Lecture by Prof. Tchrakian

Quantum Mechanics II

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Contents

1 Orbital angular momentum

1.1 Definition

$$\begin{aligned}
\vec{l} &= \vec{r} \times \vec{p} \\
l_x &= yp_z - zp_y \\
l_y &= zp_x - xp_z \\
l_z &= xp_y - yp_x
\end{aligned}$$

Canonical Quantisation:

$$\vec{l} \to \hat{\vec{l}} = \vec{L} \tag{1.1}$$

$$l_x \to L_x = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \tag{1.2}$$

$$l_y \to L_y = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \tag{1.3}$$

$$l_z \to L_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \tag{1.4}$$

It is obvious that $L_x^\dagger = L_x, L_y^\dagger = L_y, L_z^\dagger = L_z$

1.2 Commutation relations

Can all components of $\vec{L}$ be measured simultaneously? Find $[L_x, L_y], [L_y, L_z], [L_z, L_x]$:

$$\begin{aligned}
[L_x, L_y] f =&(-i\hbar)^2 \left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \left(z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z} \right) \right] - \\
&- (i\hbar)^2 \left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \left(y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y} \right) \right] \\
=&(-i\hbar)^2 \left[y\frac{\partial f}{\partial x} + yz\frac{\partial^2 f}{\partial z \partial x} - yx\frac{\partial^2 f}{\partial z \partial z} - z^2\frac{\partial^2 f}{\partial y \partial x} + zx\frac{\partial^2 f}{\partial y \partial z} \right] + \\
&(-i\hbar)^2 \left[-zy\frac{\partial^2 f}{\partial x \partial z} + z^2\frac{\partial^2 f}{\partial x \partial y} + xy\frac{\partial^2 f}{\partial z \partial z} - x\frac{\partial f}{\partial y} - xz\frac{\partial^2 f}{\partial z \partial y} \right] \\
=&(-i\hbar)^2 \left(y\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial y} \right) \\
=&i\hbar L_z f
\end{aligned}$$

$$[L_x, L_y] = i\hbar L_z \tag{1.5}$$
$$[L_y, L_z] = i\hbar L_x \tag{1.6}$$
$$[L_z, L_y] = i\hbar L_y \tag{1.7}$$

units: $[\vec{l}] = [\vec{r} \times \vec{p}] = LMLT^{-1} = ML^2T^{-1} = [\hbar]$

Commutation relations $\rightarrow$ no pair of components commute! i.e. only ONE component can be observed at a time, or: NO pair can be observed simultaneously. Contrast with linear momentum: $[p_x, p_y]\, f = (-i\hbar)^2 \left(\frac{\partial}{\partial x}\frac{\partial f}{\partial y} - \frac{\partial}{\partial y}\frac{\partial f}{\partial x}\right) = 0$

1.3 Choice of component

Criterion: reduce the eigenvalue equation to an ODE

Note. $L_x u = l_x u$ is a PDE

Solution: Go from Cartesian to spherical polar coordinates

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

$$L_x = i\hbar \left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi}\right) \tag{1.8}$$
$$L_y = i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi}\right) \tag{1.9}$$
$$L_z = -i\hbar \frac{\partial}{\partial\phi} \tag{1.10}$$

Note. Absence of r and $\frac{\partial}{\partial r}$

Choose $L_z = -i\hbar\frac{\partial}{\partial\phi}$ as the component to be measured and solve the PDE

$$L_z u(\theta, \phi) = l_z u(\theta, \phi) \tag{1.11}$$

by separability Ansatz

$$u(\theta, \phi) = P(\theta) Q(\phi) \tag{1.12}$$

$$
\begin{aligned}
P(\theta) L_z Q(\phi) &= l_z P(\theta) Q(\phi) \\
L_z Q(\phi) &= l_z Q(\phi) \\
-i\hbar \frac{\partial Q(\phi)}{\partial \phi} &= l_z Q(\phi) \\
\frac{1}{Q} \frac{\partial Q(\phi)}{\partial \phi} &= \frac{i l_z}{\hbar} \\
\frac{\partial}{\partial \phi} \ln Q(\phi) &= \frac{i l_z}{\hbar} \\
\ln Q(\phi) &= \frac{i l_z}{\hbar} \phi \\
Q(\phi) &= e^{i \frac{l_z}{\hbar} \phi}
\end{aligned}
$$

$Q(\phi)$ is not single-valued UNLESS $Q(\phi) = Q(\phi + 2\pi) = \ldots$

$$
\begin{aligned}
e^{i \frac{l_z}{\hbar} \phi} &= e^{i \frac{l_z}{\hbar} (\phi + 2\pi)} \\
1 &= e^{i \frac{l_z}{\hbar} 2\pi}
\end{aligned}
$$

i.e. $l_z = m\hbar$ where $m = 0, \pm 1, \pm 2, \ldots$ is the magnetic Quantum-number, i.e. the eigenvalue spectrum is discrete (unlike linear momentum in QM). So our solution is

$$
Q(\phi) = e^{im\phi} \tag{1.13}
$$

Note. linear motion is described on x unbounded
angular motion is described on (θ, ϕ) bounded

Next: find $P(\phi)$

Also is the magnitude observed simultaneously with $z-$ component? Only if $\left[\vec{L}^2, L_z\right] = 0$

$$
\left[\vec{L}^2, L_z\right] = \left[L_x^2, L_z\right] + \left[L_y^2, L_z\right] + 0
$$

$$
\begin{aligned}
\left[L_x^2, L_z\right] &= L_x L_x L_z - L_z L_x^2 = \\
&= L_x (L_z L_x - i\hbar L_y) - L_z L_x^2 \\
&= (L_z L_x - i\hbar L_y) L_x - i\hbar L_x L_y - L_z L_x^2 \\
&= -i\hbar (L_x L_y + L_y L_x) \\
\left[L_y^2, L_z\right] &= L_y L_y L_z - L_z L_y^2 = \\
&= L_y (i\hbar L_x + L_z L_y) - L_z L_y^2 \\
&= i\hbar L_y L_x + (i\hbar L_x + L_z L_y) L_y - L_z L_y^2 \\
&= i\hbar (L_y L_x + L_x L_y)
\end{aligned}
$$

i.e.

$$
\left[\vec{L}^2, L_z\right] = 0 \tag{1.14}
$$

i.e. solve

$$\vec{L}^2 P(\theta)Q(\phi) = \beta\hbar^2 P(\theta)Q(\phi)$$

simultaneously with

$$L_z Q(\phi) = m\hbar Q(\phi)$$

(Writing down the differential equations leads to Legendre-Polynomials. Here we will solve the problem using raising and lowering operators)

1.4 Raising/Lowering Operators

$$L_\pm = L_x \pm iL_y \tag{1.15}$$

Obviuosly: $L_+^\dagger = L_-$. The new commutations relations are:

$$\begin{aligned}
[L_z, L_\pm] &= [L_z, L_x] \pm i\,[L_z, L_y] \\
&= i\hbar L_y \mp i^2\hbar L_x = \pm\hbar L_x + i\hbar L_y \\
&= \pm\hbar(L_x \pm iL_y) \\
[L_+, L_-] &= [L_x, -iL_y] + [iL_y, L_x] = -2i\,[L_x, L_y] = -2i(i\hbar)L_z = 2\hbar L_z
\end{aligned}$$

$$[L_z, L_\pm] = \pm\hbar L_\pm \tag{1.16}$$

$$[L_+, L_-] = 2\hbar L_z \tag{1.17}$$

If $L_z u_m = m\hbar u_m$, then check if $(L_\pm u_m)$ is eigenfunction too.

$$\begin{aligned}
L_z(L_\pm u_m) &= L_z L_\pm u_m = \\
&= L_\pm L_z u_m + [L_z, L_\pm]\,u_m \\
&= L_\pm m\hbar u_m \pm \hbar L_\pm u_m \\
&= (m \pm 1)\hbar L_\pm u_m
\end{aligned}$$

$L_\pm u_m$ is eigen-function with eigen-value $(m \pm 1)$

1.5 Factorisation

Next: "factorize" $\vec{L}^2 = L_x^2 + L_y^2 + L_z^2$

$$\begin{aligned}
L_x &= \frac{1}{2}(L_+ + L_-) \\
L_y &= \frac{1}{2i}(L_+ - L_-)
\end{aligned}$$

Therefore

$$\begin{aligned}
L_x^2 + L_y^2 &= \frac{1}{4}(L_+^2 + L_-^2 + L_+L_- + L_-L_+) - \frac{1}{4}(L_+^2 + L_-^2 - L_+L_- - L_-L_+) \\
&= \frac{1}{2}(L_+L_- + L_-L_+)
\end{aligned}$$

Using the Commutation Relations we get

$$\begin{aligned}
L_x^2 + L_y^2 &= \frac{1}{2}(L_+L_- + [L_-, L_+] + L_+L_-) \\
&= \frac{1}{2}(L_+L_- - 2\hbar L_z + L_+L_-) \\
&= L_+L_- - \hbar L_z \\
\vec{L}^2 &= L_z^2 + L_+L_- - \hbar L_z \qquad (1.18) \\
L_x^2 + L_y^2 &= \frac{1}{2}([L_+, L_-] + 2L_-L_+) \\
&= \frac{1}{2}(2\hbar L_z + 2L_-L_+) \\
&= L_-L_+ + \hbar L_z \\
\vec{L}^2 &= L_z^2 + L_-L_+ + \hbar L_z \qquad (1.19)
\end{aligned}$$

1.6 Solve for eigenvalues

i) $\vec{L}^2 = L_+L_- - \hbar L_z + L_z^2$: Choose $m = -l$ (suppose this is the lowest l_z component achievable)

$$\begin{aligned}
\vec{L}^2 u_{-l} &= 0 - \hbar L_z u_{-l} + L_z^2 u_{-l} \\
&= l\hbar^2 u_{-l} + l^2\hbar^2 u_{-l} \\
&= l(l+1)\hbar^2 u_{-l}
\end{aligned}$$

i.e. $\beta = l(l+1)$ unlike classical value l^2

ii) $\vec{L}^2 = L_-L_+ + \hbar L_z + L_z^2$: Choose $m = l$ (and suppose this is the highest z-component)

$$\begin{aligned}
\vec{L}^2 u_l &= 0 + \hbar L_z u_l + L_z^2 u_l \\
&= l\hbar^2 u_l + l^2\hbar^2 u_l \\
&= l(l+1)\hbar^2 u_l
\end{aligned}$$

i.e. $\beta = l(l+1)$ again

1.7 Solve for the eigenfunctions

To get $P(\theta)$ we can either solve the DE in spherical coordinates. The angular momentum operator is

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

So we get the equation:

$$
\begin{aligned}
\vec{L}^2 u_{l,m} &= l(l+1)\hbar^2 u_{l,m} \\
-\hbar^2 \left[\frac{e^{im\phi}}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P_{l,m}}{\partial\theta}\right) + \frac{P_{l,m}e^{im\phi}(-m^2)}{\sin^2\theta}\right] &= l(l+1)\hbar^2 e^{im\phi} P_{l,m}
\end{aligned}
$$

i.e. we get the Legendre-Equation

$$
\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P_{l,m}}{\partial\theta}\right) - m^2\frac{P_{l,m}}{\sin^2\theta} + l(l+1)P_{l,m} = 0
$$

Or we can use the raising and Lowering Operators in spherical coordinates

$$
\begin{aligned}
L_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
L_y &= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
L_z &= -i\hbar\frac{\partial}{\partial\phi}
\end{aligned}
$$

