |1-1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |10\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \right] \]

\[ = 0 + \sqrt{\frac{2}{3}} \frac{1}{\sqrt{2}} k |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle + 0 \]

\[ = \frac{3}{\sqrt{3}} k |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle \]

or
\[ |\frac{3}{2}, -\frac{3}{2}\rangle = |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle . \]

But this list:

\[ |\frac{3}{2}, \frac{3}{2}\rangle = |11\rangle |\frac{1}{2}, \frac{1}{2}\rangle \]
\[ |\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{2}{3}} |10\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle \]
\[ |\frac{3}{2}, -\frac{1}{2}\rangle = \sqrt{\frac{1}{3}} |1-1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |10\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle \]
\[ |\frac{3}{2}, -\frac{3}{2}\rangle = |1-1\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle \]

contains only 4 states.

What about \[ \sqrt{\frac{1}{3}} |10\rangle |\frac{1}{2}, \frac{1}{2}\rangle - \sqrt{\frac{2}{3}} |11\rangle |1\frac{1}{2}, -\frac{1}{2}\rangle . \]

Although it has \( m_j = \frac{1}{2} \) it is orthogonal to all the states above?

What \( j \) does it correspond to?
\[
J^2 \left( \sqrt{\frac{1}{3}} \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{2}{3}} \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \right) = \\
\sqrt{\frac{1}{3}} \left\{ \frac{1}{2}(1+1)k^2 + \frac{1}{2}(\frac{1}{2}+1)k^2 + 0 \right\} \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > + \sqrt{\frac{2}{3}} k \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > + O \right\} \\
- \sqrt{\frac{2}{3}} \left\{ \left[ \frac{1}{2}(1+1)k^2 + \frac{1}{2}(\frac{1}{2}+1)k^2 + 2(1k) (-\frac{1}{2}k) \right] \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \\
+ O + \sqrt{2}k^2 \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > \right\} \\
= \sqrt{\frac{1}{3}} \left\{ (2 + \frac{3}{4})k^2 - 2k^2 \right\} \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > \\
+ \sqrt{\frac{2}{3}} \left\{ (2 + \frac{3}{4})k^2 - k^2 - k^2 \right\} \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \right\} \right. \\
= \sqrt{\frac{1}{3}} \left\{ (2 - 2 + \frac{3}{4})k^2 \right\} \left\{ \frac{1}{2} \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{2}{3}} \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \right\} \\
\right. \\
\left. \frac{1}{2}(\frac{1}{2}+1)k^2 \right. \\
\] 

This is a state with \( j = \frac{1}{2} \). By applying \( J^- \) to this state we get \( \sqrt{\frac{2}{3}} \left| 111 > \right\rangle \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{1}{3}} \left| 110 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \) corresponding to \( j = \frac{1}{2}, m_j = -\frac{1}{2} \). Thus:

\[
\left| j = \frac{1}{2}, \frac{1}{2} > = \sqrt{\frac{1}{3}} \left| 110 > \right\rangle \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{1}{3}} \left| 111 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \\
\left| j = \frac{1}{2}, -\frac{1}{2} > = \sqrt{\frac{2}{3}} \left| 111 > \right\rangle \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{1}{3}} \left| 110 > \right\rangle \frac{1}{2}, -\frac{1}{2} > \\
\right.
\]
Starting from the initial \( g \) states in a basis which diagonalizes both \( L^2 \) and \( S^2 \) and \( L_z \) and \( S_z \), we obtain a new basis which diagonalizes \( J^2 \) and \( J_z \). Alternatively, we could have just diagonalized the \( J^2 \) matrix for these values of \( L \), \( S \).

In general:

\[
|j, m_j \rangle = \sum_{m_s, m_e} |l m_e \rangle |s m_s \rangle \langle l m_e s m_s | j m_j \rangle
\]

\{ \text{Clebsch–Gordon coefficients} \}

In general, if one has a situation in which different angular momenta are added, such as the angular momenta for many particles, we obtain

\[
J = J_1 + J_2 + \cdots \quad \text{(or)} \quad S = S_1 + S_2 + S_3 + \cdots \quad \text{or} \quad L = L_1 + L_2 + \cdots
\]

we can use the above ideas. Given \( j_1 \) and \( j_2 \), the combined sets of states

\[
|j_1 m_1 \rangle |j_2 m_2 \rangle \quad \text{number} \quad (2j_1 + 1) \otimes (2j_2 + 1).
\]

Combining into eigenstates of \( J^2 \) and \( J_z \), we find

\[
j = j_1 + j_2, \quad j_1 + j_2 - 1, \quad \ldots \quad |j_1 - j_2|
\]

for a total \# of states of \((2j_1 + 1) \otimes (2j_2 + 1)\).
Consider a two particle Hamiltonian of identical particles
\[ \hat{H}(r_1, r_2) = \frac{1}{2m} \left[ \hat{p}_1^2 + \hat{p}_2^2 \right] + V(r_1) + V(r_2) + W(|r_1 - r_2|). \]

Example: two electron orbiting about a fixed center of attraction:
\[ W(|r_1 - r_2|) = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \quad \text{(electrostatic repulsion)}. \]

Note: that \( \hat{P}_{12} \) exchange operator commutes with \( \hat{H} \).

\[ \hat{P}_{12} \hat{H}(r_1, r_2) \psi(r_1, r_2) = \hat{H}(r_1, r_2) \hat{P}_{12} \psi(r_1, r_2) \]

\[ \implies \{ \hat{P}_{12}, \hat{H}(r_1, r_2) \} = 0 \]

Therefore \( \hat{P}_{12} \) is conserved. One can also find simultaneous eigenfunctions of \( \hat{H} \) and \( \hat{P}_{12} \).

Eigenvalues of \( \hat{P}_{12} \)
\[ \hat{P}_{12} \psi(r_1, r_2) = c \psi(r_1, r_2) \]
\[ (\hat{P}_{12})^2 \psi(r_1, r_2) = c^2 \psi(r_1, r_2) = \psi(r_1, r_2) \]
\[ c^2 = 1 \quad \text{or} \quad c = \pm 1. \]

\[ \hat{P}_{12} \psi(r_1, r_2) = \psi(r_2, r_1) = +\psi(r_1, r_2) \quad \text{Symmetric} \]
\[ \hat{P}_{12} \psi(r_1, r_2) = -\psi(r_2, r_1) = -\psi(r_1, r_2) \quad \text{Antisymmetric} \]
If there exist more than two particles then the procedure is more complex:
\[
\hat{P}_{13} \hat{P}_{12} \psi(1, 2, 3) = \psi^{2, 3, 1}(1, 2, 3)
\]
\[
\hat{P}_{12} \hat{P}_{13} \psi(1, 2, 3) = \psi^{2, 3, 1}(2, 3, 1)
\]

Therefore \( [\hat{P}_{13}, \hat{P}_{12}] \neq 0 \).

Although it is not possible to find a complete set of simultaneous eigenfunctions, we can find an eigenfunction of all the permutation operators. [This is similar to \( |l=0, \eta=0 > \) which is an eigenfunction of \( L_x, L_y \) and \( L_z \).]

\[
\psi_{\text{sym}} = \psi(1, 2, 3) + \psi(2, 1, 3) + \psi(1, 3, 2) + \psi(2, 3, 1)
\]
\[
2\psi(3, 1, 2) + 4\psi(3, 2, 1)
\]

\[
\psi_{\text{antisym}} = \psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 1, 2)
\]
\[
-\psi(2, 1, 3) - \psi(3, 2, 1) + \psi(1, 3, 2).
\]

Consider the electrons about two hydrogen nuclei (protons).

Clearly if the atoms are widely separated we can easily distinguish...
the two electrons. If the atoms are sufficiently close
such that the electron wavefunctions overlap then even in
principle it is not possible to distinguish them.

We therefore define the probability density as follows.

\[ |2\psi(1,2)|^2 \, dv_1 \, dv_2 = \text{probability that one electron is found in volume element } dv_1, \text{ while the other electron is found in } dv_2. \]

Note: if the two atoms are widely separated then a possible eigenfunction of \( \psi(\mathbf{r}_1, \mathbf{r}_2) \) is

\[ \psi(1,2) = \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2). \]

\[ |\psi(1,2)|^2 \, dv_1 \, dv_2 = |\psi_a(\mathbf{r}_1)|^2 \, dv_1 \otimes |\psi_b(\mathbf{r}_2)|^2 \, dv_2 \]

disjoint probabilities consistent with independent particles.

For overlapping wavefunctions, the symmetry under exchange
must be taken into account.

\[ \psi^{\pm}(1,2) = A \left( \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \right). \]

\[ |\psi^{\pm}(1,2)|^2 \, dv_1 \, dv_2 = |A|^2 \{ |\psi_a(\mathbf{r}_1)|^2 |\psi_b(\mathbf{r}_2)|^2 + |\psi_a(\mathbf{r}_2)|^2 |\psi_b(\mathbf{r}_1)|^2 - \\
\pm |\psi_a^*(\mathbf{r}_1) \psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2)|^2 \}
\otimes dv_1 \, dv_2\]
Note: if \( x_1 \) and \( x_2 \) are widely separated and \( u_a(x) \) and \( u_b(x) \) are localized then:

\[
\begin{align*}
& u_{a}^{*}(x_1) u_{b}(x_1) = 0 \\
& u_{b}^{*}(x_2) u_{a}(x_2) = 0
\end{align*}
\]

and

\[
\left| u_{(1,2)} \right|^2 \psi_1 \psi_2 = |A|^2 \left\{ \left| u_{a}(x_1) \right|^2 \left| u_{b}(x_2) \right|^2 + \left| u_{b}(x_1) \right|^2 \left| u_{a}(x_2) \right|^2 \right\}
\]

although the interference term is negligible, the probability still maintains the indistinguishability of the particles.
Consider two identical particles constrained to move on a loop of circumference \( L \). \( (L = 2\pi a) \)

\[
\text{\( \mathcal{H} = -\frac{k^2}{2m a^2} \frac{d^2}{d\phi_1^2} - \frac{k^2}{2m a^2} \frac{d^2}{d\phi_2^2} \)}
\]

which has eigenfunctions \( \psi_{1,2}(\phi_1, \phi_2) = A e^{i\phi_1} e^{i\phi_2} \)

with \( E = \frac{k^2}{2m a^2} (m^2 + n^2) \).

If we require the eigenstates of \( \mathcal{H} \) to be symmetric or antisymmetric, then we must write:

\[
\psi_{\text{sym}} = A \left\{ e^{i\phi_1} e^{i\phi_2} + e^{i\phi_2} e^{i\phi_1} \right\}
\]

Normalizing:

\[
1 = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 |\psi_{\text{sym}}|^2 = \int_0^{2\pi} \int_0^{2\pi} |A|^2 \left\{ 1 + 1 + e^{i(m-n)\phi_1} e^{i(m-n)\phi_2} + e^{i(n-m)\phi_1} e^{i(n-m)\phi_2} \right\}
\]

\[
= |A|^2 \left\{ \frac{8\pi}{4\pi} m=n \right\} \quad |A|^2 = \frac{1}{4\pi} \frac{m+n}{m-n}
\]

Rewriting \( \psi_{\text{sym}} \):

\[
\psi_{\text{sym}} = A e^{i\phi_1} e^{i\phi_2} \left[ e^{i\frac{(m+n)(\phi_1+\phi_2)}{2}} + e^{-i\frac{(m-n)(\phi_1-\phi_2)}{2}} \right]
\]

\[
= 2A e^{i\frac{m+n}{2} \cos \left( \frac{m-n}{2} \phi \right)}
\]
where $M^z$ is the total angular momentum (along z-axis) for the center of mass motion $\bar{\mathbf{M}} = \bar{\phi}_1 + \bar{\phi}_2$.

