# WEEK 15 - THE LAST CLASS

Some notes about last lecture:

We saw $\hat{J}_\pm |kjm\rangle$ produces a vector of length $\hbar\sqrt{j(j+1)-m(m\pm1)}$ and $j$ is an integer or half-integer, and $m = -j, -j+1, \dots, j-1, j$.

$$\hat{J}_\pm |kjm\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}\; |kjm\pm1\rangle e^{i\phi_{kjm}}$$

pick to be 1.

The "highest" eigenvector is $|kjj\rangle$, so $\hat{J}_+ |kjj\rangle = 0$ and any $|kjm\rangle = (\hat{J}_-)^{j-m} |kjj\rangle$ (divided by some factor)

$$|kjm\pm1\rangle = \frac{1}{\hbar\sqrt{j(j+1)-m(m\pm1)}}\hat{J}_\pm |kjm\rangle$$

## DEGENERACY

Say we have a fixed value for $j$ and $m$. For two states $|kjm\rangle$ and $|k'jm\rangle$, $\langle kjm|k'jm\rangle = \delta_{kk'}$

and $\mathcal{E}(j,m) = \text{span}\{|kjm\rangle,\ k=1,2,\dots,g(j,m)\}$

$$\begin{array}{ccc} |kjm\rangle & \perp & |k'jm\rangle \\ \downarrow \hat{J}_\pm & & \downarrow \hat{J}_\pm \\ \hat{J}_\pm|kjm\rangle & \perp & \hat{J}_\pm|k'jm\rangle \end{array}$$

j stays the same, m changes.

(still orthogonal after applying $\hat{J}_\pm$)

so the degeneracy for each $(j,m)$, where $m$ varies, stays the same.

$$\langle k'jm|\hat{J}_-\hat{J}_+|kjm\rangle = \langle k'jm|\hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z|kjm\rangle$$

$$= \hbar^2(j(j+1)-m(m+1))\langle k'jm|kjm\rangle = 0$$

(and so follows $\hat{J}_-|kjm\rangle \perp \hat{J}_-|k'jm\rangle$)

That means degeneracy depends on $j$, not $m$ at all.

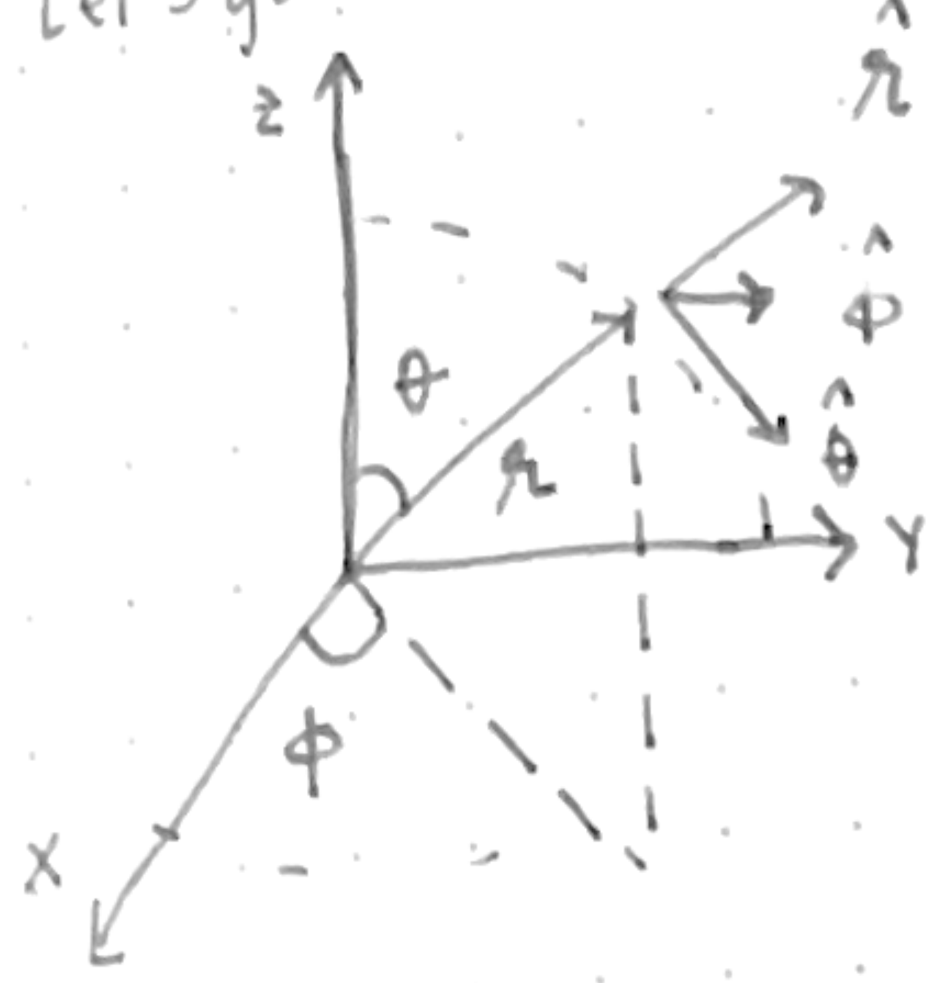
## ORBITAL ANGULAR MOMENTUM $\hat{\vec{L}}$'S EIGENVECTORS