Therefore $L_\pm$ are

$$
\begin{aligned}
L_+ &= i\hbar\left[(\sin\phi - i\cos\phi)\frac{\partial}{\partial\theta} + \cot\theta(\cos\phi + i\sin\phi)\frac{\partial}{\partial\phi}\right] \\
&= i\hbar\left[-i(\cos\phi + i\sin\phi)\frac{\partial}{\partial\theta} + \cot\theta(\cos\phi + i\sin\phi)\frac{\partial}{\partial\phi}\right] \\
&= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) \\
L_- &= i\hbar\left[(\sin\phi + i\cos\phi)\frac{\partial}{\partial\theta} + \cot\theta(\cos\phi - i\sin\phi)\frac{\partial}{\partial\phi}\right] \\
&= i\hbar\left[i(\cos\phi - i\sin\phi)\frac{\partial}{\partial\theta} + \cot\theta(\cos\phi - i\sin\phi)\frac{\partial}{\partial\phi}\right] \\
&= -\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)
\end{aligned}
$$

$$
L_\pm = \pm\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right) \tag{1.20}
$$

$L_\pm$ raise/lower m by 1 step, for each l. First find top/bottom $u_{m=\pm l} = P_{l,\pm l}e^{\pm il\phi}$

$$
L_\pm u_{m=\pm l} = 0
$$

$$\begin{aligned}
\pm\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}\pm i\cot\theta\frac{\partial}{\partial\phi}\right)P_{l,\pm l}e^{\pm il\phi}&=0\\
e^{\pm il\phi}\frac{\partial P_{l,\pm l}}{\partial\theta}\pm i\cot\theta P_{l,\pm l}(\pm il)e^{\pm il\phi}&=0\\
\frac{\partial P}{\partial\theta}-l\cot\theta P&=0
\end{aligned}$$

$$\begin{aligned}
\frac{1}{P}\frac{\partial P}{\partial\theta}&=l\frac{1}{\sin\theta}\frac{\partial\sin\theta}{\partial\theta}\\
\frac{d\ln P}{d\theta}&=l\frac{d\ln\sin\theta}{d\theta}\\
\ln|P|&=l\ln|\sin\theta|\\
P_{l,\pm l}(\theta)&=(\pm)\sin^l\theta
\end{aligned}\tag{1.21}$$

Calculate the eigen-functions for $l=1$

$$\begin{aligned}
u_{1,1}&=\sin\theta e^{i\phi}\\
u_{1,0}&=L_-u_{1,1}\\
&=-\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta e^{i\phi}\\
&=-e^{-i\phi}e^{i\phi}\cos\theta+i^2\cot\theta e^{-i\phi}\sin\theta e^{i\phi}\\
&=-2\cos\theta\\
u_{1,-1}&=-\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\phi}\right)(-\cos\theta)\\
&=-e^{-i\phi}(\sin\theta)\\
&=-\sin\theta e^{-i\phi}
\end{aligned}$$

$$\begin{aligned}
u_{1,-1}&=\sin\theta e^{-i\phi}\\
u_{1,0}&=L_+u_{1,-1}\\
&=\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta e^{-i\phi}\\
&=e^{i\phi}e^{-i\phi}\cos\theta+i^2\cot\theta e^{i\phi}\sin\theta e^{-i\phi}\\
&=2\cos\theta\\
u_{1,1}&=\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)cos\theta\\
&=e^{i\phi}(-\sin\theta)\\
&=-\sin\theta e^{i\phi}
\end{aligned}$$

Therefore two choices of eigen-functions. The convention is to use

$$u_{1,m}=\begin{cases}N_{1,1}\sin e^{i\phi}\\-N_{1,0}\cos\theta\\-N_{1,-1}\sin\theta e^{-i\phi}\end{cases}$$

The other set would be

$$u_{1,m}=\begin{cases}-N_{1,1}\sin e^{i\phi}\\N_{1,0}\cos\theta\\N_{1,-1}\sin\theta e^{-i\phi}\end{cases}$$

1.7.1 More eigenfunctions

Calculate the functions for $l = 0, 1, 2$: We have them for $l = 0, 1$, so calculate for $l = 2$

$$
\begin{aligned}
m = 2 \qquad & u_{2,2} \propto \sin^2\theta e^{2i\phi} \\
m = 1 \qquad & u_{2,1} \propto L_- \left(\sin^2\theta e^{2i\phi}\right) = -e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\sin\theta^2 e^{2i\phi}\right) = \\
& = -e^{-i\phi}\left(e^{2i\phi}2\sin\theta\cos\theta - i\cot\theta\sin^2\theta(2i)e^{2i\phi}\right) = \\
& = -e^{i\phi}\left(2\sin\theta\cos\theta + 2\sin\theta\cos\theta\right) = \\
& \propto -\sin\theta\cos\theta e^{i\phi} \\
m = 0 \qquad & u_{2,0} \propto -e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\left(-\cos\theta\sin\theta e^{i\phi}\right) = \\
& = \cos\theta^2 - \sin^2\theta - i\cot\theta(i)\sin\theta\cos\theta = \\
& = \cos^2\theta + \cos^2\theta - 1 + \cos^2\theta = \\
& = 3\cos^2\theta - 1 \\
m = -1 \qquad & u_{2,-1} \propto -e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\left(3\cos^2\theta - 1\right) = e^{-i\phi}6\cos\theta\sin\theta = \\
& \propto \sin\theta\cos\theta e^{-i\phi} \\
m = -2 \qquad & u_{2,-2} \propto -e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\sin\theta\cos\theta e^{-i\phi}\right) = \\
& = -e^{-2i\phi}\left(\cos^2\theta - \sin^2\theta - i\cot\theta\sin\theta\cos\theta(-i)\right) = \\
& = -e^{-2i\phi}\left(\cos^2\theta - \sin^2\theta - \cos^2\theta\right) = \\
& = \sin^2\theta e^{-2i\phi}
\end{aligned}
$$

Summary:

$$
\begin{aligned}
u_{0,0} &\propto 1 \\
u_{1,1} &\propto \sin\theta e^{i\phi} \\
u_{1,0} &\propto -\cos\theta \\
u_{1,-1} &\propto -\sin\theta e^{-i\phi} \\
u_{2,2} &\propto \sin^2\theta e^{2i\phi} \\
u_{2,1} &\propto -\sin\theta\cos\theta e^{i\phi} \\
u_{2,0} &\propto 3\cos^2\theta - 1 \\
u_{2,-1} &\propto \sin\theta\cos\theta e^{-i\phi} \\
u_{2,-2} &\propto \sin^2\theta e^{-2i\phi}
\end{aligned}
$$

In general

$$u^*_{l,m} = (-1)^m u_{l,-m} \tag{1.22}$$

1.8 Orthonormality

1.8.1 Normalisation

$$N_{l,m}^2 \int |u_{l,m}(\theta,\phi)|^2 d\Omega = 1$$

The eigenfunctions can be normalized, e.g. for $l = 1$

$$1 = \int |u_{1,m}|^2 d\Omega$$

$$\begin{aligned}
1 = \int |u_{1,\pm 1}|^2 d\Omega &= |N_{1,\pm 1}|^2 \int \sin^2\theta \sin\theta d\theta d\phi \\
&= |N_{1,\pm 1}|^2 2\pi \int (1-\cos^2\theta) d(-\cos\theta) \\
&= |N_{1,\pm 1}|^2 2\pi (1 - \tfrac{1}{3}) 2 \\
&= |N_{1,\pm 1}|^2 \frac{8\pi}{3} \\
N_{\pm 1} &= \sqrt{\frac{3}{8\pi}}
\end{aligned}$$

$$\begin{aligned}
1 = \int |u_{1,0}|^2 d\Omega &= |N_{1,0}|^2 \int \cos^2\theta \sin\theta d\theta d\phi \\
&= |N_1,0|^2 2\pi \int \cos^2\theta d(-\cos\theta) \\
&= |N_{1,0}|^2 2\pi \frac{1}{3} 2 \\
N_{1,0} &= \sqrt{\frac{3}{4\pi}}
\end{aligned}$$

Define the normalized states as $Y_{l,m}(\theta,\phi)$.

$$Y_{l,m}(\theta,\phi) \propto u_{l,m} \qquad \langle Y_{l,m}, Y_{l,m} \rangle = 1$$

Now in general we use raising/lowering operators, so try to calculate how the normalisation factor changes on usage of the operator.

$$\begin{aligned}
\kappa_{l,m}^{+} Y_{l,m+1} &= L_{+} Y_{l,m} \\
\kappa_{l,m}^{-} Y_{l,m-1} &= L_{-} Y_{l,m}
\end{aligned}$$

Now

$$
\begin{aligned}
|\kappa_{l,m}^{\pm}|^2 &= \langle Y_{l,m\pm1}, Y_{l,m\pm1}\rangle = \langle L_\pm Y_{l,m}, L_\pm Y_{l,m}\rangle = \langle Y_{l,m}, L_\mp L_\pm Y_{l,m}\rangle = \\
&\underset{(1.19),(1.18)}{=} \left\langle Y_{l,m}, (\vec{L}^2 - L_z^2 \mp \hbar L_z) Y_{l,m}\right\rangle = \\
&= \big(l(l+1) - m^2 \mp m\big)\,\hbar^2
\end{aligned}
$$

Choose κ positive and real

$$\kappa_{l,m}^{\pm} = \hbar\sqrt{l(l+1) - m(m\pm1)}$$

Rewrite κ in the Condon and Shortly notation

$$l(l+1) - m(m\pm1) = l^2 + l - m^2 \mp m = (l\mp m)(l\pm m+1)$$

$$
\begin{aligned}
Y_{l,m+1} &= \frac{1}{\hbar\sqrt{(l-m)(l+m+1)}} L_+ Y_{l,m} \\
Y_{l,m-1} &= \frac{1}{\hbar\sqrt{(l+m)(l-m+1)}} L_- Y_{l,m}
\end{aligned}
$$

Check for $l=1$. We had $Y_{1,\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$ and $Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$

$$Y_{1,0} = \kappa_{1,1}^{-} L_- Y_{1,1} = \frac{1}{\sqrt{2}}\sqrt{\frac{3}{8\pi}}2\cos\theta = \sqrt{\frac{3}{4\pi}}\cos\theta$$

So we only have to calculate one normalisation factor for each l.

$$
\begin{aligned}
1 &= N_{l,l}^2 2\pi \int_0^\pi \sin^{2l}\theta \sin\theta d\theta \\
1 &= 2\pi N_{l,l}^2 \int_0^\pi \sin^{2l+1}\theta d\theta \qquad (1.23)
\end{aligned}
$$

1.9 Orthogonality

Different eigenfunctions are Orthogonal, e.g.

$$\int u_{1,\pm1}^* u_{1,0} = \int \sin^2\theta\cos\theta e^{\mp i\phi} d\theta d\phi = 0$$

$$\int u_{1,-1}^* u_{1,1} = \int \sin^3\theta e^{2i\phi} d\theta d\phi = 0$$

It is obvious for different m, as we then always have a term $e^{in\phi}$ which integrated over 2π yields zero. For different $l_1 < l_2$ and same m we write the inner product as

$$\langle Y_{l_1,m}, Y_{l_2,m}\rangle = \left\langle L_-^{l_1-m} Y_{l_1,l_1}, L_-^{l_2-m} Y_{l_2,l_2}\right\rangle = \left\langle L_+^{l_2-m} L_- l_1 - m Y_{l_1,l_1}, Y_{l_2,l_2}\right\rangle$$

As $l_2 > l_1$ so is $l_2 - m > l_1 - m$ and therefore the total operator on the left annihilates Y_{l_1,l_1} as it cannot be raised anymore. So the inner product is zero.