Similarly the antisymmetric state $\psi_{\text{anti}}$ looks like:

$$\psi_{\text{anti}} = B \left\{ e^{i\phi_1} e^{i\phi_2} - e^{i\phi_2} e^{i\phi_1} \right\}.$$

Note $\psi_{\text{anti}}$ vanishes for $m=n$! (Pauli Exclusion Principle).

$$|B|^2 = \frac{1}{4\pi}.$$

Rewriting $\psi_{\text{anti}}$:

$$\psi_{\text{anti}} = B e^{i\frac{(m+n)}{2} (\phi_1 + \phi_2)} \left[ e^{i\frac{(m-n)}{2} (\phi_1 - \phi_2)} - e^{i\frac{(n-m)}{2} (\phi_1 - \phi_2)} \right].$$

The probability density for each become:

$$|\psi_{\text{sym}}|^2 \, d\phi_1 \, d\phi_2 = 4|A|^2 \cos^2 \left[ \frac{(m-n)}{2} (\phi_1 - \phi_2) \right] \, d\phi_1 \, d\phi_2.$$

$$|\psi_{\text{anti}}|^2 \, d\phi_1 \, d\phi_2 = 4|B|^2 \sin^2 \left[ \frac{(m-n)}{2} (\phi_1 - \phi_2) \right] \, d\phi_1 \, d\phi_2.$$

Although the two particles do not interact (even in principle), the probabilities show distinct correlations. In fact the $\psi_{\text{anti}}$ shows statistical repulsion is

$$|\psi_{\text{anti}}|^2 \, d\phi_1 \, d\phi_2 \rightarrow 0 \quad \text{for} \quad \phi_1 \rightarrow \phi_2.$$

If the particles avoid each other!.
This statistical repulsion can have significant consequences when there exists a physical interaction between the particles.

Consider a spring between the two particles.

\[ V(\phi_1, \phi_2) = \frac{1}{2} k a^2 (\phi_1 - \phi_2)^2 \quad |\phi_1 - \phi_2| < \pi \]

\[ = 0 \quad |\phi_1 - \phi_2| > \pi \]

Treating \( V(\phi_1, \phi_2) \) as a small perturbation to the total energy,

\[ E = \frac{k^2}{2m^2} (m^2 + n^2) \]

the correction to \( E \) is just \( \langle 4V(\phi_1, \phi_2)|4 \rangle \).

For the sym state. (for simplicity choose \( m = 2 \), \( n = 1 \)).

\[ \langle 4_{\text{sym}}|V(\phi_1, \phi_2)|4_{\text{sym}} \rangle = \]

\[ = \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\phi_2 \quad 4 |A|^2 \cos^2 \left[ \frac{\phi_1 - \phi_2}{2} \right] k (\phi_1 - \phi_2)^2 V \left( \frac{\phi_1 - \phi_2}{2} \right). \]

Variable substitution.

\[ \overline{\phi} = \frac{\phi_1 + \phi_2}{2} \]

\[ d\phi_1 d\phi_2 \Rightarrow 2 \ d\overline{\phi} \ d\Delta. \]

\[ \Delta = \frac{\phi_1 - \phi_2}{2} \]

\[ = \left| \begin{array}{cc}
\frac{\partial \phi_1}{\partial \overline{\phi}} & \frac{\partial \phi_1}{\partial \Delta} \\
\frac{\partial \phi_2}{\partial \overline{\phi}} & \frac{\partial \phi_2}{\partial \Delta}
\end{array} \right| d\overline{\phi} d\Delta \]

\[ = 2 \int_{0}^{2\pi} d\overline{\phi} \int_{-\pi/2}^{\pi/2} d\Delta \quad 4 |A|^2 \cos^2 \Delta \quad \frac{1}{2} k a^2 \Delta^2 \]
\[ \begin{align*}
&= \frac{8\pi a^2 k |A|^2}{\pi^2} \int_{-\pi/2}^{\pi/2} \Delta^2 \cos^2 \Delta \, d\Delta \\
&= 4\pi a^2 k |A|^2 \left\{ \frac{\Delta^3}{6} + \left( \frac{\Delta^2}{4} - \frac{1}{8} \right) \sin 2\Delta + \frac{\Delta \cos 2\Delta}{4} \right\} \bigg|_{-\pi/2}^{\pi/2} \\
&= 4\pi a^2 k |A|^2 \left\{ \frac{\pi^3}{24} - \frac{\pi}{4} \right\} = \pi^2 a^2 k |A|^2 \left( \frac{\pi^2}{6} - 1 \right). \\
\end{align*} \]

Similarly for the antisymmetric state. \((n=2, \pi=1)\)

\[ \langle \psi_{\text{anti}} | \mathcal{V}(\phi_1, \phi_2) | \psi_{\text{anti}} \rangle \]

\[ \begin{align*}
&= \int_0^{2\pi} d\phi_1 \int_0^{2\pi} \sin^2 \left( \frac{\phi_1 - \phi_2}{2} \right) \frac{\pi}{2} k (\phi_1 - \phi_2)^2 \sin^2 \left( \frac{\phi_1 - \phi_2}{2} \right) \\
&= 2 \int_0^{\pi/2} d\Phi \int_{-\pi/2}^{\pi/2} \sin^2 \Delta \frac{\pi}{2} k a^2 \Delta^2 \\
&= \pi^2 k a^2 |B|^2 \left( \frac{\pi^2}{6} + 1 \right)
\end{align*} \]

The effect of the statistical repulsion is to keep the particles apart. Therefore, the spring remains stretched more than in the sym. state. The correction to the unperturbed energy is larger.
Consider two identical particles with spin \( \frac{1}{2} \).

\( \chi_+ \) "spin up" \quad \( S_2 \chi_+ = \frac{1}{2} \hbar \chi_+ \)

\( \chi_- \) "spin down" \quad \( S_2 \chi_- = -\frac{1}{2} \hbar \chi_- \)

**Combined spin state of total spin.**

\[
\begin{align*}
\chi_+(1) \chi_+(2) \\
\chi_+(1) \chi_-(2) \\
\chi_-(1) \chi_+(2) \\
\chi_-(1) \chi_-(2)
\end{align*}
\]

\[
\rightarrow \quad \frac{1}{2} \left[ \chi_+(1) \chi_-(2) + \chi_-(1) \chi_+(2) \right]
\]

\[
\frac{1}{2} \left[ \chi_+(1) \chi_-(2) - \chi_-(1) \chi_+(2) \right]
\]

**Eigenstates of** \( S^2, S_z \)

**where** \( S = S_1 + S_2 \)

**Note:** The states of total spin are also eigenstates of the exchange operator \( \hat{P}_{12} \) with the \( S=1 \) state being symmetric and the \( S=0 \) state being antisymmetric.

This property could have been predicted since

\[
[S, \hat{P}_{12}] = 0 \quad S = S_1 + S_2
\]

implies that the eigenfunctions of \( S^2 \) and \( S_z \) can be chosen as eigenfunctions of \( \hat{P}_{12} \).
This is a general property.

\[ L = l_1 + l_2 \]

Clearly commutes with \( \hat{P}_{12} \) and so if

\[ l_1 = 1 \quad \text{and} \quad l_2 = 1 \]

\[ l = 2 \quad 2l + 1 = 5 \]

\[ l = 1 \quad 2l + 1 = 3 \]

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

\( 9 \) states \( = (2l_1 + 1) \times (2l_2 + 1) \)

have definite exchange symmetry, i.e.

\[ l = 2 \quad \text{Symmetric states} \]

\[ l = 1 \quad \text{Antisymmetric} \]

\[ l = 0 \quad \text{Symmetric states} \]

Such

The symmetry of the angular momentum states can have profound effects in the energy of a system and can lead to interesting effects: molecular binding, magnetism...
Electron Configurations

1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 

Consider two inequivalent p electrons, 2p3p. Each contributes one unit of angular momentum. From our previous discussions we should have for the total \( L = (L_1^2 + L_2^2)^{1/2} \)

\[ L = 0, 2, 1, 0 \quad l_1 + l_2, l_1 + l_2 - 1 \ldots \quad |l_1 - l_2| \]

Similarly for the spin the total \( S \)

\[ S = 1, 0 \]

How would one write a \( L = 2 \) \( M_L = 2 \) wavefunction?

Since \( \Psi_{nlm}(r, \theta, \phi) = R_{nl}(\rho) Y_l^m(\theta, \phi) \) we have

\[ \Psi(l_1, 2, l_2, M_L = 2) = R_{21}(1) Y_{1}^{1}(1) R_{31}(2) Y_{1}^{1}(2) \]

The combination \( Y_{1}^{1}(1) Y_{1}^{1}(2) \) is an eigenstate of \( L_2 \) and \( L^2 \)

But \( Y_{1}^{1}(2) Y_{1}^{1}(1) \) is also an eigenstate and so we can form

\[ \Psi^{\pm} = R_{21}(1) R_{31}(2) Y_{1}^{1}(1) Y_{1}^{1}(2) \pm R_{21}(2) R_{31}(1) Y_{1}^{1}(2) Y_{1}^{1}(1) \]

Thus we can form both a symmetric and antisymmetric orbital state. For other \( L, M_L \) values we can form the eigenstates of \( L_2 \), \( L^2 \) and the symmetrizing the result.
so that,

\[ \psi(1, 2, L=2, M_L=1) = \frac{R_{21(1)} R_{31(2)}}{\sqrt{2}} \left[ Y^*(1) Y^T(2) + Y^0(1) Y^T(1) \right] + \frac{R_{12(1)} R_{31(1)}}{\sqrt{2}} \left[ Y^T(1) Y^T(2) + Y^0(1) Y^T(1) \right] \]

The total # of states 

9 states

4 states

= 36 states

Coupling \( L \) and \( S \) we have

\[
\begin{array}{cccc}
L = 2 \quad & S = 1 & J = 3, 2, 1 & 3 \text{D}_{3, 2, 1} \\
& S = 0 & J = 2 & 1 \text{D}_2 \\
L = 1 \quad & S = 1 & J = 2, 1, 0 & 3 \text{P}_{2, 1, 0} \\
& S = 0 & J = 1 & 1 \text{P}_1 \\
L = 0 \quad & S = 1 & J = 1 & 3 S_1 \\
& S = 0 & J = 0 & 1 S_0 \\
\end{array}
\]

If the two electrons are equivalent \( \psi^2 \) then the Pauli exclusion principle removes states.
Our previous state

\[ R_{21}(1) R_{21}(2) Y_1(1) Y_1(2) \]

can not be made into an antisymmetric state.

Therefore the \( L=2 \) (symmetric) can only be combined with \( S=0 \).

Similarly \( L=1 \) (antisymmetric) can only be combined with \( S=1 \)

\[ L=0 \] (symmetric) \[ S=0 \].

And so...

\[ ^1D_2 \]

\[ ^3P_{2,1,0} \]

\[ ^1S_0 \]

15 states.

So the requirement of symmetry greatly reduces the number of states.

//

higher configuration of more than 2 electrons reduces the number of states even further until you fill an orbital and thereby quench all the angular momentum.
Fermions

- half-integer spin

\( \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \)

electron, proton, quark,

neutron, neutrinos, \( ^3\text{He}, \)

Antisymmetric

Bosons

- integer spin

\( 0, 1, 2, 3, \ldots \)

photons, pions, deuterons

\( ^4\text{He}, \) graviton \( W\)'s.

Symmetric

Composite systems (such as \( ^3\text{He}, \) \( ^4\text{He} \)) can be considered as

a fermion or boson if the experiment under consideration does not

probe the internal structure.

The requirement of an antisymmetric wavefunction for fermions

leads to the Pauli exclusion principle.

2-particle wavefunction:

\[ \psi = \frac{1}{\sqrt{2}} \left[ \psi_n(1) \psi_m(2) - \psi_m(1) \psi_n(2) \right] \]

if the quantum number \( n \) and \( m \) are equal, the wavefunction

vanishes. Two fermions can not occupy the same state.