1.10 Spherical functions

$$
\begin{aligned}
Y_{0,0} &= \frac{1}{\sqrt{4\pi}} \\
Y_{1,1} &= \sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \\
Y_{1,0} &= -\sqrt{\frac{3}{4\pi}}\cos\theta \\
Y_{1,-1} &= -\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \\
Y_{2,2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi} \\
Y_{2,1} &= -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi} \\
Y_{2,0} &= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \\
Y_{2,-1} &= \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi} \\
Y_{2,-2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}
\end{aligned}
$$

2 Intrinsic angular momentum

In the last chapter we discussed the orbital angular momentum using differential operators. We can also express the operators as matrices

$$\begin{aligned} \vec{J}^j_{m,n} &= \left\langle u_{j,m}, \vec{J}^j u_{j,n} \right\rangle \\ \left(J^j_z\right)_{m,n} &= \left\langle u_{j,m}, J^j_z u_{j,n} \right\rangle \end{aligned}$$

We denote the rows and coloumns in the following way:

$$J = \begin{pmatrix} m = j, n = j & m = j, n = j-1 & \dots & m = j, n = -j \\ m = j-1, n = j & m = j-1, n = j-1 & \dots & m = j-1, n = -j \\ \vdots & & & \vdots \\ m = -j, n = j & \dots & \dots & m = -j, n = -j \end{pmatrix}$$

For each j we have $2j+1$ different possible eigenfunctions, i.e. we get a $2l+1$ dimensional matrices. So we can choose j to be integer or half-integer.

Recall from the last chapter

$$\begin{aligned} \hbar\sqrt{(j \mp m)(j \pm m + 1)} Y_{j,m+1} &= L_+ Y_{j,m} \\ \hbar\sqrt{(j \mp m)(j \pm m + 1)} Y_{j,m-1} &= L_- Y_{j,m} \end{aligned}$$

So for $J^j_\pm$ we get

$$\begin{aligned} (J^{\frac{1}{2}}_\pm)_{mn} &= \left\langle u_{\frac{1}{2},m}, L_\pm u_{\frac{1}{2},n} \right\rangle = \kappa^\pm_{\frac{1}{2},n} \left\langle u_{\frac{1}{2},m}, u_{\frac{1}{2},n\pm 1} \right\rangle = \\ &= \kappa^\pm_{\frac{1}{2},n} \delta_{m,n\pm 1} \end{aligned}$$

2.1 $j = \frac{1}{2}$

So for $j = \frac{1}{2}$ we get

$$J^{\frac{1}{2}}_+ = \hbar \begin{pmatrix} 0 & \sqrt{\left(\frac{1}{2} + \frac{1}{2}\right)\left(\frac{1}{2} - \frac{1}{2} + 1\right)} \\ 0 & 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J^{\frac{1}{2}}_- = \left(J^{\frac{1}{2}}_+\right)^\dagger \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

So we get

$$J_x^{\frac{1}{2}} = \frac{1}{2}\left(J_+^{\frac{1}{2}} + J_-^{\frac{1}{2}}\right) = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$
$$J_y^{\frac{1}{2}} = \frac{1}{2i}\left(J_+^{\frac{1}{2}} - J_-^{\frac{1}{2}}\right) = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$
$$J_z^{\frac{1}{2}} = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

2.2 Pauli Matrices

Define the Pauli Spin matrices

$$\sigma_1 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_2 = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_3 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

Properties:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$

And the magnitude of the spin is

$$\vec{J}^2 = J_x^2 + J_y^2 + J_z^2 = \frac{\hbar^2}{4}(\sigma_x^2 + \sigma_y^2 + \sigma_z^2) = \frac{3\hbar^2}{4}$$

2.3 $j = 1$

$$\vec{J}^2 = 2\hbar^2 1$$
$$J_z^1 = \hbar\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}$$
$$J_+^1 = \hbar\begin{pmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{pmatrix}$$
$$J_-^1 = \hbar\begin{pmatrix}0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{pmatrix}$$

Therefore

$$J_x^1 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$J_x^1 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

And check that $J_x^2 + J_y^2 + J_z^2 = \vec{J}^2$

3 Hydrogen Atom

In 3 dimensions, 2 (interacting) particles

3.1 Effective Schrödinger equation for Hydrogen atom

0. 2 non-interacting particles.
   i.e. we have m_1 at $\vec{x}_1$ with $\psi_1(\vec{x}_1)$ and m_2 at $\vec{x}_2$ with $\psi_2(\vec{x}_2)$. The separate stationary state Schrödinger equations are

$$
\begin{aligned}
H_1\psi_1 &= -\frac{\hbar^2}{2m}\Delta_1\psi_1 + V_1(x_1)\psi_1 = E_1\psi_1 \\
H_2\psi_2 &= -\frac{\hbar^2}{2m}\Delta_2\psi_2 + V_2(x_2)\psi_2 = E_2\psi_2
\end{aligned}
$$

   The total wave function is $\Psi(\vec{x}_1, \vec{x}_2) = \psi_1(\vec{x}_1), \psi_2(\vec{x}_2)$ because probabilities multiply and $E = E_1 + E_2$. So we get

$$
\begin{aligned}
H\Psi &= (H_1 + H_2)(\psi_1\psi_2) = \psi_2 H_1\psi_1 + \psi_1 H_2\psi_2 = \\
&= E_1\psi_2\psi_1 + E_2\psi_1\psi_2 = (E_1 + E_2)\psi_1\psi_2 = \\
&= E\Psi
\end{aligned}
$$

1. Now introduce interaction (in 1 dimension)=, i.e. the Hamiltonian has the form

$$\hat{H} = H_1 + H_2 + V(x_1 - x_2) \tag{3.1}$$

   Now change variables to center of mass coordinates

$$
\begin{aligned}
x &= x_1 - x_2 && (3.2) \\
\bar{x} &= \frac{x_1m_1 + x_2m_2}{m_1 + m_2} = \frac{x_1m_1 + x_2m_2}{M} && (3.3)
\end{aligned}
$$

   Now the partial derivatives transform as follows

$$
\begin{aligned}
\frac{\partial}{\partial x_1} &= \frac{\partial \bar{x}}{\partial x_1}\frac{\partial}{\partial \bar{x}} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} = \frac{m_1}{M}\frac{\partial}{\partial \bar{x}} + \frac{\partial}{\partial x} \\
\frac{\partial}{\partial x_2} &= \frac{\partial \bar{x}}{\partial x_2}\frac{\partial}{\partial \bar{x}} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} = \frac{m_2}{M}\frac{\partial}{\partial \bar{x}} - \frac{\partial}{\partial x}
\end{aligned}
$$

And the Laplacians transform like

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} = \frac{1}{m_1}\left(\frac{m_1^2}{M^2}\frac{\partial^2}{\partial \bar{x}^2} + 2\frac{m_1}{M}\frac{\partial^2}{\partial x\bar{x}} + \frac{\partial^2}{\partial x}\right) = \frac{m_1}{M^2}\frac{\partial^2}{\partial \bar{x}^2} + 2\frac{1}{M}\frac{\partial^2}{\partial x\bar{x}} + \frac{1}{m_1}\frac{\partial^2}{\partial x^2}$$
$$\frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{m_2}\left(\frac{m_2^2}{M^2}\frac{\partial^2}{\partial \bar{x}^2} - 2\frac{m_2}{M}\frac{\partial^2}{\partial x\bar{x}} + \frac{\partial^2}{\partial x^2}\right) = \frac{m_2}{M^2}\frac{\partial^2}{\partial \bar{x}^2} - 2\frac{1}{M}\frac{\partial^2}{\partial x\bar{x}} + \frac{1}{m_2}\frac{\partial^2}{\partial x^2}$$

The cross-terms get killed

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{m_1+m_2}{M^2}\frac{\partial^2}{\partial \bar{x}^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} = \frac{1}{M}\frac{\partial^2}{\partial \bar{x}^2} + \frac{1}{\mu}\frac{\partial^2}{\partial x^2}$$

with the reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$. Now the full Hamiltonian is

$$H = -\frac{\hbar^2}{2}\left(\frac{1}{M}\frac{\partial^2}{\partial \bar{x}^2} + \frac{1}{\mu}\frac{\partial^2}{\partial x^2}\right) + V(x) \tag{3.4}$$

Try separability ansatz

$$\Psi(x_1, x_2) = \Psi(\bar{x}, x) = \phi(\bar{x})\psi(x) \tag{3.5}$$

So the Schrödinger eqution becomes

$$H\Psi = -\frac{\hbar^2}{2M}\psi\frac{\partial^2}{\partial \bar{x}^2}\phi - \frac{\hbar^2}{2\mu}\phi\frac{\partial^2}{\partial x^2}\psi + V(x)\phi\psi = E_{tot}\phi\psi$$

Write the total energy as sum of the energy of the centre of mass and the energy of relative motion: $E_{tot} = E_{CM} + E$ and divide by $\phi\psi$ so we get

$$-\frac{\hbar^2}{2M}\frac{1}{\phi}\frac{\partial^2}{\partial \bar{x}^2}\phi - E_{CM} = E + \frac{\hbar^2}{2\mu}\frac{1}{\psi}\frac{\partial^2}{\partial x^2}\psi - V(x)$$

And as x and $\bar{x}$ are linearly independent we get two separate equations

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \bar{x}^2}\phi = E_{CM}\phi \tag{3.6}$$
$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\psi = E\psi - V(x)\psi \tag{3.7}$$

So the Schrödinger equation reduces to the free particle equation for the motion of centre of mass and a stationary state equation for the relative motion. Now if $m_1 \gg m_2$

$$M = m_1 + m_2 \approx m_1$$
$$\mu = \frac{m_1 m_2}{m_1 + m_2} \approx m_2$$

We can treat the relative motion as the motion of m_2 in the force field $V(x)$ of m_1

In 3 dimensions we get a similiar result

$$\vec{\nabla}_1 = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1}\right) \qquad \vec{r}_1 = (x_1, y_1, z_1)$$
$$\vec{\nabla}_2 = \left(\frac{\partial}{\partial x_2}, \frac{\partial}{\partial y_2}, \frac{\partial}{\partial z_2}\right) \qquad \vec{r}_2 = (x_2, y_2, z_2)$$
$$\vec{\nabla}_r = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \qquad \vec{r} = \vec{r}_1 - \vec{r}_2 = (x, y, z)$$
$$\vec{\nabla}_R = \left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z}\right) \qquad \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} = (X, Y, Z)$$

So the Schrödinger equations are

$$-\frac{\hbar^2}{2M}\vec{\nabla}_R\vec{\nabla}_R\phi = E_{CM}\phi \tag{3.8}$$
$$-\frac{\hbar^2}{2\mu}\vec{\nabla}_r\vec{\nabla}_r\psi = (E - V(r))\psi \tag{3.9}$$

The effective Schrödinger equation we have to solve is

$$-\frac{\hbar^2}{2\mu}\vec{\nabla}_r\vec{\nabla}_r\psi = (E - V(r))\psi \tag{3.10}$$

with $\mu \approx m_2$ the electron mass and the Coloumb potential $V(r) = -\frac{e^2}{r}$

3.2 Separationn of variables

Aim: separate variables such that the PDE becomes an ODE
Transform coordinates to spherical polar coordinates:

$$x = r\sin\theta\cos\phi = r\hat{x}$$
$$y = r\sin\theta\sin\phi = r\hat{y}$$
$$z = r\cos\theta = r\hat{z}$$

Recall:

$$L_i = -i\hbar\epsilon_{ijk}x_j\frac{\partial}{\partial x_k}$$

and in terms of (r, θ, ϕ), L_i had no $\frac{\partial}{\partial r}$ operator, i.e. $Y_{l,m} = Y_{l,m}(\theta, \phi)$. Now prove the following identity

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\frac{1}{\hbar^2}|\vec{L}|^2 \tag{3.11}$$

We will use the identities $x_i\frac{\partial f}{\partial x_i} = r\frac{\partial f}{\partial r}$ which follows from

$$\frac{\partial f}{\partial r} = \frac{\partial x_i}{\partial r}\frac{\partial f}{\partial x_i} = \hat{x}_i\frac{\partial f}{\partial x_i}$$

And the identity

$$\epsilon_{ijk}\epsilon_{imn} = \delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}$$

Now

$$\begin{aligned}
-\frac{1}{\hbar^2}|\vec{L}|^2 f &= \left(\epsilon_{ijk} x_j \frac{\partial}{\partial x_k}\right)\left(\epsilon_{imn} x_m \frac{\partial f}{\partial x_n}\right) = \\
&= \epsilon_{ijk}\epsilon_{imn} x_j \frac{\partial}{\partial x_k}\left(x_m \frac{\partial f}{\partial x_n}\right) = \\
&= \left(\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}\right) x_j \frac{\partial}{\partial x_k}\left(x_m \frac{\partial f}{\partial x_n}\right) = \\
&= x_j \frac{\partial}{\partial x_k}\left(x_j \frac{\partial f}{\partial x_k} - x_k \frac{\partial f}{\partial x_j}\right) = \\
&= x_j \delta_{jk} \frac{\partial f}{\partial x_k} + x_j x_j \frac{\partial^2 f}{\partial x_k x_k} - x_j \delta_{kk} \frac{\partial f}{\partial x_j} - x_j x_k \frac{\partial^2 f}{\partial x_j x_k} = \\
&= x_k \frac{\partial f}{\partial x_k} + r^2 \Delta f - 3 x_j \frac{\partial f}{\partial x_j} - x_j x_k \frac{\partial^2 f}{\partial x_j x_k} = \\
&= r^2 \Delta f - 2r \frac{\partial f}{\partial r} - x_j \frac{\partial}{\partial x_j}\left(x_k \frac{\partial f}{\partial x_k}\right) + x_j \delta_{jk} \frac{\partial f}{\partial x_k} = \\
&= r^2 \Delta f - 2r \frac{\partial f}{\partial r} - r \frac{\partial}{\partial r}\left(r \frac{\partial f}{\partial r}\right) + r \frac{\partial f}{\partial r} = \\
&= r^2 \Delta f - r \frac{\partial f}{\partial r} - r \frac{\partial}{\partial r}\left(r \frac{\partial f}{\partial r}\right) = \\
&= r^2 \Delta f - r \frac{\partial f}{\partial r} - \frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) + r \frac{\partial f}{\partial r} = \\
&= r^2 \Delta f - \frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right)
\end{aligned}$$

i.e.

$$\Delta f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) - \frac{1}{r^2}\frac{1}{\hbar^2}|\vec{L}|^2 f$$

So the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{1}{r^2}\frac{1}{\hbar^2}|\vec{L}|^2\right]\psi = (E - V(r))\psi$$

Separate ψ:

$$\psi(r, \theta, \phi) = u(r) Y_{lm}(\theta, \phi) \tag{3.12}$$

since we know $|\vec{L}|^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$

$$-\frac{\hbar^2}{2m}\left[Y_{lm}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) - u\frac{1}{r^2}\frac{1}{\hbar^2}|\vec{L}|^2 Y_{lm}\right] = (E - V(r))uY_{lm}$$
$$-\frac{\hbar^2}{2m}\left[Y_{lm}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) - u\frac{1}{r^2}l(l+1)Y_{lm}\right] = (E - V(r))uY_{lm}$$
$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) - u\frac{l(l+1)}{r^2}\right] = (E - V(r))u$$

So we have 1 dimensional st.st. Sch. eq. but not in standard form

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Define $u = r^\alpha \chi$. So we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\alpha r^{\alpha-1}\chi + r^\alpha\frac{\partial \chi}{\partial r}\right)\right] =$$
$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left[\alpha r^{\alpha+1}\chi + r^{\alpha+2}\frac{\partial \chi}{\partial r}\right] =$$
$$= \frac{1}{r^2}\left[\alpha(\alpha+1)r^\alpha\chi + \alpha r^{\alpha+1}\frac{\partial \chi}{\partial r} + (\alpha+2)r^{\alpha+1}\frac{\partial \chi}{\partial r} + r^{\alpha+2}\frac{\partial^2 \chi}{\partial r^2}\right) =$$
$$= \alpha(\alpha+1)r^{\alpha-2}\chi + (\alpha+\alpha+2)r^{\alpha-1}\frac{\partial \chi}{\partial r} + r^\alpha\frac{\partial^2 \chi}{\partial r^2} =$$

To get the standard form we only want to have the second order derivate so choose $\alpha = -1$ i.e.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) = \frac{1}{r}\frac{\partial^2 \chi}{\partial r^2}$$

Now the Sch. eq is

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

And finally with the Coloumb potential

$$\frac{\partial^2 \chi}{\partial r^2} - \left[\frac{l(l+1)}{r^2} - \frac{2me^2}{\hbar^2 r}\right]\chi + \frac{2m}{\hbar^2}E\chi = 0 \tag{3.13}$$

Now rescale $r = \lambda\rho$ with ρ dimensionless

$$\frac{1}{\lambda^2}\frac{\partial^2\chi}{\partial\rho^2} - \frac{1}{\lambda^2}\left[\frac{l(l+1)}{\rho^2} - \frac{2me^2\lambda}{\hbar^2\rho}\right]\chi + \frac{2m}{\hbar^2}E\chi = 0$$

Now choose $\lambda = \frac{\hbar^2}{me^2}$ (Bohr's radius) i.e.

$$\frac{\partial^2\chi}{\partial\rho^2} - \left[\frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right]\chi + \frac{2m}{\hbar^2}\frac{\hbar^4}{m^2e^4}E\chi = 0$$

And define a dimensionless energy $\epsilon = \frac{2\hbar^2}{me^4}E$ to get the Schrödinger equation we need to solve

$$\frac{\partial^2\chi_l}{\partial\rho^2} - \left[\frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right]\chi_l + \epsilon_l\chi_l = 0 \tag{3.14}$$

3.3 Raising and Lowering operators

"Factorise" the differential operator $\frac{\partial^2}{\partial\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho}$, i.e. find raising and lowering operators. Try $\left(\frac{\partial}{\partial x} + \frac{a}{x} + b\right)$ and $\left(\frac{\partial}{\partial x} - \frac{a}{x} - b\right)$:

$$\begin{aligned}
\left(\frac{\partial}{\partial x} + \frac{a}{x} + b\right)\left(\frac{\partial}{\partial x} - \frac{a}{x} - b\right)f =& \frac{\partial^2}{\partial x^2} - \frac{a}{x}\frac{\partial f}{\partial x} + \frac{a}{x^2}f - b\frac{\partial f}{\partial x} + \\
&+ \frac{a}{x}\frac{\partial f}{\partial x} - \frac{a^2}{x^2}f - \frac{ab}{x}f + \\
&+ b\frac{\partial f}{\partial x} - \frac{ab}{x}f - b^2 f = \\
=& \frac{\partial^2 f}{\partial x^2} - \frac{2ab}{x}f - b^2 f + \frac{a-a^2}{x^2}f = \\
=& \frac{\partial^2 f}{\partial x^2} - \frac{2ab}{x}f + \frac{a-a^2}{x^2}f - b^2 f \\
\left[\frac{\partial^2}{\partial\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho}\right]f =& \left[\frac{\partial^2}{\partial x^2} + \frac{a-a^2}{x^2} - \frac{2ab}{x}\right]f - b^2 f
\end{aligned}$$

i.e. $a^2 - a = l(l+1) \Rightarrow a = l+1$ and $-ab = 1 \Rightarrow b = -\frac{1}{l+1}$. Now we define the two operators as

$$a_+ = \left(\frac{\partial}{\partial x} - \frac{l+1}{x} + \frac{1}{l+1}\right) \tag{3.15}$$

$$a_- = \left(\frac{\partial}{\partial x} + \frac{l+1}{x} - \frac{1}{l+1}\right) \tag{3.16}$$

and

$$
\begin{aligned}
a_+a_-f = &\left(\frac{\partial}{\partial x} - \frac{l+1}{x} + \frac{1}{l+1}\right)\left(\frac{\partial f}{\partial x} + \frac{l+1}{x}f - \frac{f}{l+1}\right) = \\
=&\frac{\partial^2 f}{\partial x^2} + \frac{l+1}{x}\frac{\partial f}{\partial x} - \frac{l+1}{x^2}f - \frac{1}{l+1}\frac{\partial f}{\partial x} - \\
&- \frac{l+1}{x}\frac{\partial f}{\partial x} - \frac{(l+1)^2}{x^2}f + \frac{f}{x} + \\
&+ \frac{1}{l+1}\frac{\partial f}{\partial x} + \frac{f}{x} - \frac{1}{(l+1)^2}f = \\
=&\frac{\partial^2 f}{\partial x^2} - \frac{f}{x^2}(l+1+(l+1)^2) + \frac{2}{x}f - \frac{1}{(l+1)^2}f = \\
=&\frac{\partial^2 f}{\partial x^2} - \frac{(l+1)(l+2)}{x^2}f + \frac{2}{x}f - \frac{1}{(l+1)^2}f
\end{aligned}
$$

i.e. the differential operator for $l+1$. Summarize:

$$a_-a_+ = \frac{\partial^2}{\partial x^2} - \frac{l(l+1)}{x^2} + \frac{2}{x} - \frac{1}{(l+1)^2} \tag{3.17}$$

$$a_+a_- = \frac{\partial^2}{\partial x^2} - \frac{(l+1)(l+2)}{x^2} + \frac{2}{x} - \frac{1}{(l+1)^2} \tag{3.18}$$

i.e. we can write the reduced Schödinger equation in the two alternative "factorisations"

$$\left[a_-a_+ + \epsilon_l + \frac{1}{(l+1)^2}\right]\chi_l = 0 \tag{3.19a}$$

$$\left[a_+a_- + \epsilon_{l+1} + \frac{1}{(l+1)^2}\right]\chi_{l+1} = 0 \tag{3.19b}$$

Now act on (3.19a) with a_+ and on (3.19b) with a_-

$$\left[a_+a_- + \epsilon_l + \frac{1}{(l+1)^2}\right](a_+\chi_l) = 0 \tag{3.20a}$$

$$\left[a_-a_+ + \epsilon_{l+1} + \frac{1}{(l+1)^2}\right](a_-\chi_{l+1}) = 0 \tag{3.20b}$$