Note: the above function can be written as a determinant

\[ \psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_n(1) & \psi_m(1) \\ \psi_n(2) & \psi_m(2) \end{vmatrix} \]

or if one has more than two particles.
\[ \psi \left( n! \right)^{-1/2} \begin{vmatrix} \alpha_1(1) & \alpha_2(1) & \alpha_3(1) & \cdots & \alpha_n(1) \\ \alpha_1(2) & \alpha_2(2) & & \cdots \\ \vdots & \vdots & \ddots & \vdots \\ \alpha_1(n) & \alpha_2(n) & \alpha_3(n) & \cdots & \alpha_n(n) \end{vmatrix} \]

which is called the Slater determinant.
Approximation Schemes

Perturbation Theory.

In Q.M., one is often presented with a Hamiltonian which is only slightly different from one that has been solved previously.

\[ H = H_0 + H_1 \]

where the eigenfunctions and eigenvalues of \( H_0 \) are known.

\[ H_0 |E_n^0\rangle = E_n^0 |E_n^0\rangle \quad \text{eigenvector} \]

\[ E_n^0 \quad \text{eigenvalue} \]

Note: We shall work with discrete states although the formalism equally applies to the continuum as well.

If \( H_1 \) is indeed "small" (and we shall discuss what small means later) one would guess that an eigenfunction of \( H \) would look very much like an eigenfunction of \( H_0 \) i.e.

\[ |E_n\rangle = |E_n^0\rangle + |\delta E_n\rangle \]

Similarly for the energy eigenvalue.

\[ E_n = E_n^0 + \Delta E_n \]

Substituting into our equation \( H |E_n\rangle = E_n |E_n\rangle \) we have.

\[ (H_0 + H_1)\left[ |E_n^0\rangle + |\delta E_n\rangle \right] = (E_n^0 + \Delta E_n) \left( |E_n^0\rangle + |\delta E_n\rangle \right) \]

\[ H_0 |E_n^0\rangle + H_0 |\delta E_n\rangle + H_1 |E_n\rangle = E_n^0 |E_n^0\rangle + E_n^0 |\delta E_n\rangle + \Delta E_n |E_n\rangle \]

These two terms cancel.

Taking an inner product with \( \langle E_n^0 \rangle \) we obtain
\[ \langle E_\eta | H, 1\delta^4 \rangle + \langle E_\eta | H, 1E_\eta \rangle \]
\[ = E_\eta \langle E_\eta | H, 1\delta^4 \rangle + \Delta E_\eta \langle E_\eta | E_\eta \rangle \]

Since \( H_0 \) is Hermitian
\[ \langle E_\eta | H_0, 1\delta^4 \rangle = \langle \delta^4 \ E_\eta | H_0 \rangle \]
\[ = E_\eta \langle E_\eta | \delta^4 \rangle \]

and we have
\[ (E_\eta - E_\eta) \langle E_\eta | \delta^4 \rangle + \langle E_\eta | H, 1E_\eta \rangle = \Delta E_\eta \langle E_\eta | E_\eta \rangle \]

1. For \( m = n \)
\[ \Delta E_\eta = \frac{\langle E_\eta | H, 1E_\eta \rangle}{\langle E_\eta | E_\eta \rangle} \]

2. For \( m \neq n \)
\[ (E_\eta - E_\eta) \langle E_\eta | \delta^4 \rangle = \langle E_\eta | H, 1E_\eta \rangle - \Delta E_\eta \langle E_\eta | E_\eta \rangle \]

Now if \( H_0 \) is indeed small we would be only making a slight error if we replace \( 1E_\eta \) by \( 1E_\eta^0 \) in the above equations.

\[ 1E_\eta \Rightarrow 1E_\eta^0 \] gives for \( m = n \).
\[ \frac{\langle E_\eta^0 | H, 1E_\eta^0 \rangle}{\langle E_\eta | E_\eta^0 \rangle} \]
\[ \Delta E_\eta \approx \frac{\langle E_\eta^0 | H, 1E_\eta^0 \rangle}{\langle E_\eta^0 | E_\eta \rangle} \]

and for \( m \neq n \).
\[ \langle E_\eta^0 | \delta^4 \rangle \approx \frac{\langle E_\eta^0 | H, 1E_\eta \rangle}{(E_\eta^0 - E_\eta^0)} \]
\[ \langle E_\eta^0 | E_\eta \rangle = 0 \]

for \( m \neq n \).
The first result \( \Delta E_n < \langle E_m^0 | H | E_n^0 \rangle \) can be interpreted physically if the change in \( E_n \) is a change on the potential. In this case \( \Delta E_n \) is just the average value of this potential for the state in question.

The second result

\[
\langle E_m^0 | \delta \psi_n \rangle = \frac{\langle E_m^0 | H | E_n^0 \rangle}{E_n^0 - E_m^0}
\]

suggests that the component of \( \delta \psi_n \) along the \( E_m^0 \) direction will be large if the energy of \( E_m^0 \) is close to that of the original state.

The above result suggests that we expand \( \delta \psi_n \) in a series of states orthogonal to \( E_m^0 \) i.e.

\[
\delta \psi_n = \sum_{m \neq n} C_m | E_m \rangle
\]

where our normal def. of \( C_m = \langle E_m^0 | \delta \psi_n \rangle \) holds. Therefore to this level of approximation

\[
| E_n \rangle = | E_m \rangle + \sum_{m \neq n} \frac{\langle E_m^0 | H | E_n^0 \rangle}{E_n^0 - E_m^0} | E_m \rangle
\]

0th order in \( \delta \psi \), 1st order in \( H \).

We can go back now with this corrected \( | E_n \rangle \) and subst. again into our expressions 1 and 2.

\[
\Delta E_n = \langle E_m^0 | H | E_n^0 \rangle = \langle E_m^0 | H | E_n^0 \rangle + \sum_{m \neq n} \frac{\langle E_m^0 | H | E_n^0 \rangle \langle E_n^0 | H | E_m \rangle}{E_n^0 - E_m^0}
\]

\[
= \langle E_m^0 | H | E_n^0 \rangle + \sum_{m \neq n} \frac{\langle E_m^0 | H | E_n^0 \rangle}{E_n^0 - E_m^0} \frac{\langle E_n^0 | H | E_m \rangle}{E_n^0 - E_m^0}
\]

1st order in \( \delta \psi \), 2nd order in \( H \).

Note: to get 1st order in \( \delta \psi \), we only need \( n^{th} \) order eigenfunctions.
We could also substitute up to $O$ to obtain a higher order correction for $1_{\mathcal{H}_n}$ and continue to iterate our results to obtain higher order corrections for $\Delta E_n$ as well.

A more systematic approach which is more conducive to obtaining higher order terms involves introducing an expansion parameter $\lambda$:

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_1,$$

$\lambda$ is chosen to be sufficiently small in order to do the expansion. (at the end we will however set $\lambda = 1$ to return to our original problem).

Again we assume solutions of $\mathcal{H}$ are close to solutions of $\mathcal{H}_0$:

$$1_{E_n} = 1_{E_n^0} + 1_{\mathcal{H}_n},$$

where $1_{\mathcal{H}_n}$ is expanded in eigenfunctions which are orthogonal to $1_{E_n^0}$:

$$1_{\mathcal{H}_n} = \sum_{m \neq n} C_m 1_{E_m^0}$$

Assume $1_{E_m^0}$ non-degenerate.

Our notation can be simplified by defining $C_n = 1$ so that:

$$1_{E_n} = \sum_m C_m 1_{E_m^0}$$

Substituting into our equation for $\mathcal{H}$:

$$\mathcal{H} 1_{E_n} = (\mathcal{H}_0 + \lambda \mathcal{H}_1) \sum_m C_m 1_{E_m^0} = E_n \sum_m C_m 1_{E_m^0}$$

Taking the inner product with $\langle E_k^0 |$

$$\sum_m \langle E_k^0 | \mathcal{H}_0 | E_m^0 \rangle + \lambda \sum_m \langle E_k^0 | \mathcal{H}_1 | E_m^0 \rangle = E_n \sum_m C_m \langle E_k^0 | E_m^0 \rangle$$

$$\sum_{E_m^0} \sum_k <E_k^0|E_m^0> C_m = E_n \sum_{E_m^0} \sum_k <E_k^0|E_m^0> C_m$$
\[ C_k E_k^0 + \lambda \sum_m C_m \left< E_k^0 | H_m | E_m^0 \right> = E_n C_k \quad \text{or} \]

\[ C_k (E_n - E_k^0) = \lambda \sum_m C_m \left< E_k^0 | H_m | E_m^0 \right> \]

One can treat the above equation as a definition for \( E_n \) and \( C_k \)'s which are functions of the parameter \( \lambda \). Since \( \lambda \) is supposed to be small we can try expanding \( E_n \) and \( C_k \) in a Taylor series in \( \lambda \), i.e.

\[ E_n (\lambda) = E_n(0) + \frac{\lambda}{1!} \left( \frac{dE_n}{d\lambda} \right)_{\lambda=0} + \frac{\lambda^2}{2!} \left( \frac{d^2E_n}{d\lambda^2} \right)_{\lambda=0} + \cdots \]

\[ k \neq 0 \quad C_k (\lambda) = C_k(0) + \frac{\lambda}{1!} \left( \frac{dC_k}{d\lambda} \right)_{\lambda=0} + \frac{\lambda^2}{2!} \left( \frac{d^2C_k}{d\lambda^2} \right)_{\lambda=0} + \cdots \]

\[ k = n \quad C_n (\lambda) = 1 \]

From above \* at \( \lambda = 0 \) we have

\[ C_k(0) \quad (E_n(0) - E_k^0) = 0 \]

Since \( C_n (\lambda) = 1 \) then \( E_n(0) = E_n^0 \) but if this is true then for \( k \neq n \).

\[ C_k(0) \quad (E_n^0 - E_k^0) = 0 \quad \Rightarrow \quad C_k(0) = 0 \quad \text{or} \quad C_k(0) = \delta_{kn} \quad \text{for all} \ k. \]

Differentiating \* \[ \frac{dC_k}{d\lambda} (E_n - E_k^0) + C_k \left( \frac{dE_n}{d\lambda} \right) = \sum_m C_m \left< E_n^0 | H_m | E_m^0 \right> \]

\[ + \lambda \sum_m \left( \frac{dC_m}{d\lambda} \right) \left< E_k^0 | H_m | E_m^0 \right> \]
Again let \( \lambda = 0 \).

\[
\left( \frac{dC_k}{d\lambda} \right) \bigg|_0 (E_n(0) - E^0_n) + C_k(0) \left( \frac{dE_n}{d\lambda} \right) \bigg|_0 = \sum_m C_m(0) \langle E^0_n | \mathcal{H}_n | E^0_m \rangle
\]

But \( E_n(0) = E^0_n \) AND \( C_m(0) = \delta_{mn} \). Substitute.

\[
\left( \frac{dC_k}{d\lambda} \right) \bigg|_0 (E^0_n - E^0_k) + C_k(0) \left( \frac{dE_n}{d\lambda} \right) \bigg|_0 = \langle E^0_k | \mathcal{H}_n | E^0_n \rangle
\]

For \( k \neq n \)

\[
\left( \frac{dC_k}{d\lambda} \right) \bigg|_0 = \frac{\langle E^0_k | \mathcal{H}_n | E^0_n \rangle}{(E^0_n - E^0_k)}
\]

For \( k = n \)

\[
\left( \frac{dE_n}{d\lambda} \right) \bigg|_0 = \langle E^0_n | \mathcal{H}_n | E^0_n \rangle
\]

Differentiate twice.

\[
\frac{d^2C_k}{d\lambda^2} (E_n - E^0_n) + 2 \left( \frac{dC_k}{d\lambda} \right) \left( \frac{dE_n}{d\lambda} \right) + \frac{d^2E_n}{d\lambda^2} + C_k \left( \frac{d^2E_n}{d\lambda^2} \right)
\]

\[
= 2 \sum_m \left( \frac{dC_m}{d\lambda} \right) \langle E^0_n | \mathcal{H}_m | E^0_m \rangle + \lambda \sum_m \left( \frac{d^2C_m}{d\lambda^2} \right) \langle E^0_n | \mathcal{H}_m | E^0_m \rangle.
\]

Let \( \lambda = 0 \).

\[
\left( \frac{d^2C_k}{d\lambda^2} \right) \bigg|_0 (E_n(0) - E^0_n) + 2 \left( \frac{dC_k}{d\lambda} \right) \bigg|_0 \left( \frac{dE_n}{d\lambda} \right) \bigg|_0 + C_k(0) \left( \frac{d^2E_n}{d\lambda^2} \right) \bigg|_0 = \]

\[
= 2 \sum_m \left( \frac{dC_m}{d\lambda} \right) \bigg|_0 \langle E^0_n | \mathcal{H}_m | E^0_m \rangle
\]

Subst. our previous results.
\[
\left( \frac{\partial C_k}{\partial \lambda} \right)_0 (E_n^0 - E_k^0) + 2 \left( \frac{\partial C_k}{\partial \lambda} \right)_0 \langle E_n^0 \mid \hat{H}_1 \mid E_n^0 \rangle + \sum_{\eta \neq n} \left( \frac{\partial^2 E_k}{\partial \lambda^2} \right)_0 \langle E_k^0 \mid \hat{H}_1 \mid E_m^0 \rangle
\]

Since \( \left( \frac{\partial C_n}{\partial \lambda} \right)_0 = 0 \), \( C_n(\lambda) \equiv 1 \)

For \( k \neq n \)

\[
\left( \frac{\partial^2 C_k}{\partial \lambda^2} \right)_0 (E_n^0 - E_k^0) + 2 \langle E_k^0 \mid \hat{H}_1 \mid E_n^0 \rangle \langle E_n^0 \mid \hat{H}_1 \mid E_n^0 \rangle \frac{\langle E_n^0 \mid \hat{H}_1 \mid E_m^0 \rangle \langle E_k^0 \mid \hat{H}_1 \mid E_m^0 \rangle}{(E_n^0 - E_m^0)}
\]

\[
= 2 \sum_{m \neq n} \frac{\langle E_n^0 \mid \hat{H}_1 \mid E_m^0 \rangle \langle E_k^0 \mid \hat{H}_1 \mid E_m^0 \rangle}{(E_n^0 - E_m^0)}
\]

or

\[
\frac{1}{2} \left( \frac{\partial^2 C_k}{\partial \lambda^2} \right)_0 = \sum_{m \neq n} \frac{\langle E_k^0 \mid \hat{H}_1 \mid E_m^0 \rangle \langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle - \langle E_k^0 \mid \hat{H}_1 \mid E_n^0 \rangle \langle E_n^0 \mid \hat{H}_1 \mid E_m^0 \rangle}{(E_n^0 - E_m^0)(E_n^0 - E_k^0)}
\]

For \( k = n \)

\[
\left( \frac{\partial^2 E_n}{\partial \lambda^2} \right)_0 = 2 \sum_{m \neq n} \frac{\langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle \left( \langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle \right)^2}{(E_n^0 - E_m^0)}
\]

And so on.

\[
E_n = E_n^0 + \chi \langle E_n^0 \mid \hat{H}_1 \mid E_n^0 \rangle + \chi^2 \sum_{m \neq n} \frac{\langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle \left( \langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle \right)^2}{(E_n^0 - E_m^0)} + \ldots
\]

And

\[
|E_n\rangle = |E_n^0\rangle + \chi \sum_{m \neq n} \frac{\langle E_m^0 \mid \hat{H}_1 \mid E_n^0 \rangle}{(E_n^0 - E_m^0)} |E_m^0\rangle + \chi^2 \left\{ \ldots \right\}
\]
Examples.

Let the unperturbed Hamiltonian be that of an infinite square well potential.

Eigenfunctions: \( \langle x | n \rangle = \sqrt{\frac{2}{a}} \sin \left( \frac{n \pi x}{a} \right) \) \( n = 1, 2, 3 \).

Eigenvalues: \( E_n = \frac{k_n^2 \pi^2}{2ma^2} \).

Add a small piece to the bottom of the well

\( F_1 = 0 \) for \( 0 \leq x \leq \frac{a}{2} \)

\( = 0 \) for \( \frac{a}{2} \leq x \leq a \).

1. Calculate the correction to 1st order of the ground state energy.

\[
E_1 = E_1^0 + \langle E_1^0 | F_1 | E_1^0 \rangle
= \frac{k_1^2 \pi^2}{2ma^2} + \int_0^{a/2} \left[ \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \right] \phi_1 \left[ \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \right] dx

= \frac{k_1^2 \pi^2}{2ma^2} + \frac{\pi}{2a} \int_0^{a/2} \sin^2 \left( \frac{\pi x}{a} \right) dx

= \frac{k_1^2 \pi^2}{2ma^2} + \frac{\pi}{2a} \frac{a}{2} \sin \left( \frac{\pi a}{2} \right)

E_1 = \frac{k_1^2 \pi^2}{2ma^2} + \frac{\pi}{2}.
2. Calculate the correction to the ground state wave function to 1st order in the perturbation.

\[ |E_i> = |E_i^0> + \sum_{\eta \neq 1} \frac{\langle E_m^0 | H_1 | E_i^0 \rangle}{E_i^0 - E_m^0} |E_m^0> \]

where \( \langle E_m^0 | H_1 | E_i^0 \rangle = \int_{0}^{a} \left[ \left( \frac{2\alpha}{a} \right)^2 \sin \frac{\pi x}{a} \right]^{\eta} \left[ \left( \frac{2\alpha}{a} \right)^2 \sin \frac{\pi x}{a} \right] \ dx \)

\[ = \frac{2\xi}{a} \int_{0}^{a} \sin \left( \frac{\pi x}{a} \right) \sin \left( \frac{\pi x}{a} \right) \ dx \]

but \( \sin A \sin B = \frac{1}{2} \left[ \cos (A - B) - \cos (A + B) \right] \) and

\[ \langle E_m^0 | H_1 | E_i^0 \rangle = \frac{\xi}{a} \int_{0}^{a/2} \left[ \cos \left( \frac{(m+1)\pi x}{a} \right) - \cos \left( \frac{(m+1)\pi x}{a} \right) \right] \ dx \]

\[ = \frac{\xi}{\pi} \left\{ \frac{\sin (m+1)\pi/2}{(m+1)} - \frac{\sin (m+1)\pi/2}{(m+1)} \right\} \]

\[ \text{if } m \text{ odd, the } \sin (m+1)\pi/2 = \sin (m+1)\pi/2 = 0 \]

\[ \text{if } m \text{ even, } (m = 2n) \]

\[ \langle E_m^0 | H_1 | E_i^0 \rangle = \frac{\xi}{\pi} \left\{ \frac{-(-1)^n}{2n-1} - \frac{(-1)^n}{2n+1} \right\} = \frac{(-1)^{n+1} 4\eta}{(4\eta^2-1)} \left( \frac{\xi}{\pi} \right) \]

and

\[ |E_i> = |E_i^0> + \frac{4\xi/\pi}{(\pi^2/2\eta a^2)} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(4n^2-1)} \frac{n}{(1 - 4n^2)} |E_{2n}^0> \]
\[ |E_i\rangle = |E_i^0\rangle + \frac{2m\alpha^2}{k^2} \sum_{n=1}^{\infty} \frac{(-1)^n \frac{n^2}{(4n^2-1)^2}}{|E_i^0 - E_{m^2/1}|^2} \]

Corrections fall off rapidly \( \propto 1/n^3 \)

\[ \langle E_i \rangle \approx \langle E_i^0 \rangle \]

\[ |E_i^0\rangle \quad \text{shift probability away from higher potential region} \]

\[ (3) \text{ The correction to the ground state energy to } 2^{\text{nd}} \text{ order becomes} \]

\[ E_i = E_i^0 + \langle E_i^0 | \hat{H} | E_i^0 \rangle + \sum_{m^2/1} \left| \frac{\langle E_i^0 \rangle | \hat{H} | E_i^0 \rangle}{E_i^0 - E_{m^2/1}} \right|^2 \]

\[ = \frac{k^2\alpha^2}{2\eta a^2} + \varepsilon/2 + \sum_{n=1}^{\infty} \frac{\left(4\varepsilon/k\right)^2 \frac{n^2}{(4n^2-1)^2}}{\frac{k^2\alpha^2}{2\eta a^2} (1 - 4n^2)} \]

\[ = \frac{k^2\alpha^2}{2\eta a^2} + \varepsilon/2 - \left(\frac{2m\alpha^2}{k^2}\right) \left(\frac{4\varepsilon}{\pi^2}\right)^2 \sum_{n=1}^{\infty} \frac{n^2}{(4n^2-1)^3} \]

\[ = \frac{k^2\alpha^2}{2\eta a^2} + \varepsilon/2 - \left[ \frac{\varepsilon^2}{\left(k^2\alpha^2/2\eta a^2\right)} \right] (0.062 \ldots) \]
Note: If $\varepsilon$ were to become large, then the ground state wave function would approach that of a well with $\frac{a}{4}$ of the width.

The energy of the ground state should approach

$$E_1 = \frac{k^2 \pi^2}{2m (a/4)^2} = 4 \left( \frac{k^2 \pi^2}{2ma^2} \right).$$

The energy rolls over initially due to $-\varepsilon^2$ term.
One approach to estimating the relativistic corrections to the energy would be to look at

\[ E^2 = \left( c^2 p^2 + m_0^2 c^4 \right) \]

Then

\[ E = \left( c^2 p^2 + m_0^2 c^4 \right)^{1/2} \]

but at small momenta,

\[ E = m_0 c^2 \left( 1 + \frac{p^2}{2m_0^2 c^2} \right)^{1/2} \]

\[ = m_0 c^2 \left( 1 + \frac{1}{2} \frac{p^2}{m_0^2 c^2} + \frac{1}{2} \left( \frac{1}{2} \right) \left( \frac{p^2}{m_0^2 c^2} \right)^2 + \cdots \right) \]

\[ = m_0 c^2 + \frac{p^2}{2m_0} - \frac{1}{8} \frac{p^4}{m_0^3 c^2} + \cdots \]

The first term is just a constant; the second term is the familiar classical term \( \frac{p^2}{2m} \); the third term is the first order correction to the energy. It is negative since the quadratic dependence on \( p \) overestimates the energy at large \( p \).