Now $\epsilon_l = \epsilon_{l+1}$. Identify (3.19a) with (3.20b)

$$
\begin{aligned}
&a_-\chi_{l+1} \propto \chi_l \\
&a_-\chi_{l+1} = \kappa_l^- \chi_l
\end{aligned} \tag{3.21}
$$

i.e. a_- is a lowering operator. Identify (3.19b) with (3.20a)

$$
\begin{aligned}
&a_+\chi_l \propto \chi_{l+1} \\
&a_-\chi_l = \kappa_l^+ \chi_{l+1}
\end{aligned} \tag{3.22}
$$

i.e. a_+ is a raising operator. ϵ is degenerate with respect to quantum number l

3.4 Calculate $\kappa_l^{(\pm)}$

Take $\mathcal{H}$ space inner product of both sides of (3.21)

$$\begin{aligned} \langle a_- \chi_{l+1}, a_- \chi_{l+1} \rangle &= \langle \kappa_l^- \chi_l, \kappa_l^- \chi_l \rangle \\ &= |\kappa_l^-|^2 \\ |\kappa_l^-|^2 &= \left\langle \chi_{l+1}, a_-^\dagger a_- \chi_{l+1} \right\rangle \end{aligned}$$

Take the inner product of (3.22)

$$|\kappa_l^+|^2 = \left\langle \chi_l, a_+^\dagger a_+ \chi_l \right\rangle$$

Evaluate $a_\pm^\dagger$:

$$\begin{aligned} \langle \chi, a_\pm \chi \rangle &= \left\langle a_\pm^\dagger \chi, \chi \right\rangle \\ \langle \chi, a_\pm \chi \rangle &= \int \chi^* \left(\frac{\partial}{\partial \rho} \mp \frac{l+1}{\rho^2} \pm \frac{1}{l+1} \right) \chi d\rho = \\ &= \int \left[\chi^* \frac{\partial \chi}{\partial \rho} \mp \frac{l+1}{\rho^2} \chi^* \chi \pm \frac{1}{l+1} \chi^* \chi \right] d\rho = \\ &= \left[|\chi|^2 \right]_0^\infty + \int \left[-\frac{\partial \chi^*}{\partial \rho} \chi \mp \frac{l+1}{\rho^2} \chi^* \chi \pm \frac{1}{l+1} \chi^* \chi \right] d\rho = \\ &= \left[|\chi|^2 \right]_0^\infty - \int \left(\frac{\partial}{\partial \rho} \pm \frac{l+1}{\rho^2} \mp \frac{1}{l+1} \right) \chi^* \chi d\rho = \\ &= \left[|\chi|^2 \right]_0^\infty - \int a_\mp \chi^* \chi d\rho = \\ &= \left[|\chi|^2 \right]_0^\infty + \langle -a_\mp \chi, \chi \rangle \end{aligned}$$

Now $\chi \xrightarrow{\rho \to \infty} 0$ since norm has to be finite and $\chi(\rho = 0) = 0$ since $u(\rho) = \frac{\chi}{r}$ has to be analytic. So we get:

$$a_\pm^\dagger = -a_\mp \tag{3.23}$$

and

$$|\kappa_l^+|^2 = -\langle \chi_l, a_- a_+ \chi_l \rangle$$

but from (3.19a) we have $a_- a_+ \chi_l = -\left(\epsilon_l + \frac{1}{(l+1)^2} \right) \chi_l$, so

$$\begin{aligned} |\kappa_l^+|^2 &= -\left\langle \chi_l, -\left(\epsilon_l + \frac{1}{(l+1)^2} \right) \chi_l \right\rangle = \left(\epsilon_l + \frac{1}{(l+1)^2} \right) \langle \chi_l, \chi_l \rangle = \\ &= \epsilon_l + \frac{1}{(l+1)^2} \end{aligned}$$

$$
\begin{aligned}
|\kappa_l^-|^2 &= -\langle \chi_{l+1}, a_+ a_- \chi_{l+1}\rangle = -\left\langle \chi_{l+1}, -\left(\epsilon_{l+1} + \frac{1}{(l+1)^2}\right)\chi_{l+1}\right\rangle = \\
&= \epsilon_l + \frac{1}{(l+1)^2}
\end{aligned}
$$

So we have

$$
|\kappa_l^{\pm}|^2 = \epsilon_l + \frac{1}{(l+1)^2} \tag{3.24}
$$

We have a negative potential, so to have a bound state we require the energy to be negative, i.e. $\epsilon_l = -\frac{1}{c^2}$ for $c \in \mathbb{R}$. But positivity of norm requires that $\epsilon_l + \frac{1}{(l+1)^2}$ be real, i.e. $-\frac{1}{c^2} + \frac{1}{(l+1)^2} \geq 0$, so

$$
l \leq c - 1
$$

3.5 Eigenfunction and energy eigenvalue

This tells us, there is a l_{max}. Now take this $l_{max} = n-1$, $n \in \mathbb{N}$ and annihilate it with raising operator.

$$
\begin{aligned}
a_+ \chi_{n-1} &= 0 \\
\frac{\partial}{\partial \rho}\chi_{n-1} &= \frac{n}{\rho}\chi_{n-1} - \frac{1}{n}\chi_{n-1} \\
\frac{\partial}{\partial \rho}\ln \chi_{n-1} &= \frac{n}{\rho} - \frac{1}{n} \\
\ln \chi_{n-1} &= \int \frac{n}{\rho} d\rho - \frac{\rho}{n} \\
\ln \chi_{n-1} &= n \ln \rho - \frac{\rho}{n} \\
\chi_{n-1} &\propto \rho^n e^{-\frac{\rho}{n}}
\end{aligned}
$$

The energy can be calculated from (3.19a): $\left[a_- a_+ + \epsilon_l + \frac{1}{(l+1)^2}\right]\chi_l = 0$, i.e. as $a_+\chi_{n-1} = 0$

$$
\epsilon = -\frac{1}{n^2}
$$

So we have a new quantum number determining the energy. And $l = 0, \ldots, n-1$. For each energy level there are $n-1$ possibilities for l and for each l there are $2l+1$ possibilities for m, i.e. each energy level is $\sum_{l=0}^{n-1}(2l+1) = (n-1)n + n = n^2$ fold degenerate.

3.6 Normalisation

$$
\begin{aligned}
N_{n,l,m} &= \int |\psi_{n,l,m}|^2 d\vec{r} = \\
&= \int |u_{n,l}(r)|^2 |Y_{l,m}(\theta,\phi)|^2 r^2 dr \sin\theta d\theta d\phi = \\
&= \int |u_{n,l}(r)|^2 r^2 dr = \\
&= \int \frac{|\chi_{n,l}(r)}{r^2} r^2 dr = \\
&= \int \lambda |\chi_{n,l}(\rho)|^2 d\rho
\end{aligned}
$$

So $N_{n,l,m} = N_{n,l}$. We know the normalisation factors when using the raising and lowering operators, i.e. we only need to calculate one normalisation factor for each n. ($I_n = \frac{N_{n,n-1}}{\lambda}$)
For $n = 1$

$$
\begin{aligned}
I_1 &= \int_0^\infty \rho^2 e^{-2\rho} d\rho = 2\frac{1}{2}\int \rho e^{-2\rho} d\rho = \\
&= \frac{1}{2}\int e^{-2\rho} d\rho = \frac{1}{4}
\end{aligned}
$$

General formula:

$$
I_n = (2n)! \left(\frac{n}{2}\right)^{2n+1}
$$

This can be easily seen from the partial integration. So for $l = n-1$ we have $c_n = \frac{1}{\sqrt{N_{n,n-1}}} = \sqrt{\frac{1}{\lambda(2n)!}} \left(\frac{2}{n}\right)^{n+\frac{1}{2}}$ and

$$
\chi_{n,n-1} = c_n \rho^n e^{-\frac{\rho}{n}} \tag{3.25}
$$

Now calculate some eigenfunctions for $l = n-2, n-3, \ldots$. Use $\chi_{n,l} = \frac{1}{\kappa_l^-} a_- \chi_{n,l+1}$

$$
\begin{aligned}
\chi_{n,n-2} &= \frac{1}{\sqrt{-\frac{1}{n^2} + \frac{1}{(n-1)^2}}} \left[\frac{\partial}{\partial\rho} - \frac{n-1}{\rho} + \frac{1}{n-1}\right] c_n \rho^n e^{-\frac{\rho}{n}} = \\
&= c_n \frac{n(n-1)}{\sqrt{2n-1}} \left[n\rho^{n-1} - \frac{\rho^n}{n} + (n-1)\rho^{n-1} - \frac{1}{n-1}\rho^n\right] e^{-\frac{\rho}{n}} = \\
&= c_n \frac{n(n-1)}{\sqrt{2n-1}} \left[\frac{2n-1}{\rho} - \left(\frac{1}{n} + \frac{1}{n-1}\right)\right] \rho^n e^{-\frac{\rho}{n}} = \\
&= c_n \frac{n(n-1)}{\sqrt{2n-1}} \left[\frac{2n-1}{\rho} - \frac{2n-1}{n(n-1)}\right] \rho^n e^{-\frac{\rho}{n}} = \\
&= c_n n(n-1)\sqrt{2n-1} \left[\frac{1}{\rho} - \frac{1}{n(n-1)}\right] \rho^n e^{-\frac{\rho}{n}}
\end{aligned}
$$

for $n = 2, 3$:

$$\chi_{2,0} = c_2 2\sqrt{3}\left[\frac{1}{\rho} - \frac{1}{2}\right]\rho^2 e^{-\frac{\rho}{2}}$$
$$\chi_{3,1} = c_3 6\sqrt{5}\left[\frac{1}{\rho} - \frac{1}{6}\right]\rho^3 e^{-\frac{\rho}{3}}$$

Excercise: Show that $\chi_{2,0}$ and $\chi_{3,1}$ are energy eigenfunctions for the Hydrogen atom for certain quantum numbers n, l i.e. find the energy eigenvalues.

3.7 Visualisation

Now the complete eigenfunctions $\psi_{n,l,m}(r, \theta, \phi)$ are

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$
$$Y_{1,1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$
$$Y_{1,0} = -\sqrt{\frac{3}{4\pi}}\cos\theta$$
$$Y_{1,-1} = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$
$$Y_{2,2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$
$$Y_{2,1} = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}$$
$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$
$$Y_{2,-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}$$
$$Y_{2,-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$$

$c_n = \frac{1}{\sqrt{N_{n,n-1}}} = \sqrt{\frac{1}{\lambda(2n)!}}\left(\frac{2}{n}\right)^{n+\frac{1}{2}}$

$$\chi_{n,n-1} = c_n \rho^n e^{-\frac{\rho}{n}}$$
$$\chi_{n,n-2} = c_n n(n-1)\sqrt{2n-1}\left(\frac{1}{\rho} - \frac{1}{n(n-1)}\right)\rho^n e^{-\frac{\rho}{n}}$$

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}} e^{-\rho} \tag{3.26}$$

$$\psi_{2,0,0} = \frac{1}{\sqrt{8\pi}} \left(1 - \frac{\rho}{2}\right) e^{-\frac{\rho}{2}} \tag{3.27}$$

$$\psi_{2,1,-1} = -\frac{1}{\sqrt{64\pi}} \rho e^{-\frac{\rho}{2}} \sin\theta e^{-i\phi} \tag{3.28}$$

$$\psi_{2,1,0} = -\frac{1}{\sqrt{32\pi}} \rho e^{-\frac{\rho}{2}} \cos\theta \tag{3.29}$$

$$\psi_{2,1,1} = \frac{1}{\sqrt{64\pi}} \rho e^{-\frac{\rho}{2}} \sin\theta e^{i\phi} \tag{3.30}$$

3.8 Zeeman effect

Removal of m-degeneracy. Switch on an external magnetic field $\vec{B}$. Electron has magnetic moment $\vec{\mu}$ (by virtue of its orbital motion $\vec{\mu} \propto \vec{l} \Rightarrow \hat{\mu} \propto L$). The energy of the electron changes by $-\vec{\mu}\vec{B}$.

$$H \to H_0 - \vec{\mu}\vec{B}$$

$$\begin{aligned} H &= H_0 - \mu \vec{B}\vec{L} = \\ &= H_0 - \mu B L_z \end{aligned}$$

with the choice of $\vec{B} = (0, 0, B)$. So we have a new Sch. eq.

$$H\psi = (H_0 - \mu B L_z)\psi = E'\psi$$

Separate again $\psi = u(r) Y_{l,m}(\theta, \phi)$. Now

$$\begin{aligned} H\psi &= H_0(uY_{l,m}) - \mu B L_z(uY_{l,m}) = \\ &= H_0(uY_{l,m}) - \mu B u m\hbar Y_{l,m} = \qquad = \left[H_0 - \mu B m\hbar\right]\psi = E'\psi \\ H_0\psi &= \underbrace{\left[E' + \mu B m\hbar\right]}_{-\frac{1}{n^2}} \psi \end{aligned}$$

Now the new energy eigenvalues are

$$E_{n,l,m} = -\frac{1}{n^2} - \mu B m\hbar$$

4 Stationary State Perturbation Theory

(Rayleigh Schrödinger Theory); Approximate solutions to eigenvalue equations (2nd order)

4.1 Idea

We have the Eigenvalue (Schrödinger) Problem

$$H\psi = E\psi$$

with no solutions in closed form. But the corresponding problem

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

is solved in closed form! Where $H = H_0 + gV$ with g being a (real) perturbation parameter and V being "very small" i.e.

$$\langle V\rangle_0 \ll \langle H_0\rangle = E_n^{(0)}$$

To each exact eigenvalue $E_n^{(0)}$ there exists a perturbed eigenvalue

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots$$

To each exact eigenfunction $\psi_n^{(0)}$ there exists a perturbed eigenfunction

$$\psi_n = \psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots$$

The criterion for validity is

$$E_n^{(0)} \gg E_n^{(1)} \gg E_n^{(2)} \gg \dots$$

4.2 Non degenerate case

Assume our exact eigenvalues are not degenerate, i.e. $E_n \neq E_m$ for $n \neq m$. In this rewritten form our eigenvalue equation has the form

$$\begin{aligned}(H_0 + gV)\left(\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots\right) &= \\ = \left(E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots\right)&\left(\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots\right)\end{aligned}$$

Now equate the coefficients of all powers of g

$$\begin{aligned}
H_0\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(0)} \\
H_0\psi_n^{(1)} + V\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \\
H_0\psi_n^{(2)} + V\psi_n^{(1)} &= E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \\
&\vdots
\end{aligned}$$

rewritten:

$$\left(E_n^{(0)} - H_0\right)\psi_n^{(0)} = 0 \tag{4.1}$$

$$\left(E_n^{(0)} - H_0\right)\psi_n^{(1)} = \left(V - E_n^{(1)}\right)\psi_n^{(0)} \tag{4.2}$$

$$\left(E_n^{(0)} - H_0\right)\psi_n^{(2)} = \left(V - E_n^{(1)}\right)\psi_n^{(1)} - E_n^{(2)}\psi_n^{(0)} \tag{4.3}$$

each is a 2nd order differential equation, to be solved in succession.

4.2.1 $E_n^{(1)}$ and $\psi_n^{(1)}$

Take inner product of Act on (4.2) with $\psi_n^{(0)}$ (Hilbert space inner product)

$$E_n^{(0)}\left\langle\psi_n^{(0)},\psi_n^{(1)}\right\rangle - \left\langle\psi_n^{(0)},H_0\psi_n^{(1)}\right\rangle = \left\langle\psi_n^{(0)},V\psi_n^{(0)}\right\rangle - E_n^{(1)}\underbrace{\left\langle\psi_n^{(0)},\psi_n^{(0)}\right\rangle}_{=1}$$

Now

$$\left\langle\psi_n^{(0)},H_0\psi_n^{(1)}\right\rangle = \left\langle H_0^{\dagger}\psi_n^{(0)},\psi_n^{(1)}\right\rangle = \left\langle E_n^{(0)}\psi_n^{(0)},\psi_n^{(1)}\right\rangle$$

and so

$$E_n^{(1)} = \left\langle\psi_n^{(0)},V\psi_n^{(0)}\right\rangle = V_{nn} \tag{4.4}$$

Now find $\psi_n^{(1)}$: Take the inner product of (4.2) with $\psi_k^{(0)}, k \neq n$

$$\begin{aligned}
E_n^{(0)}\left\langle\psi_k^{(0)},\psi_n^{(1)}\right\rangle - E_k^{(0)}\left\langle\psi_k^{(0)},\psi_n^{(1)}\right\rangle &= \left\langle\psi_k^{(0)},V\psi_n^{(0)}\right\rangle - E_n^{(1)}\left\langle\psi_k^{(0)},\psi_n^{(0)}\right\rangle \\
\left(E_n^{(0)} - E_k^{(0)}\right)\left\langle\psi_k^{(0)},\psi_n^{(1)}\right\rangle &= V_{kn} \\
\left\langle\psi_k^{(0)},\psi_n^{(1)}\right\rangle &= \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}
\end{aligned}$$

Now we can express $\psi_n^{(1)}$ in the complete orthonormal set $\psi_k^{(0)}$. For $k \neq n$ the coefficients are given.

$$\psi_n^{(1)} = \lambda\psi_n^{(0)} + \sum_{k\neq n}\frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}\psi_k^{(0)}$$

We choose $\lambda = 0$, so $\left\langle \psi_n^{(1)}, \psi_n^{(0)} \right\rangle = 0$

$$\psi_n^{(1)} = \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} \tag{4.5}$$

4.2.2 $E_n^{(2)}$ and $\psi_n^{(2)}$

Similarly evaluate $E_n^{(2)}$ and $\psi_n^{(2)}$: Take inner product of (4.3) with $\psi_n^{(0)}$

$$\begin{aligned}
E_n^{(0)} \left\langle \psi_n^{(0)}, \psi_n^{(2)} \right\rangle - E_n^{(0)} \left\langle \psi_n^{(0)}, \psi_n^{(2)} \right\rangle &= \\
&= \left\langle \psi_n^{(0)}, V\psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \psi_n^{(0)}, \psi_n^{(1)} \right\rangle - E_n^{(2)} \left\langle \psi_n^{(0)}, \psi_n^{(0)} \right\rangle \\
0 &= \left\langle \psi_n^{(0)}, V\psi_n^{(1)} \right\rangle - E_n^{(2)} \\
E_n^{(2)} &= \left\langle \psi_n^{(0)}, V\psi_n^{(1)} \right\rangle = \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \left\langle \psi_n^{(0)}, V\psi_k^{(0)} \right\rangle = \\
&= \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} V_{nk} = \\
&= \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}
\end{aligned}$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{4.6}$$

Evaluate $\psi_n^{(2)}$: Take inner product of (4.3) with $\psi_l^{(0)}, l \neq n$

$$\begin{aligned}
E_n^{(0)} \left\langle \psi_l^{(0)}, \psi_n^{(2)} \right\rangle - E_l^{(0)} \left\langle \psi_l^{(0)}, \psi_n^{(2)} \right\rangle &= \\
&= \left\langle \psi_l^{(0)}, V\psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \psi_l^{(0)}, \psi_n^{(1)} \right\rangle - E_n^{(2)} \left\langle \psi_l^{(0)}, \psi_n^{(0)} \right\rangle \\
\left(E_n^{(0)} - E_l^{(0)} \right) \left\langle \psi_l^{(0)}, \psi_n^{(2)} \right\rangle &= \left\langle \psi_l^{(0)}, V\psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \psi_l^{(0)}, \psi_n^{(1)} \right\rangle
\end{aligned}$$

$$\begin{aligned}
\left\langle \psi_l^{(0)}, \psi_n^{(2)} \right\rangle &= \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_l^{(0)}} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \left[\left\langle \psi_l^{(0)}, V\psi_k^{(0)} \right\rangle - E_n^{(1)} \left\langle \psi_l^{(0)}, \psi_k^{(0)} \right\rangle \right] = \\
&= \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_l^{(0)}} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \left[V_{lk} - V_{nn}\delta_{lk} \right]
\end{aligned}$$

Again express $\psi_n^{(2)}$ in terms of $\psi_l^{(0)}$ and choose $\left\langle \psi_n^{(2)}, \psi_n^{(0)} \right\rangle = 0$

$$\psi_n^{(2)} = \sum_{l \neq n} \frac{1}{E_n^{(0)} - E_l^{(0)}} \left[\sum_{k \neq n} \left(\frac{V_{kn}V_{lk}}{E_n^{(0)} - E_k^{(0)}} \right) - \frac{V_{nn}V_{ln}}{E_n^{(0)} - E_l^{(0)}} \right] \psi_l^{(0)} \tag{4.7}$$

and etc.

4.3 Criterion of validity

Do cross check of the ansatz and the results up to order g^2

$$E_n = \langle \psi_n, H\psi_n \rangle \, E_n \quad = \left\langle \psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)}, (H+gV)\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} \right\rangle$$

$$\begin{aligned} \langle \psi_n, gV\psi_n \rangle &= g\left\langle \psi_n^{(0)}, V\psi_n^{(0)} \right\rangle + g^2\left\langle \psi_n^{(0)}, V\psi_n^{(1)} \right\rangle + g^2\left\langle \psi_n^{(1)}, V\psi_n^{(0)} \right\rangle + o(g^3) = \\ &= gE_n^{(1)} + 2g^2E_n^{(2)} \end{aligned}$$

$$\begin{aligned} \langle \psi_n, H_0\psi_n \rangle =& \left\langle \psi_n^{(0)}, H_0\psi_n^{(0)} \right\rangle + g\left\langle \psi_n^{(0)}, H_0\psi_n^{(1)} \right\rangle + g\left\langle \psi_n^{(1)}, H_0\psi_n^{(0)} \right\rangle + \\ &+ g^2\left\langle \psi_n^{(0)}, H_0\psi_n^{(2)} \right\rangle + g^2\left\langle \psi_n^{(2)}, H_0\psi_n^{(0)} \right\rangle + g^2\left\langle \psi_n^{(1)}, H_0\psi_n^{(1)} \right\rangle = \\ =& E_n^{(0)} + 0 + 0 + 0 + 0 + g^2\left\langle \psi_n^{(1)}, H_0\psi_n^{(1)} \right\rangle \end{aligned}$$

To evaluate the last term take the inner product of (4.2) with $\psi_n^{(1)}$:

$$\begin{aligned} E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle - \left\langle \psi_n^{(1)}, H_0\psi_n^{(1)} \right\rangle &= \left\langle \psi_n^{(1)}, V\psi_n^{(0)} \right\rangle - \left\langle \psi_n^{(1)}, \psi_n^{(0)} \right\rangle \\ E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle - \left\langle \psi_n^{(1)}, H_0\psi_n^{(1)} \right\rangle &= E_n^{(2)} \\ E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle - E_n^{(2)} &= \left\langle \psi_n^{(1)}, H_0\psi_n^{(1)} \right\rangle \end{aligned}$$

So we finally get

$$\langle \psi_n, H_0\psi_n \rangle = E_n^{(0)} + g^2\left(E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle - E_n^{(2)}\right)$$

Together:

$$\begin{aligned} E_n &= \langle \psi_n, H_0\psi_n \rangle + \langle \psi_n, gV\psi_n \rangle = \\ &= E_n^{(0)} + g^2\left(E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle - E_n^{(2)}\right) + gE_n^{(1)} + 2g^2E_n^{(2)} = \\ &= E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + g^2E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle \end{aligned}$$

So by solving our equations we got an additional term. For our calculation to be valid, this extra term must not change the result significantly, i.e.

$$E_n^{(2)} \gg E_n^{(0)}\left\langle \psi_n^{(1)}, \psi_n^{(1)} \right\rangle \tag{4.8}$$

4.4 Application

Restrict to $E_n^{(1)}, {}_n^{(2)}$ and $\psi_n^{(1)}$.