In quantum mechanics we can ignore the constant term \( m_0 c^2 \) since it only shifts the zero of the energy. We therefore take \(-\frac{1}{8} \frac{p^4}{m_0^3 c^2}\) to be the perturbation term.
\[ \hat{H}_1 = -\frac{1}{8} \frac{P^4}{m_0^3 c^2} \quad \text{where} \quad P = -i\hbar \nabla \]

Since the hydrogen Hamiltonian can be written as
\[ \hat{H}_1 = T + \hat{V} = \frac{P^2}{2m_0} - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{we can write} \]
\[ \hat{H}_1 = -\frac{1}{8} \frac{1}{m_0^3 c^2} \left[ 2m_0 (\hat{H} - \hat{V}) \right] \left[ 2m_0 (\hat{H} - \hat{V}) \right] \]
and so since \[ \hat{H}_1 \psi_{100} = E_1 \psi_{100} \]
\[ \Delta E^{(1)} = \psi_{100} \rangle \langle \hat{H}_1 \psi_{100} \rangle \]
\[ = -\frac{1}{8} \frac{(4m_0^2)}{m_0^3 c^2} \psi_{100} \rangle \langle \hat{H}_1 \psi_{100} \rangle \psi_{100} \rangle - \psi_{100} \rangle \langle \hat{V} \psi_{100} \rangle \psi_{100} \rangle \]
\[ = -\frac{1}{2} (m_0 c^2) \left\{ \langle \psi_{100} \vert \hat{H}_1 \phi \vert \psi_{100} \rangle - \langle \psi_{100} \vert \hat{V} \psi_{100} \rangle \right\} \]
\[ - \langle \psi_{100} \vert \hat{V} \psi_{100} \rangle + \langle \psi_{100} \vert V^2 \psi_{100} \rangle \]
\[ = -\frac{1}{2} \frac{(m_0 c^2)}{m_0 c^2} \left\{ \langle \psi_{100} \vert \hat{H}_1 \psi_{100} \rangle - \langle \psi_{100} \vert \hat{V} \psi_{100} \rangle \right\} \]
\[ = -\frac{1}{2} \frac{(m_0 c^2)}{m_0 c^2} \left\{ \psi_{100} \rangle \langle \hat{H}_1 \psi_{100} \rangle - \psi_{100} \rangle \langle \hat{V} \psi_{100} \rangle \right\} \]
\[ = -\frac{1}{2} \frac{(m_0 c^2)}{m_0 c^2} \left\{ E_1 - 2 E_1 \langle \psi_{100} \vert \hat{V} \psi_{100} \rangle + \frac{e^4}{(4\pi\epsilon_0)^2} \langle \psi_{100} \vert V^2 \psi_{100} \rangle \right\} \]
Note: from the virial theorem \( \langle \psi | V | \psi \rangle = -2 \langle \psi | T | \psi \rangle \)

or \( \langle E \rangle = \langle T \rangle + \langle V \rangle = \frac{1}{2} \langle V \rangle \) and so

\[
\Delta E^{(1)} = \frac{-1}{2 m_0 c^2} \left\{ E_1^2 - 2 E_1 \left( 2 E_1 + \frac{e^4}{(4 \pi \epsilon_0)^2} \langle \psi_{100} | \frac{1}{r^2} | \psi_{100} \rangle \right) \right\}
\]

and using \( \psi_{100} = \frac{1}{\pi a_0} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \)

\[
\langle \psi_{100} | \frac{1}{r^2} | \psi_{100} \rangle = \int_0^\infty r^2 dr \int_0^{2\pi} d\theta \int_0^\pi d\varphi \sin \varphi d\varphi \left( \frac{1}{r a_0} \right)^3 e^{-2r/a_0} \frac{1}{r^2}
\]

\[
= \frac{4\pi}{\pi} \frac{1}{a_0^3} \int_0^\infty dr \ e^{-2r/a_0}
\]

\[
= \frac{4}{a_0^3} \left( \frac{a_0}{2} \right) e^{-2r/a_0} \bigg|_0^\infty = \left( \frac{2}{a_0^2} \right)
\]

and

\[
\frac{e^4}{(4 \pi \epsilon_0)^2} \langle \frac{1}{r^2} \rangle = \frac{2}{\pi} \left( \frac{e^2}{a_0} \right)^2 = 2 \left( \frac{e^2}{a_0} \right)^2
\]

\[
\Delta E^{(1)} = \frac{-1}{2 m_0 c^2} \left\{ E_1^2 - 4 E_1^2 + 8 E_1^2 \right\}
\]

\[
= - \frac{E_1^2}{m_0 c^2} \left( \frac{5}{2} \right)
\]

Since \( E_1 = \frac{-1}{\sqrt{\epsilon_0}} \frac{e^2}{2a_0} \) and \( \alpha = \frac{e^2}{4 \pi \epsilon_0 \hbar c} \) and \( a_0 = \frac{4 \pi \epsilon_0 k^2}{m_0 e^2} \)

Then

\[
\frac{E_1}{m_0 c^2} = -\frac{\alpha}{2} \frac{c}{2a_0 m_0 c^2} = -\frac{\alpha}{2} \frac{e^2}{4 \pi \epsilon_0 \hbar c} = -\frac{\alpha^2}{2}
\]

or

\[
\Delta E^{(1)} = E_1 \frac{\alpha^2}{4}
\]

where \( \alpha \) is the fine structure constant

\[
\alpha \approx \frac{1}{137}
\]
Consider the following Hamiltonian

\[ H = \frac{p^2}{2m} + \frac{1}{2} k x^2 + \frac{1}{2} k' x'^2 \]

Obviously this is just the harmonic oscillator with a spring constant \( k_{\text{eff}} = k + k' \) and therefore the eigenstates and eigenvalues can be written as

\[ \psi_n(x) = N_n e^{-\alpha x^2/2} H_n(\alpha x) \quad \text{where} \quad \alpha = \left( \frac{m k_{\text{eff}}}{\hbar} \right)^{1/4} = \left( \frac{m k_{\text{eff}}}{\hbar} \right)^{1/2} \]

with energies \( E_n = (n + \frac{1}{2}) \hbar \omega_{\text{eff}} = \hbar \left( \frac{k_{\text{eff}}}{m} \right)^{1/2} (n + \frac{1}{2}) \)

Let us try to solve this problem using perturbation theory in which we assume that \( k' \ll k \) and

\[ H_0 = \frac{p^2}{2m} + \frac{1}{2} k x^2 \quad \text{with eigenstates} \quad \psi_n^0(x) = \psi_n(x) \]

where \( E_n^0 = (n + \frac{1}{2}) \hbar \omega = \hbar \left( \frac{k}{m} \right)^{1/2} (n + \frac{1}{2}) \). The energy of the \( n^{th} \) state is given by.

\[ E_n = E_n^0 + \langle \psi_n^0 | H | \psi_n^0 \rangle + \sum_{\ell \neq n} \frac{|\langle \psi_n^0 | H | \psi_{n} \rangle|^2}{(E_n^0 - E_{\ell}^0)} \]

where \( H_1 = \frac{1}{2} k' x'^2 \) using the raising and lowering operators

\[ x = \left( \frac{\hbar}{2m \omega} \right)^{1/2} (a + a^+) \quad \frac{1}{2} k' x'^2 = \frac{k' \hbar}{2m \omega} (aa + a^+a + aa^+ + a^+a^+) \]

\[ \langle n | \frac{1}{2} k' x'^2 | \ell \rangle = \frac{1}{4} \frac{k' \hbar}{k} \langle n | (aa + a^+a + aa^+ + a^+a^+) | \ell \rangle \]

\[ a | n \rangle = \sqrt{n} | n-1 \rangle \quad a^+ | n \rangle = \sqrt{n+1} | n+1 \rangle \]

\[ \langle n | aa | \ell \rangle = (\ell (\ell - 1))^{1/2} \delta_{n \ell -2} \quad \langle n | a^+ a^+ | \ell \rangle = (\ell (\ell + 1))^{1/2} \delta_{n \ell +2} \]

\[ \langle n | a^+ a + aa^+ | \ell \rangle = \left( [\ell^2]^{1/2} + [\ell (\ell + 1)]^{1/2} \right) \delta_{n \ell} \]
\[ \langle \psi_n^0 | \hat{H}, | \psi_n^0 \rangle = \frac{i}{4} \mathcal{E}_k' \omega (2n+1) \]

\[ \langle \psi_n^2 | \hat{H}, | \psi_n^0 \rangle = \frac{1}{4} \mathcal{E}_k \left[ \left( \frac{n(n-1)}{2} \right)^{1/2} s_{n-2} + \left[ (n+1)(n+2) \right]^{1/2} s_{n+2} \right] \quad \text{for } n \geq 2 \]

\[
\sum_{\ell \neq n} \left| \frac{\langle \psi_\ell^0 | \hat{H}, | \psi_n^0 \rangle}{(E_n^0 - E_\ell^0)} \right|^2 = \left( \frac{1}{4} \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right)^2 \left\{ \frac{n(n-1)}{(n+1/2)^2 \mathcal{E}_k - (n-2+1/2)^2 \mathcal{E}_k} + \frac{(n+1)(n+2)}{(n+1/2)^2 \mathcal{E}_k - (n+2+1/2)^2 \mathcal{E}_k} \right\}
\]

\[
= \frac{1}{16} \left( \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right)^2 \omega^2 \mathcal{E}_k^2 \left[ \begin{array}{c} n(n-1) - (n+1)(n+2) \end{array} \right]
\]

\[
= -\frac{1}{32} \left( \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right)^2 \mathcal{E}_k \left[ 4n + 2 \right]
\]

\[
= -\frac{1}{8} \left( \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right)^2 \mathcal{E}_k \left( n + \frac{1}{2} \right)
\]

So that

\[ E_\ell = \mathcal{E}_k \left( n + \frac{1}{2} \right) + \mathcal{E}_k \left( n + \frac{1}{2} \right) \frac{1}{2} \left( \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right) - \mathcal{E}_k \left( n + \frac{1}{2} \right) \frac{1}{8} \left( \frac{\mathcal{E}_k'}{\mathcal{E}_k} \right)^2 \]

This can be seen as an expansion of the true energy

\[ E_\ell = \mathcal{E}_k \left( n + \frac{1}{2} \right) = \mathcal{E}_k \left( \frac{k+k'}{m} \right) \left( n + \frac{1}{2} \right) = \mathcal{E}_k \left( 1 + \frac{k'}{\mathcal{E}_k} \right)^{1/2} \left( n + \frac{1}{2} \right) \]

\[
= \mathcal{E}_k \left( n + \frac{1}{2} \right) \left[ 1 + \frac{1}{2} \left( \frac{k'}{\mathcal{E}_k} \right) + \frac{1}{2} \left( \frac{k'}{\mathcal{E}_k} \right)^2 + \cdots \right]
\]

\[
= \mathcal{E}_k \left( n + \frac{1}{2} \right) \left[ 1 + \frac{1}{2} \left( \frac{k'}{\mathcal{E}_k} \right) - \frac{1}{8} \left( \frac{k'}{\mathcal{E}_k} \right)^2 + \cdots \right]
\]
Similarly, the corrections to the wave function can be written as $n \geq 2$

$$|E_n\rangle = |E_n^0\rangle + \sum_{k \neq n} \frac{\langle E_k^0 | H | E_n^0 \rangle}{E_n^0 - E_k^0} |E_k^0\rangle$$

$$= |E_n^0\rangle + \frac{1}{4} \left( \frac{k'}{k} \right)_{kW} \left[ n(n-1) \right]^{1/2} |E_{n-2}\rangle$$

$$- \frac{1}{4} \left( \frac{k'}{k} \right)_{kW} \left[ (n+1)(n+2) \right]^{1/2} |E_{n+2}\rangle$$

$$|E_n\rangle = |E_n^0\rangle + \frac{1}{8} \left( \frac{k'}{k} \right)^2 \left[ [n(n-1)]^{1/2} |E_{n-2}\rangle - [(n+1)(n+2)]^{1/2} |E_{n+2}\rangle \right]$$