Physical case e.g. Helium atom, 2 electrons.
Start with two non-interacting electrons in the same coloumb potential, i.e.

$$H_0 = H(\vec{x}_1) + H(\vec{x}_2)$$

the unperturbed solutions are

$$\begin{aligned}
\psi_n^{(0)} &= \psi_{n_1,l_1,m_1}(\vec{x}_1)\psi_{n_2,l_2,m_2}(\vec{x}_2) \\
E_n^{(0)} &= E_{n_1} + E_{n_2}
\end{aligned}$$

The interaction term of the electrons is

$$V = \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}$$

Now solve the 1st order perturbation theory for

$$H = H_0 + \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}$$

e.g. for the ground state: $n_1 = 1, n_2 = 1$

$$\begin{aligned}
\psi_{n_1} &= e^{-\lambda r_1} \\
\psi_{n_2} &= e^{-\lambda r_2}
\end{aligned}$$

and our perturbation in the energy is

$$\begin{aligned}
E_n^{(1)} &= \left\langle \psi_1^{(0)}, V\psi_1^{(0)} \right\rangle = \\
&= e^2 \int \frac{e^{-\lambda(r_1-r_2)}}{|\vec{x}_1 - \vec{x}_2|} r_1^2 r_2^2 dr_1 dr_2 d\Omega(\theta_1,\phi_1) d\Omega(\theta_2,\phi_2)
\end{aligned}$$

This is too tedious to solve, and in any case, the obtained values have to be improved by the use of other approximation methods.

4.5 Degenerate energy level perturbation (for solid state course

Start with the exactly solvable problem

$$H_0\psi^{(0)} = E^{(0)}\psi^{(0)}$$

And assume there exist two distinc solutions with the same (degenerate) $E^{(0)}$

$$H_0\psi_1^{(0)} = E^{(0)}\psi_1^{(0)}$$
$$H_0\psi_2^{(0)} = E^{(0)}\psi_2^{(0)}$$

As they are distinct we can assume $\left\langle \psi_1^{(0)}, \psi_2^{(0)} \right\rangle = 0$. Now introduce a small perturbing potential V

$$H = H_0 + gV$$

And we have to solve the Schrödinger equations

$$H\psi_1 = E_1\psi_1 \tag{4.9}$$
$$H\psi_2 = E_2\psi_2 \tag{4.10}$$

where $E_1 \neq E_2$ (degeneracy removed) and

$$E_1 = E^{(0)} + gE_1^{(1)} + \dots$$
$$E_2 = E^{(0)} + gE_2^{(2)} + \dots$$

and

$$\psi_1 = c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)} + g\psi_1^{(1)} + \dots$$
$$\psi_2 = c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)} + g\psi_2^{(1)} + \dots$$

Substituting these into (4.9) and (4.10) and comparing coefficients up to g^1 we get

$$c_{11}\left(E^{(0)} - H_0\right)\psi_1^{(0)} + c_{12}\left(E^{(0)} - H_0\right)\psi_2^{(0)} = 0 \tag{4.11}$$
$$\left(E^{(0)} - H_0\right)\psi_1^{(1)} + \left(E_1^{(1)} - V\right)\left(c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)}\right) = 0 \tag{4.12}$$
$$c_{21}\left(E^{(0)} - H_0\right)\psi_1^{(0)} + c_{22}\left(E^{(0)} - H_0\right)\psi_2^{(0)} = 0 \tag{4.13}$$
$$\left(E^{(0)} - H_0\right)\psi_2^{(1)} + \left(E_2^{(1)} - V\right)\left(c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)}\right) = 0 \tag{4.14}$$

Now taking inner product of (4.12) with $\psi_1^{(0)}$ we get

$$E^{(0)}\left\langle \psi_1^{(0)}, \psi_1^{(1)} \right\rangle - \left\langle \psi_1^{(0)}, H_0\psi_1^{(1)} \right\rangle + c_{11}E_1^{(1)} - c_{11}\left\langle \psi_1^{(0)}, V\psi_1^{(0)} \right\rangle - c_{12}\left\langle \psi_1^{(0)}, V\psi_2^{(0)} \right\rangle = 0$$

So in our matrix notation we get

$$V_{11}c_{11} + V_{12}c_{12} = E_1^{(1)}c_{11}$$

And take inner product of (4.12) with $\psi_2^{(0)}$

$$E^{(0)}\left\langle \psi_2^{(0)}, \psi_1^{(1)} \right\rangle - \left\langle \psi_2^{(0)}, H_0\psi_1^{(1)} \right\rangle + c_{12}E_1^{(1)} - c_{11}V_{21} - c_{12}V_{22} = 0$$

$$V_{21}c_{11} + V_{22}c_{12} = E_1^{(1)}c_{12}$$

Doing the same with (4.14) yields

$$V_{11}c_{21} + V_{12}c_{22} = E_2^{(1)}c_{21}$$
$$V_{21}c_{21} + V_{22}c_{22} = E_2^{(1)}c_{22}$$

So both first order corrections can be calculated from solving the eigenvalue equation

$$\begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

So we get the two corrections by solving

$$\det \begin{bmatrix} V_{11} - E^{(1)} & V_{12} \\ V_{21} & V_{22} - E^{(1)} \end{bmatrix} = 0$$

4.6 Examples

4.6.1 Anharmonic oscillators

Start with the Harmonic oscillator and perturb it with x^4 and x^6 potentials

$$H = H_0 + \lambda x^4$$
$$H = H_0 + \lambda x^6$$

The unperturbed energy levels are

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) = c\left(n + \frac{1}{2}\right)$$

Recall:

$$\left(aa^\dagger - \frac{1}{2}\right) u_n = \epsilon u_n$$
$$\left(a^\dagger a + \frac{1}{2}\right) u_n = \epsilon u_n$$

And

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega}\hat{p}\right) \qquad \text{lowering operator} \tag{4.15}$$
$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) \qquad \text{raising operator} \tag{4.16}$$

with

$$au_n = \sqrt{n}u_{n-1}$$
$$a^\dagger u_n = \sqrt{n+1}u_{n+1}$$

So we can express the space-operator x in terms of $a, a^\dagger$.

$$x = K(a + a^\dagger)$$

Now our first order energy corrections are given as

$$\begin{aligned} E_n^{(1)} &= \left\langle \psi_n^{(0)}, \lambda x^{2m} \psi_n^{(0)} \right\rangle = \\ &= \lambda \left\langle x^m u_n, x^m u_n \right\rangle = \\ &= \lambda \| x^m u_n \|^2 \end{aligned}$$

So we need to calculate $x^m u_n$

$$\begin{aligned} \frac{1}{K^2} x^2 u_n &= \left(a + a^\dagger\right)^2 u_n = \\ &= \left(a + a^\dagger\right) \left(\sqrt{n} u_{n-1} + \sqrt{n+1} u_{n+1}\right) = \\ &= \sqrt{n(n-1)} u_{n-2} + \sqrt{n^2} u_n + \sqrt{(n+1)^2} u_n + \sqrt{(n+1)(n+2)} u_{n+2} = \\ &= \sqrt{n(n-1)} u_{n-2} + (2n+1) u_n + \sqrt{(n+1)(n+2)} u_{n+2} \end{aligned}$$

$$\begin{aligned} \frac{1}{K^3} x^3 u_n = &\left(a + a^\dagger\right) \left(\sqrt{n(n-1)} u_{n-2} + (2n+1) u_n + \sqrt{(n+1)(n+2)} u_{n+2}\right) = \\ =&\sqrt{n(n-1)(n-2)} u_{n-3} + \sqrt{n(n-1)^2} u_{n-1} + \\ &+ (2n+1)\sqrt{n} u_{n-1} + (2n+1)\sqrt{n+1} u_{n+1} + \\ &+ \sqrt{(n+1)(n+2)^2} u_{n+1} + \sqrt{(n+1)(n+2)(n+3)} u_{n+3} = \\ =&\sqrt{n(n-1)(n-2)} u_{n-3} + \sqrt{n}(3n) u_{n-1} + \\ &+ \sqrt{n+1}(3n+3) u_{n+1} + \sqrt{(n+1)(n+2)(n+3)} u_{n+3} \end{aligned}$$

So the first order energy correction for the x^4 perturbation is

$$\begin{aligned} E_n^{(1)} &= \lambda K^4 \left(n(n-1) + (2n+1)^2 + (n+1)(n+2)\right) = \\ &= \lambda K^4 \left(n^2 - n + 4n^2 + 4n + 2 + n^2 + 3n + 2\right) = \\ &= \lambda K^4 \left(6n^2 + 6n + 4\right) = \\ &= 2\lambda K^4 \left(3n^2 + 3n + 2\right) \end{aligned}$$

For the x^6 perturbation the correction is

$$\begin{aligned} E_n^{(1)} =&\lambda K^6 \left(n(n-1)(n-2) + 9n^3 + 9(n+1)^3 + (n+1)(n+2)(n+3)\right) = \\ =&\lambda K^6 \left(n^3 - 3n^2 + 2n + 9n^3 + 9n^3 + 27n^2 + 27n + 9 + \right. \\ &\left. n^3 + 5n^2 + 6n + n^2 + 5n + 6\right) = \\ =&\lambda K^6 \left(20n^3 + 30n^2 + 40n + 15\right) = \\ =&5\lambda K^6 \left(4n^3 + 6n^2 + 8n + 3\right) \end{aligned}$$

The second order correction is

$$E_n^{(2)} = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$$

Our matrix elements are

$$V_{kn} = \lambda \langle x^m u_k, x^m u_n \rangle$$

For the x^4 perturbation we get:

$$\begin{aligned}
V_{kn} =& \lambda K^4 \Big\langle \sqrt{k(k-1)} u_{k-2} + (2k+1) u_k + \sqrt{(k+1)(k+2)} u_{k+2}, \\
& \sqrt{n(n-1)} u_{n-2} + (2n+1) u_n + \sqrt{(n+1)(n+2)} u_{n+2} \Big\rangle = \\
=& \lambda K^4 \Big[\sqrt{k(k-1)n(n-1)} \delta_{k-2,n-2} + (2n+1)\sqrt{k(k-1)} \delta_{k-2,n} + \\
& + \sqrt{k(k-1)(n+1)(n+2)} \delta_{k-2,n+2} + (2k+1)\sqrt{n(n-1)} \delta_{k,n-2} + \\
& + (2k+1)(2n+1)\delta_{kn} + (2k+1)\sqrt{(n+1)(n+2)} \delta_{k,n+2} + \\
& + \sqrt{(k+1)(k+2)n(n-1)} \delta_{k+2,n-2} + (2n+1)\sqrt{(k+1)(k+2)} \delta_{k+2,n} + \\
& + \sqrt{(k+1)(k+2)(n+1)(n+2)} \delta_{k+2,n+2} \Big]
\end{aligned}$$

as $k \neq n$ we can reduce this to

$$\begin{aligned}
V_{kn} =& \lambda K^4 \Big[(2n+1)\sqrt{k(k-1)} \delta_{k-2,n} + \sqrt{k(k-1)(n+1)(n+2)} \delta_{k-2,n+2} + \\
& + (2k+1)\sqrt{n(n-1)} \delta_{k,n-2} + (2k+1)\sqrt{(n+1)(n+2)} \delta_{k,n+2} + \\
& + \sqrt{(k+1)(k+2)n(n-1)} \delta_{k+2,n-2} + (2n+1)\sqrt{(k+1)(k+2)} \delta_{k+2,n} \Big]
\end{aligned}$$