To compare this to the exact result we must expand

$$\Psi_n(x) = N_n e^{-\alpha^2 x^2/2} H_n(\alpha x) \quad \text{where} \quad \alpha = \left( \frac{m k_{\text{eff}}}{\hbar^2} \right)^{1/2} \quad N_n = \left( \frac{\alpha}{\sqrt{n!}} \right)^{1/2}$$

where $k_{\text{eff}} = k + k'$. Expanding in a Taylor's sense,

$$|\Psi_n(x)\rangle = |\Psi_n^0\rangle + \left( \frac{\partial \Psi_n}{\partial k'} \right)_{k'=0} k' \quad \text{and so}$$

$$\left( \frac{2 \Psi_n^0}{\partial k'} \right) = \left( \frac{\partial N_n}{\partial k'} \right) e^{-\alpha^2 x^2} H_n(\alpha x) = \frac{z \alpha^2 x^2}{2} N_n e^{-\alpha^2 x^2} H_n(\alpha x) \frac{\partial x}{\partial k'}$$

$$+ N_n e^{-\alpha^2 x^2} H_n''(\alpha x) \frac{\partial x}{\partial k'}$$

$$\frac{\partial N_n}{\partial k'} = \frac{1}{2} \alpha N_n \frac{\partial x}{\partial k'} = \frac{1}{2} \alpha N_n \frac{1}{k_{\text{eff}}} \frac{1}{k_{\text{eff}}} \frac{1}{k_{\text{eff}}} = \frac{1}{8} N_n$$

$$H_n'(\alpha x) = 2n H_{n-1}(\alpha x) = \frac{2n}{2 \alpha x} \left[ H_n(\alpha x) + z \partial H_n(\alpha x) \right]$$
\[ \chi^2 H_\alpha (\lambda x) = \frac{\chi}{2 \kappa} \left[ H_{\alpha + 1} (\lambda x) + 2 \alpha H_{\alpha} (\lambda x) \right] \]

\[ = \left( \frac{1}{2\alpha} \right)^2 \left[ H_{\alpha + 2} (\lambda x) + 2(\alpha + 1) H_{\alpha} (\lambda x) \right. \]
\[ \left. + 2 \alpha \left( H_{\alpha} (\lambda x) + 2(\alpha - 1) H_{\alpha - 2} (\lambda x) \right) \right] \]

\[ = \left( \frac{1}{2\alpha} \right)^2 \left[ H_{\alpha + 2} (\lambda x) + (4 \alpha + 2) H_{\alpha} (\lambda x) + 4 \alpha(\alpha - 1) H_{\alpha - 2} (\lambda x) \right] \]

\[ \left( \frac{\partial H_{\alpha}}{\partial \kappa^2} \right)_{\kappa = 0} = \frac{\kappa}{4 \kappa} e^{-\kappa^2 x^2} \left[ \frac{1}{2 \alpha} H_{\alpha} (\lambda x) - \frac{1}{2 \kappa} \left[ H_{\alpha + 2} (\lambda x) + (4 \alpha + 2) H_{\alpha} (\lambda x) \right. \right. \]
\[ \left. \left. + 4 \alpha(\alpha - 1) H_{\alpha - 2} (\lambda x) \right] + \frac{2 \alpha}{2 \alpha} \left[ H_{\alpha} (\lambda x) + 2(\alpha - 1) H_{\alpha - 2} (\lambda x) \right] \right] \]

\[ = \frac{N_\alpha}{8 \kappa} e^{-\kappa^2 x^2} \left[ - \frac{1}{2} H_{\alpha + 2} (\lambda x) + 2 \alpha(\alpha - 1) H_{\alpha - 2} (\lambda x) \right] \]

but \( N_\alpha = \left( \frac{\alpha}{\sqrt{\pi} 2^{\alpha} \alpha!} \right)^{1/2} \) and so

\[ N_{\alpha + 2} = \left( \frac{\alpha}{\sqrt{\pi} 2^{\alpha + 2} (\alpha + 2)!} \right)^{1/2} = \frac{N_\alpha}{2 \sqrt{\alpha + 1} \alpha + 1} \]

\[ N_{\alpha - 2} = \left( \frac{\alpha}{\sqrt{\pi} 2^{\alpha - 2} (\alpha - 2)!} \right)^{1/2} = \frac{N_\alpha}{2 \sqrt{\alpha - 1} \alpha - 1} \]

\[ \left( \frac{\partial H_{\alpha}}{\partial \kappa^2} \right)_{\kappa = 0} = \frac{1}{8 \kappa} e^{-\kappa^2 x^2} \left[ - \frac{1}{2} \sqrt{\alpha + 1} \alpha + 1 H_{\alpha + 2} (\lambda x) + \frac{N_\alpha}{2 \sqrt{\alpha - 1} \alpha - 1} H_{\alpha - 2} (\lambda x) \right] \]

which gives

\[ |E_n\rangle = |E_0\rangle + \frac{1}{8} (\kappa / \kappa) \left[ - \sqrt{\alpha + 1} \alpha + 1 |E_{\alpha + 2}\rangle + \sqrt{\alpha - 1} \alpha - 1 |E_{\alpha - 2}\rangle \right] \]

which is our previous result.
How does one deal with states which are initially degenerate?

2.B. Rigid Rotator

\[ \psi_0 = \frac{1}{2} \frac{k^2}{I} \]

has eigenfunctions \( |k, m\rangle \equiv \psi_n(r, \theta, \phi) \) with energy eigenvalues \( E_k = \frac{k^2 l(l+1)}{2I} \) which does not depend upon the values of \( m \). Therefore each energy eigenstate is \( 2l+1 \) degenerate. In the development of the normal (non-degenerate) perturbation series we implicitly assumed that all states are non-degenerate.

To develop a new formalism denote the energy eigenstates of \( \psi_0 \) by

\[ |E_n, \alpha\rangle \]

where \( \alpha \) denotes the \( \alpha \)th degenerate eigenstate with energy \( E_n^0 \).

\[ \psi_0 |E_n, \alpha\rangle = E_n^0 |E_n, \alpha\rangle \]

and

\[ \langle E_n^0, \alpha | E_m^0 \rangle = \delta_{nm} \delta_{\alpha \alpha} \]

We have already used the Gram-Schmidt procedure to give us an orthogonal set.

Again we perturb \( \psi_0 \) by \( \psi \), and we are looking for solutions of the problem

\[ \psi |E_n\rangle = E_n |E_n\rangle \]

where \( \psi = \psi_0 + \psi \).

This time try expanding \( |E_n\rangle \) in terms of a complete set of states (which is always possible)

\[ |E_n\rangle = \sum_{m, \alpha} C_{n, \alpha} |E_m^0, \alpha\rangle \]

in general both indices are involved.

Upon Substitution up to \( \psi |E_n\rangle = E_n |E_n\rangle \) we get.
\[ \rho \left| \text{En} \right\rangle = \sum_{m, \alpha} \left( \rho_{m, \alpha} \right) C_{m, \alpha} \left( 1 \right) \text{En} \alpha \rangle = \text{En} \sum_{m, \alpha} C_{m, \alpha} \left( 1 \right) \text{En} \alpha \rangle \]

\[ = \sum_{m, \alpha} C_{m, \alpha} \left\{ E_{m, \alpha} \left( 1 \right) \text{En} \alpha \rangle + \rho \left( 1 \right) \text{En} \alpha \rangle \right\} = \text{En} \sum_{m, \alpha} C_{m, \alpha} \left( 1 \right) \text{En} \alpha \rangle \]

Taking the inner product with \( \langle E_k^0 \rangle \) we find:

\[ \sum_{m, \alpha} C_{m, \alpha} \left\{ E_{m, \alpha} \langle E_k^0 | 1 \rangle \text{En} \alpha \rangle + \langle E_k^0 | \rho \rangle \text{En} \alpha \rangle \} = \text{En} \sum_{m, \alpha} C_{m, \alpha} \langle E_k^0 | 1 \rangle \text{En} \alpha \rangle \]

\[ \sum_{k, m, \alpha} \delta_{km} \delta_{\alpha k} \]

\[ C_{k, \beta} E_k^0 + \sum_{m, \alpha} C_{m, \alpha} \langle E_k^0 \rangle \rho \left| \text{En} \alpha \rangle \right\rangle = \text{En} C_{k, \beta} \]

or

\[ \rightarrow C_{k, \beta} \left( \text{En} - E_k^0 \right) = \sum_{m, \alpha} C_{m, \alpha} \left( \langle E_k^0 \rangle \right) \rho \left| \text{En} \alpha \rangle \right\rangle \]

Now if as before \( \rho \) is "small" then I might expect to find the corrections to \( \alpha \)th order by ignoring \( \rho \) on the RHS. i.e.

\[ C_{k, \beta} \left( \text{En} - E_k^0 \right) \rightarrow 0 \]

Since for \( \rho \rightarrow 0 \) I expect \( E_{k, \beta} E_k^0 \) we can say that

For \( k = n \) All \( C_{n, \beta} \) will be non-zero (for all \( \beta \))

\[ E_n = E_n^0 \]

For \( k \neq n \) \( C_{k, \beta} = 0 \)

Again we can use this \( m \)th order result to get a \( 1 \)st order correction by subst. the above \( m \)th order result in our master equation *
Substituting $C_{n\beta} = 0$ for all $m \neq n$ we have:

$$C_{k\beta}(E_n - E_n) = \sum_{\alpha} C_{n\alpha} \langle E_k^\beta | \psi_n | E_n \alpha \rangle$$

Examining the particular case for $k = n$

$$C_{n\beta}(E_n - E_n) = \sum_{\alpha} C_{n\alpha} \langle E_n^\beta | \psi_n | E_n \alpha \rangle$$

the equation resembles our matrix formulation of $H$. i.e.

$$\sum_{\alpha} C_{n\alpha} \left[ \langle E_n^\beta | \psi_n + \psi_n | E_n \alpha \rangle - E_n \delta_{n\beta} \right] = 0$$

or

$$\begin{bmatrix}
E_n^0 + \langle \psi_1 \rangle_{11} - E_n & \langle \psi_1 \rangle_{12} & \cdots \\
\langle \psi_1 \rangle_{21} & E_n^0 + \langle \psi_1 \rangle_{22} - E_n & \cdots \\
\langle \psi_1 \rangle_{31} & \langle \psi_1 \rangle_{32} & \cdots \\
\langle \psi_1 \rangle_{41} & & & \\
\vdots & & & \\
\end{bmatrix}
\begin{bmatrix}
C_{n1} \\
C_{n2} \\
C_{n3} \\
\vdots \\
\end{bmatrix} = 0$$

This matrix equation can be solved in the standard fashion by taking the determinant and setting it equal to zero.

Although it may seem as if we are just diagonalizing the original $H$ Hamiltonian, we are making a great simplification by restricting our diagonalization to only the degenerate wavefunctions!

Thus to first order, the perturbation selects from the set of degenerate eigenfunctions those linear combinations which best suit it.
Our example problem was \( \mathfrak{H}_0 = \frac{1}{2} \mathbf{p}^2 \) with \( E_\epsilon = \frac{k^2 \ell(\ell+1)}{2 I} = \epsilon_\ell \)
and has therefore degenerate eigenfunctions.

\[
\begin{array}{cccccccc}
Y_0^0 & Y_1^0 & Y_1^{-1} & Y_2^1 & Y_2^{-1} & Y_2^0 \\
Y_0^0 & \epsilon_0 & 0 & 0 & 0 & 0 & \rightarrow \\
Y_1^0 & 0 & \epsilon_1 \\
Y_1^{-1} & 0 & 0 & \epsilon_1 \\
Y_2^1 & & & & \epsilon_2 \\
Y_2^{-1} & & & & \epsilon_2 \\
Y_2^0 & & & & & \epsilon_2 \\
\end{array}
\]

Now if we introduce a perturbation of the form

\[
\mathfrak{H}_1 = 4\pi V_0 \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_2)
\]

we obtain the following matrix elements of \( \mathfrak{H} = \mathfrak{H}_0 + \mathfrak{H}_1 \).
\[
\begin{align*}
\mathbf{H} &= \mathbf{H}_0 + \mathbf{H}_1 + \frac{L}{2I} + \frac{1}{I}\pi V_0 \mathbf{d}(\theta - \pi \xi_4) \mathbf{d}(\phi - \pi \xi_4).
\end{align*}
\]

\[\begin{array}{cccccccc}
Y_0^0 & Y_0^1 & Y_1^0 & Y_1^1 & Y_2^0 & Y_2^1 & Y_2^2 & Y_2^3 \\
\varepsilon_0 + V_0 & -\frac{3}{4} \sqrt{2} e^{i\pi/4} & 0 & \frac{1}{4} \sqrt{2} e^{-i\pi/4} & 0 & -\frac{1}{4} \sqrt{2} e^{i\pi/4} & 0 & -\frac{1}{4} \sqrt{2} e^{-i\pi/4} \\
-\frac{3}{4} \sqrt{2} e^{-i\pi/4} & e_1 + \frac{3}{2} V_0 & 0 & -\frac{1}{2} e^{-i\pi/4} V_0 & -\frac{3}{4} \sqrt{2} e^{i\pi/4} V_0 & 0 & -\frac{1}{4} \sqrt{2} e^{-i\pi/4} V_0 & 0 \\
0 & 0 & e_1 + 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{3}{4} \sqrt{2} e^{i\pi/4} & -\frac{3}{4} \sqrt{2} e^{-i\pi/4} & 0 & e_1 + \frac{3}{2} V_0 & -\frac{1}{4} \sqrt{2} e^{i\pi/4} V_0 & 0 & -\frac{1}{4} \sqrt{2} e^{-i\pi/4} V_0 & 0 \\
\frac{1}{4} \sqrt{2} e^{-i\pi/4} & e_2 + \frac{1}{2} V_0 & 0 & \frac{1}{4} \sqrt{2} e^{i\pi/4} V_0 & e_2 + \frac{15}{8} V_0 & 0 & -\frac{1}{4} \sqrt{2} e^{-i\pi/4} V_0 & 0 \\
0 & 0 & 0 & 0 & 0 & e_2 + 0 & 0 & 0 \\
\frac{1}{2} \sqrt{2} V_0 & -\frac{1}{8} \sqrt{2} e^{i\pi/4} V_0 & 0 & -\frac{1}{8} \sqrt{2} e^{-i\pi/4} V_0 & -\frac{1}{8} \sqrt{2} e^{i\pi/4} V_0 & 0 & e_2 + \frac{3}{4} V_0 & 0 \\
\end{array}\]

where \(\xi_L = \frac{l(l+1)\hbar^2}{2I}.\)
To proceed with degenerate perturbation theory, we might be interested in determining the change in energy of the $l=1$ eigenfunctions. We therefore take the $l=1$ submatrix and diagonalize it:

$$
\begin{bmatrix}
\varepsilon_1 + \frac{3}{2} V_0 & 0 & +\frac{3}{2} i V_0 \\
0 & \varepsilon_1 & 0 \\
-\frac{3}{2} i V_0 & 0 & \varepsilon_1 + \frac{3}{2} V_0
\end{bmatrix}
$$

\[\Downarrow\]

$$
\begin{bmatrix}
\varepsilon_1 + \frac{3}{2} V_0 - E_1 & 0 & +\frac{3}{2} i V_0 \\
0 & \varepsilon_1 - E_1 & 0 \\
-\frac{3}{2} i V_0 & 0 & \varepsilon_1 + \frac{3}{2} V_0 - E_1
\end{bmatrix}
$$

$$(\varepsilon_1 + \frac{3}{2} V_0 - E_1)^2 (\varepsilon_1 - E_1) - \frac{9}{4} V_0^2 (\varepsilon_1 - E_1) = 0$$

$$(\varepsilon_1 - E_1)\left[ (\varepsilon_1 + \frac{3}{2} V_0 - E_1) - \frac{9}{4} V_0^2 \right] = 0$$

Three solutions:

$\varepsilon_1$: \(\varepsilon_1\) (no change)

$\varepsilon_1$: \(\varepsilon_1 + \frac{3}{2} V_0 \pm \frac{3}{2} V_0 = \varepsilon_1, \varepsilon_1 + 3 V_0\)

Substituting this back into our matrix we can find our new eigenfunctions.

$$\varepsilon_1 = \varepsilon_1$$

$$
\begin{bmatrix}
\varepsilon_1 + \frac{3}{2} V_0 - \varepsilon_1 & 0 & +\frac{3}{2} i V_0 \\
0 & \varepsilon_1 - \varepsilon_1 & 0 \\
-\frac{3}{2} i V_0 & 0 & \varepsilon_1 + \frac{3}{2} V_0 - \varepsilon_1
\end{bmatrix}
\begin{bmatrix}
a \\
b \\
c
\end{bmatrix} = 0
$$
$$\begin{bmatrix}
\frac{3}{2} V_0 & 0 & +\frac{3}{2} i V_0 \\
0 & 0 & 0 \\
-\frac{3}{2} i V_0 & 0 & \frac{3}{2} V_0
\end{bmatrix}\begin{bmatrix} a \\ b \\ c \end{bmatrix} = \frac{3}{2} V_0 \begin{bmatrix} a + i c \\ 0 \\ -i a + c \end{bmatrix} = 0$$

Two solutions:

\begin{align*}
a - c &= 0 \quad b = 1 \\
a &= 1, \quad c = i \quad b = 0 \quad \Rightarrow \quad \psi_1 &= \frac{1}{\sqrt{2}} (Y_1' + i Y_1^{-1}) \end{align*}

and for $E_1 = E_1 + 3V_0$

$$\begin{bmatrix}
-\frac{3}{2} V_0 & 0 & \frac{3}{2} i V_0 \\
0 & -3 V_0 & 0 \\
-\frac{3}{2} i V_0 & 0 & -\frac{3}{2} V_0
\end{bmatrix}\begin{bmatrix} a \\ b \\ c \end{bmatrix} = \frac{3}{2} V_0 \begin{bmatrix} -a + i c \\ -2 b \\ -i a - c \end{bmatrix} = 0$$

\begin{align*}
b &= 0 \\
a &= 1, \quad c = -i \\
\psi_3 &= \frac{1}{\sqrt{2}} (Y_1' - i Y_1^{-1}).\end{align*}

\[\psi_1 = Y_1^0 = \frac{1}{\sqrt{2}} \sqrt{\frac{3}{\pi}} \cos \psi \]

\[\psi_2 = \frac{1}{\sqrt{2}} (Y_1' + i Y_1^{-1}) = \frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2 \pi}} \right) \sin \psi \left( -e^{-i \phi} + i e^{-i \phi} \right) \]

\[= \frac{1}{\sqrt{2}} \left( \frac{3}{\pi} \right) \sqrt{\frac{3}{\pi}} \sin \psi e^{i \pi/4} \left[ -e^{-i (\psi - \pi/4)} + e^{-i (\psi - \pi/4)} \right] \]

\[\psi_2 = -i \left( \frac{3}{\pi} \right) \sqrt{\frac{3}{\pi}} \sin \psi e^{i \pi/4} \sin (\psi - \pi/4) \]

Similarly:

\[\psi_3 = -i \left( \frac{3}{\pi} \right) \sqrt{\frac{3}{\pi}} \sin \psi e^{i \pi/4} \cos (\psi - \pi/4) \]
So our perturbing Hamiltonian $f_1 = 4\pi V_0 \delta (y - \pi/2) \delta (\phi - \pi/4)$ has a large contribution to eigenfunctions with a finite value at $\phi = \pi/4$ and $y = \pi/4$.

One initial degenerate state $\psi_0$ is unaffected by $f_1$, as it has a node at $\phi = \pi/2, y = \pi/2$. But the other two $\psi_1, \psi_1^*$ both have non-zero values but neither takes advantage of the symmetry of the perturbation (both are cylindrical symmetric).

In fact the new eigenfunctions $\psi_2$ and $\psi_3$ show the broken symmetry:

$\psi_2 \propto \sin(\phi - \pi/4)$ has a node at $\phi = \pi/4$ while

$\psi_3 \propto \cos(\phi - \pi/4)$ is max there. Thus the perturbation forces a choice among the degenerate states which has the correct symmetry for further work.

Having made this choice of linear combinations of the degenerate states, we can now proceed with non-degenerate perturbation theory.

The state $\psi_3$ is no longer degenerate with any other state, so

$$E_1^{(3)} = \epsilon_1 + \langle \psi_3 | f_1 | \psi_3 \rangle + \sum_{m \neq 0} \frac{|\langle m | f_1 | \psi_3 \rangle|^2}{\epsilon_1 - \epsilon_m}$$

Everything looks ok except for the denominator $\frac{1}{\epsilon_1 - \epsilon_m}$ in principle this will still diverge when I use the states $\psi_1$ or $\psi_2$. But since we have already chosen these to diagonalize $H_0 + f_1$, the matrix element in the numerator also vanishes giving zero contribution.
\[ \langle \psi_1, \phi, \psi_2 \rangle = 0 \quad \text{since } \cos(\frac{\pi}{2}) = 0 \]
\[ \langle \psi_3, \phi, \psi_2 \rangle = 0 \quad \text{since } \sin(\phi - \frac{\pi}{4}) \text{ vanishes at } \phi = \frac{\pi}{4}. \]

All other states have different energies and so the procedure works as before.

The same applies to the states \( \psi_1 \) and \( \psi_2 \). Although they are still degenerate, the matrix elements of \( \psi_1 \) between them vanish and so again we can use the non-degenerate formulae.
- Nearly Degenerate Levels.

If we have two states which are nearly degenerate initially, then we can show how these levels behave under a small perturbation.

Consider a set of states \( |E_1^o \rangle \) which are eigenstates of \( \hat{H} \) with energy \( E_1^o \) and that for \( m=1 \) and \( m=2 \) we have:

\[
E_1^o = E_0 + \epsilon \quad \text{and} \quad E_2^o = E_0 - \epsilon
\]

i.e. these states are nearly degenerate being separated by a small energy \( \epsilon \).

As before we can expand our true eigenstates in terms of the eigenstates of \( \hat{H}_0 \), i.e.

\[
|E_n \rangle = \sum_{\eta=1}^{\infty} C_\eta \ |E_\eta^o \rangle
\]

As before, sub. into \( \hat{H} |E_n \rangle = E_n |E_n \rangle \) we obtain

\[
C_k \ (E_n - E_k^o) = \sum_\eta C_\eta \ |E_\eta^o \rangle \langle \eta | \hat{H} \rangle \langle \hat{H} | E_k^o \rangle
\]

As with our discussion in the degenerate case, if \( E_n \approx E_0 \) then only \( C_{k=1} \) and \( C_{k=2} \) will be non-zero, whereas \( C_{\eta \neq 1,2} \) will be small of order \( \mathcal{O}(\epsilon^2) \). Continuing our discussion involves them diagonalizing the \( 2 \times 2 \) matrix corresponding to the state \( |E_1^o \rangle \) and \( |E_2^o \rangle \) which are nearly degenerate.
\[\begin{align*}
\alpha \left[ \begin{array}{cc}
E_0 + \epsilon + \langle \mathcal{H}_1 \rangle_{11} - E & \langle \mathcal{H}_1 \rangle_{12} \\
\langle \mathcal{H}_1 \rangle_{21} & E_0 - \epsilon + \langle \mathcal{H}_2 \rangle_{22} - E
\end{array} \right] \left[ \begin{array}{c}
c_1 \\
c_2
\end{array} \right] = 0.
\end{align*}\]

Setting the determinant to zero we have:

\[\begin{align*}
&[E_0 - \epsilon + \langle \mathcal{H}_1 \rangle_{11} - E][E_0 + \epsilon + \langle \mathcal{H}_2 \rangle_{22} - E] - |\langle \mathcal{H}_1 \rangle_{12}|^2 = 0 \\
&[E_0 - E - \epsilon + \langle \mathcal{H}_1 \rangle_{11}][E_0 - E + \epsilon + \langle \mathcal{H}_2 \rangle_{22}] - |\langle \mathcal{H}_1 \rangle_{12}|^2 = 0 \\
&(E_0 - E)^2 + (E_0 - E)[\langle \mathcal{H}_1 \rangle_{11} + \langle \mathcal{H}_2 \rangle_{22}] + \langle \mathcal{H}_2 \rangle_{22} \langle \mathcal{H}_1 \rangle_{11} + \\
&- 4\epsilon (\langle \mathcal{H}_1 \rangle_{11} - \langle \mathcal{H}_1 \rangle_{22}) - \epsilon^2 - |\langle \mathcal{H}_1 \rangle_{12}|^2 = 0
\end{align*}\]