So our infinite sum for the second order correction reduces to a finite number of terms.

$$\begin{aligned}
E_n^{(2)} =& \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} = \\
=& \frac{\lambda^2 K^8}{c} \Bigg[\frac{(2n+1)\sqrt{(n+2)(n+1)}}{n-(n+2)} + \frac{\sqrt{(n+4)(n+3)(n+1)(n+2)}}{n-(n+4)} + \\
& + \frac{(2(n-2)+1)\sqrt{n(n-1)}}{n-(n-2)} + \frac{(2(n+2)+1)\sqrt{(n+1)(n+2)}}{n-(n+2)} + \\
& + \frac{\sqrt{(n-3)(n-2)(n-1)n}}{n-(n-4)} + \frac{(2n+1)\sqrt{(n-1)n}}{n-(n-2)} \Bigg] = \\
=& \frac{\lambda^2 K^8}{c} \Bigg[-(2n+3)\sqrt{(n+1)(n+2)} - \frac{\sqrt{(n+1)(n+2)(n+3)(n+4)}}{4} + \\
& + (2n-1)\sqrt{n(n-1)} + \frac{\sqrt{n(n-1)(n-2)(n-3)}}{4} \Bigg]
\end{aligned}$$

The last term is only valid if $n \geq 4$, the second last only if $n \geq 2$. So for example, the first energy level will be up to second order perturbation:

$$
\begin{aligned}
E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} &= \\
&= \frac{1}{2}c + 4\lambda K^4 + \frac{\lambda^2 K^8}{c}\left[-3\sqrt{2} - \frac{\sqrt{24}}{4}\right] = \\
&= \frac{1}{2}c + 4\lambda K^4 - \sqrt{2}\frac{\lambda^2 K^8}{c}\left[3 + \frac{\sqrt{3}}{2}\right]
\end{aligned}
$$

4.6.2 Infinitely deep square well

Perturb the infinitely deep square well with a harmonic oscillator potential λx^2. Our unperturbed eigenfunctions are

$$
u_n(x)^{(0)} = \frac{1}{\sqrt{a}} \begin{cases} \sin \frac{n\pi}{2a}x & n \text{ even} \\ \cos \frac{n\pi}{2a}x & n \text{ odd} \end{cases}
$$

As $n \in \mathbb{N}$ we get either symmetric or antisymmetric solutions. Our unperturbed energy spectrum is

$$
E_n^{(0)} = \frac{\hbar^2 \pi^2}{8ma^2} n^2
$$

Now calculate first order pertubation

$$
E_n^{(1)} = \int_{-a}^{a} \lambda x^2 u_n^2(x)\ dx
$$

In the symmetric case, i.e. n odd:

$$\begin{aligned}
E_n^{(1)} &= \lambda \int_{-a}^{a} x^2 \cos^2 \frac{n\pi}{2a}x \; dx = \\
&= \lambda \int_{-a}^{a} x^2 \frac{1}{2} \left(1 + \cos \frac{n\pi}{a}x\right) dx = \\
&= \frac{\lambda}{2} \int_{-a}^{a} x^2 \; dx + \frac{\lambda}{2} \int_{-a}^{a} x^2 \cos \frac{n\pi}{a}x \; dx = \\
&= \frac{\lambda}{2}\frac{2a^3}{3} + \frac{\lambda}{2}\left[x^2 \frac{a}{n\pi} \sin \frac{n\pi}{a}x \Big|_{-a}^{a} - \int_{-a}^{a} 2x \frac{a}{n\pi} \sin \frac{n\pi}{a}x \; dx \right] = \\
&= \frac{\lambda a^3}{3} + \frac{\lambda}{2}\left[0 + 2\frac{a^2}{n^2\pi^2} x \cos \frac{n\pi}{a}x \Big|_{-a}^{a} - 2\frac{a^2}{n^2\pi^2} \int \cos \frac{n\pi}{a}x \; dx \right] = \\
&= \frac{\lambda a^3}{3} + \frac{\lambda}{2}\left[2\frac{2a^2}{n^2\pi^2} a(-1)^n - \frac{2a^3}{n^3\pi^3} \sin \frac{n\pi}{a}x \Big|_{-a}^{a} \right] = \\
&= \frac{\lambda a^3}{3} + \frac{\lambda}{2}(-1)^n \frac{4a^3}{n^2\pi^2} = \\
&= \lambda\frac{a^3}{3} + \lambda(-1)^n \frac{2a^3}{n^2\pi^2} = \\
&= \lambda\frac{a^3}{3} - \lambda\frac{2a^3}{n^2\pi^2}
\end{aligned}$$

In the antisymmetric case:

$$\begin{aligned}
E_n^{(1)} &= \lambda \int_{-a}^{a} x^2 \sin^2 \frac{n\pi}{2a}x \; dx = \\
&= \lambda \int_{-a}^{a} x^2 \frac{1}{2} \left(1 - \cos \frac{n\pi}{a}x\right) dx = \\
&= \lambda\frac{a^3}{3} - \lambda(-1)^n \frac{2a^3}{n^2\pi^2} = \\
&= \lambda\frac{a^3}{3} - \lambda\frac{2a^3}{n^2\pi^2}
\end{aligned}$$

So in both cases the energy correction is

$$E_n^{(1)} = \lambda\frac{a^3}{3} - \lambda\frac{2a^3}{n^2\pi^2} \tag{4.17}$$

The second order energy correction is given by

$$E_n^{(2)} = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$$

Our matrix elements are

$$V_{kn} = \int_{-a}^{a} u_k^*(x) \lambda x^2 u_n(x) \; dx =$$

Symmetric in k and n so, we only have to check three cases:

- k, n even

$$V_{kn} = \lambda \int_{-a}^{a} x^2 \sin\frac{k\pi}{2a}x \sin\frac{n\pi}{2a}x \; dx$$

Using the trigonometric identity $\sin\alpha\sin\beta = \frac{1}{2}\left[\cos(\alpha-\beta) - \cos(\alpha+\beta)\right]$ we get

$$V_{kn} = \frac{\lambda}{2} \int_{-a}^{a} x^2 \left[\cos\frac{(n-k)\pi}{2a}x - \cos\frac{(n+k)\pi}{2a}x\right] \; dx$$

Both $n-k$ and $n+k$ are even. We calculated that integral for the first order:

$$\begin{aligned}
V_{kn} &= \lambda\frac{2a^3}{\pi^2}\left[(-1)^{\frac{n-k}{2}}\frac{4}{(n-k)^2} - (-1)^{\frac{n+k}{2}}\frac{4}{(n+k)^2}\right] = \\
&= \lambda\frac{8a^3}{\pi^2}(-1)^{\frac{n}{2}}\left[(-1)^{-\frac{k}{2}}\frac{1}{(n-k)^2} - (-1)^{\frac{k}{2}}\frac{1}{(n+k)^2}\right] = \\
&= \lambda\frac{8a^3}{\pi^2}(-1)^{\frac{n+k}{2}}\frac{(n+k^2)-(n-k^2)}{(n-k)^2(n+k)^2} = \\
&= \lambda(-1)^{\frac{n+k}{2}}\frac{8a^3}{\pi^2}\frac{4nk}{(n^2-k^2)^2}
\end{aligned}$$

- k, n odd

$$V_{kn} = \lambda \int_{-a}^{a} x^2 \cos\frac{k\pi}{2a}x \cos\frac{n\pi}{2a}x \; dx$$

Using the trigonometric identity $\sin\alpha\sin\beta = \frac{1}{2}\left[\cos(\alpha-\beta) + \cos(\alpha+\beta)\right]$ we get

$$V_{kn} = \frac{\lambda}{2} \int_{-a}^{a} x^2 \left[\cos\frac{(n-k)\pi}{2a}x + \cos\frac{(n+k)\pi}{2a}x\right] \; dx$$

Both $n-k$ and $n+k$ are even. We calculated that integral for the first order:

$$\begin{aligned}
V_{kn} &= \lambda\frac{2a^3}{\pi^2}\left[(-1)^{\frac{n-k}{2}}\frac{4}{(n-k)^2} + (-1)^{\frac{n+k}{2}}\frac{4}{(n+k)^2}\right] = \\
&= \lambda\frac{8a^3}{\pi^2}(-1)^{\frac{n+k}{2}}\left[(-1)^{-k}\frac{1}{(n-k)^2} + \frac{1}{(n+k)^2}\right] = \\
&= \lambda(-1)^{\frac{n+k}{2}}\frac{8a^3}{\pi^2}\left[\frac{-(n+k)^2+(n-k)^2}{(n^2-k^2)^2}\right] = \\
&= \lambda(-1)^{\frac{n+k}{2}}\frac{8a^3}{\pi^2}\frac{-4kn}{(n^2-k^2)^2}
\end{aligned}$$

- k even, n odd

$$V_{kn} = \lambda \int_{-a}^{a} x^2 \sin \frac{k\pi}{2a} x \cos \frac{n\pi}{2a} x \; dx$$

Using the trigonometric identity $\sin\alpha\cos\beta = \frac{1}{2}\left[\sin(\alpha-\beta)+\sin(\alpha+\beta)\right]$ we get

$$V_{kn} = \frac{\lambda}{2} \int_{-a}^{a} x^2 \left[\sin \frac{(k-n)\pi}{2a} x + \sin \frac{(n+k)\pi}{2a} x\right] \; dx$$

The sines are antisymmetric, x^2 is symmetric and as we have we have symmetric limits, the integral is zero

$$V_{kn} = 0$$

In our energy correction, we only need $|V_{kn}|^2$, so the different sines do not matter:

$$|V_{kn}|^2 = \lambda^2 \frac{1024a^6}{\pi^4} \frac{n^2k^2}{(n^2-k^2)^4}$$

So the second order energy correction is

$$\begin{aligned}
E_n^{(2)} &= \sum_{k\neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} = \\
&= \sum_{k\neq n} \lambda^2 \frac{1024a^6}{\pi^4} \frac{n^2k^2}{(n^2-k^2)^4} \frac{1}{\frac{\hbar^2\pi^2}{8ma^2}n^2 - \frac{\hbar^2\pi^2}{8ma^2}k^2} = \\
&= \sum_{k\neq n} \lambda^2 \frac{1024a^6}{\pi^4} \frac{n^2k^2}{(n^2-k^2)^4} \frac{8ma^2}{\hbar^2\pi^2} \frac{1}{n^2-k^2} = \\
&= \sum_{k\neq n} 2\lambda^2 \frac{64^2ma^8}{\hbar^2\pi^6} \frac{n^2k^2}{(n^2-k^2)^5}
\end{aligned}$$

subject to $k = n + 2l$ for any integer l