Solving for \(E\) we have:

\[E = E_0 \pm \frac{1}{2} \left[ \langle \mathcal{H}_1 \rangle_{11} + \langle \mathcal{H}_2 \rangle_{22} \right] \pm \frac{1}{2} \left\{ \frac{\langle \mathcal{H}_1 \rangle_{11} - \langle \mathcal{H}_1 \rangle_{22} + \epsilon}{2} \right\}^{1/2}
\]

or

\[E = E_0 \pm \frac{1}{2} \left[ \langle \mathcal{H}_1 \rangle_{11} + \langle \mathcal{H}_2 \rangle_{22} \right] \pm \frac{1}{2} \left\{ \langle \mathcal{H}_1 \rangle_{11} - \langle \mathcal{H}_1 \rangle_{22} + \epsilon \right\}^{1/2}
\]

or

\[E_{\pm} = \bar{E} \pm \left\{ \frac{\langle \mathcal{H}_1 \rangle_{11} + \langle \mathcal{H}_2 \rangle_{22} - \epsilon}{2} \right\}^{1/2} \left\{ \langle \mathcal{H}_1 \rangle_{11} - \langle \mathcal{H}_1 \rangle_{22} \right\}^{1/2}.
\]
Calling \( \Delta E = 2E \pm \langle \mathcal{H}_1 \rangle_{12} - \langle \mathcal{H}_1 \rangle_{22} \) then
\[
E_{\pm} = \bar{E} \pm \left\{ \left( \frac{\Delta E}{\bar{E}} \right)^2 + 4 \left| \langle \mathcal{H}_1 \rangle_{12} \right|^2 \right\}^{1/2}
\]

Thay as a function of \( \Delta E \) or effectively of \( \bar{E} \) we have.

Levels repel each other due to the coupling of the \( \mathcal{H}_1 \) perturbation. Only if \( \langle \mathcal{H}_1 \rangle_{12} \approx 0 \) will the two levels cross. (usually up cases a symmetry.)
VARIATIONAL CALCULATION

Given \( \mathcal{H} \) with eigenfunctions \( |4n\rangle \) which form an orthonormal basis. with \( \mathcal{H}|4n\rangle = E_n|4n\rangle \) and \( E_0 < E_n \) the ground state. (Spectrum must be bounded from below).

Then any arbitrary \( |4\rangle \) can be expanded in the basis:

\[
|4\rangle = \sum_{j} c_j |4_j\rangle
\]

The expectation value of \( \mathcal{H} \) for \( |4\rangle \) is then just

\[
\frac{\langle 4 | \mathcal{H} | 4 \rangle}{\langle 4 | 4 \rangle} = \frac{\sum_j E_j |c_j|^2}{\sum_j |c_j|^2}
\]

but since \( E_j \geq E_0 \) we have:

\[
\frac{\langle 4 | \mathcal{H} | 4 \rangle}{\langle 4 | 4 \rangle} = \frac{\sum E_0 |c_j|^2}{\sum |c_j|^2} = E_0
\]

Thus, any arbitrary state \( |4\rangle \) has an energy expectation value which is greater than or equal to the ground state energy.

We take advantage of this by choosing a state \( |4\rangle \) with variational parameter one can minimize \( \langle E \rangle \) to obtain a rigorous upper bound for \( E_0 \).
Example: Anharmonic Oscillator \[ \psi = \frac{p^2}{2m} + \lambda x^4. \]

To obtain a guess for the ground state consider the dependence of \( \psi(x) \) at large \( x \):

\[ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \lambda \psi(x) = E \psi(x) \] becomes:

\[ \frac{d^2 \psi(x)}{dx^2} = \frac{2m \lambda}{\hbar^2} x^4 \psi(x). \]

If \( \psi(x) = Ae^{-x^n} \), then

\[ \frac{\partial \psi}{\partial x} = A(-nx^{n-1})e^{-x^n}, \]

\[ \frac{\partial^2 \psi}{\partial x^2} = A(n^2x^{2n-2} - n(n-1)x^{n-2})e^{-x^n} \]

\[ = (n^2x^{2n-2} - n(n-1)x^{n-2})\psi(x). \]

Therefore \( n = 3 \) and our trial wavefunction should be

\[ \psi(x) = Ae^{-\frac{8|x|^3}{3}}. \]

Unfortunately the necessary integrals cannot be done analytically so we choose to use instead:

\[ \psi(x) = Ae^{-\frac{\sqrt{2}\pi}{2}x^2}. \]

Then \[ \langle 4\mid \psi \mid 4 \rangle = \langle 4\mid \frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \lambda x^4 \mid 4 \rangle. \]

\[ \frac{\partial \psi}{\partial x} = A(-x)e^{-\frac{\sqrt{2}\pi}{2}x^2}. \]

\[ \frac{\partial^2 \psi}{\partial x^2} = A(-x^2 + x^2)e^{-\frac{\sqrt{2}\pi}{2}x^2}. \] and.
\[
\langle \psi | -\frac{k^2}{2m} \frac{\partial^2}{\partial x^2} | \psi \rangle = -\frac{k^2}{2m} |A|^2 \left\{ -\alpha (\frac{\pi}{\alpha^2})^\frac{1}{2} + \frac{\alpha^2}{2} \left( \frac{\pi}{\alpha^3} \right)^\frac{1}{2} \right\}
\]

Since
\[
\int_{-\infty}^{\infty} dx x^n e^{-\alpha x^2} = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^n \alpha^n} \left( \frac{\pi}{\alpha^2} \right)^\frac{n}{2}
\]

\[
\langle \psi | -\frac{k^2}{2m} \frac{\partial^2}{\partial x^2} | \psi \rangle = -\frac{k^2}{2m} |A|^2 \left\{ -(\alpha \pi)^\frac{1}{2} + \frac{1}{2} (\alpha \pi)^\frac{1}{2} \right\}
\]

\[
= \frac{k^2}{4m} (\alpha \pi)^\frac{1}{2} |A|^2
\]

\[
\langle \psi | xx^4 | \psi \rangle = \frac{\lambda |A|^2}{4 \alpha^2} (\frac{\pi}{\alpha})^\frac{1}{2}
\]

\[
\langle \psi | \psi \rangle = |A|^2 (\frac{\pi}{\alpha})^\frac{1}{2}
\]

\[
\langle E \rangle = \frac{\langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{k^2}{2m} (\alpha \pi)^\frac{1}{2} |A|^2 + \frac{\lambda |A|^2 (\pi/\alpha)^\frac{1}{2}}{|A|^2 (\pi/\alpha)^\frac{1}{2}} (3/4 \alpha^2)
\]

\[
\langle E \rangle = \frac{k^2}{2m} \alpha + \frac{3 \lambda}{4} \alpha^2
\]

\[
\frac{d\langle E \rangle}{d\alpha} = \frac{k^2}{2m} - \frac{3 \lambda}{4} \alpha^2 = 0 \text{ or } \alpha^2 = \frac{6 \lambda m}{k^2}
\]

\[
\alpha = \left( \frac{6 \lambda m}{k^2} \right)^\frac{1}{2} \text{ minimizes the energy.}
\]
Substituting into the expression for $\langle E \rangle$,

$$\langle E \rangle = \frac{k^2}{4m} \left( \frac{6 \lambda m}{k^2} \right)^{\frac{1}{3}} + \frac{3\lambda}{4} \left( \frac{6 \lambda m}{k^2} \right)^{-\frac{3}{2}}$$

$$= \lambda^{\frac{1}{3}} \left( \frac{k^2}{2m} \right)^{\frac{2}{3}} \left[ \frac{24}{4} + \frac{3}{4} \frac{1}{3} \right]$$

$$= \frac{3\lambda^{\frac{3}{2}}}{4} \lambda^{\frac{1}{3}} \left( \frac{k^2}{2m} \right)^{\frac{2}{3}} = 1.0817 \lambda^{\frac{1}{3}} \left( \frac{k^2}{2m} \right)^{\frac{2}{3}}.$$

Solving the problem numerically we obtain $E_{\text{ground state}} = 1.060 \lambda^{\frac{1}{3}} \left( \frac{k^2}{2m} \right)^{\frac{2}{3}}$.

Example #2.

Estimate the ground state of the infinite potential well of width $L$.

$V(x) = 0$ if $0 \leq x \leq L$

$V(x) = \infty$ outside.

Try $\psi(x) = x (L - x)$ Note: $\psi(x) = 0$ at $x=0$ and $x=L$

$$\langle \psi | \psi \rangle = \int_0^L \left| x(L-x) \right|^2 dx = \int_0^L dx \left( x^2 L^2 - 2x^3 L + x^4 \right)$$

$$= \left. \frac{x^3}{3} L^2 - \frac{X^4}{4} L + \frac{x^5}{5} \right|_0^L = L^5 \left( \frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right) = \frac{8}{30}.$$

$$\langle \psi | \hat{H} | \psi \rangle = \int_0^L x(L-x) \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] x(L-x) dx.$$

$$= \int_0^L \left( xL - x^2 \right) \frac{\hbar^2}{2m} = \left. \frac{\hbar^2}{2m} \left( \frac{xL^2}{2} - \frac{x^3}{3} \right) \right|_0^L$$

$$= \frac{\hbar^2}{2m} \frac{L^3}{6}.$$
\[ \langle E \rangle = \frac{\langle 4 \ 1 \ 2 \ 1 \ 4 \rangle}{\langle 4 \ 1 \ 4 \rangle} = \frac{k^2}{m} \frac{L}{L^2} > E_0 = \frac{k^2}{m} \left( \frac{\pi^2}{2L^2} \right) \]

Now to get a better estimate one could introduce a variation parameter such as \( \lambda \)

\[ \Psi(x) = x^\lambda (L^2 - x^2) \]

Now \( \langle E \rangle \) will depend on \( \lambda \).

Note: What if instead of \( x(L-x) \) we had chosen \( \Psi(x) = 1 \)

Then \( \langle 4 \ 1 \ 2 \ 1 \ 4 \rangle = 0 \) which means \( \langle E \rangle < E_0 \).

This particular guess does not satisfy the appropriate boundary conditions and therefore cannot be expanded in terms of the basis and invalidates the theory. If we had forces \( \Psi \to 0 \) at \( x=0,L \) then the large slopes would have increased the kinetic energy term to agree with our expectations of \( \langle E \rangle \geq E_0 \).

One can also use the variational technique to obtain estimates of higher states if there is sufficient symmetry in the problem's \( \Psi \).
For the case of the Anharmonic Oscillator $H$ commutes with the parity operator telling us that the eigenstates of $H$ have a definite parity. Therefore if the ground state has even parity, then by choosing a trial wavefunction which has odd parity we know that the trial wavefunction will be orthogonal to the ground state. In our expansion of the trial wavefunction then

$$|\psi_{\text{odd}}\rangle = \sum C_j |\psi_j\rangle$$

the ground state will not appear since $C_0 = \langle \psi_0 | \psi_{\text{odd}} \rangle \equiv 0$. If $|\psi_j\rangle$ has odd parity then we find that

$$\frac{\langle \psi_{\text{odd}} | H | \psi_{\text{odd}} \rangle}{\langle \psi_{\text{odd}} | \psi_{\text{odd}} \rangle} = \sum_{j=1}^{(\text{odd})} |C_j|^2 E_j \geq \sum_{j=1}^{(\text{odd})} |C_j|^2 E_j = E_1$$

Therefore $\langle E \rangle$ will be an upper bound for the first excited state.