$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{P}}$, so: $\hat{L}_i = \varepsilon_{ijk}\hat{X}_j\hat{P}_k$ (and $j \neq k$, else 0...)

$\langle \vec{r}|\hat{\vec{L}} = -i\hbar\,\vec{r}\times\vec{\nabla}\langle\vec{r}|$ (3D: $\langle\vec{r}|\hat{\vec{P}} = -i\hbar\vec{\nabla}\langle\vec{r}|$ not $-i\hbar\frac{d}{dx}\langle x|$)

Because $\vec{r}$ scales with the distance from the origin and $\vec{\nabla} = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$

so is scaling inversely with length, we expect $\vec{r} \times \vec{\nabla}$ to be invariant under scaling of $r$. so, we are motivated to use spherical coordinates.
Let's go into depth on spherical coordinates first:




a vector $\vec{r}$ with length $r$ can be written as $\vec{r} = r \cdot \hat{r}$

We can also write $\hat{r}$ in terms of $\theta$ and $\phi$:
$$\hat{r} = (\hat{z}\cos\theta + \sin\theta(\hat{x}\cos\phi + \hat{y}\sin\phi))$$

Thus all we need to do is find $\vec{\nabla}$ in spherical coordinates, and we can write $\langle \vec{r} | \hat{L}$ in spherical coordinates (and find $\hat{L}$'s eigenvectors).

Given function $f(\vec{r})$, where $\vec{r}$ is in terms of $\hat{r}$, $\hat{\theta}$, and $\hat{\phi}$ (see above)

any $\frac{\partial f(\vec{r}(r,\theta,\phi))}{\partial q_i}$ where $q$ can be coordinate $r, \theta$, or $\phi$, is

$\frac{\partial \vec{r}}{\partial q_i} \cdot \vec{\nabla} f$ (think $\left(\frac{\partial x}{\partial q}, \frac{\partial y}{\partial q}, \frac{\partial z}{\partial q}\right) \cdot \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}\right) \ldots$ )

Based on $\vec{r}$ in spherical coordinates,

$$\frac{\partial \vec{r}}{\partial r} = \hat{r} = \hat{z}\cos\theta + \sin\theta(\hat{x}\cos\phi + \hat{y}\sin\phi)$$

$$\frac{\partial \vec{r}}{\partial \theta} = r\hat{\theta} = r\left(-\sin\theta\,\hat{z} + \cos\theta(\hat{x}\cos\phi + \hat{y}\sin\phi)\right)$$

$$\frac{\partial \vec{r}}{\partial \phi} = r\sin\theta\,\hat{\phi} = r(-\sin\phi\,\hat{x} + \cos\phi\,\hat{y})\sin\theta$$

We can use this to find $\frac{\partial f}{\partial r}$, $\frac{\partial f}{\partial \theta}$, and $\frac{\partial f}{\partial \phi}$, and then $\vec{\nabla} f$ in turn.

$$\frac{\partial f}{\partial r} = \frac{\partial \vec{r}}{\partial r} \cdot \vec{\nabla} f = \hat{r} \cdot \vec{\nabla} f, \quad \frac{\partial f}{\partial \theta} = \frac{\partial \vec{r}}{\partial \theta} \cdot \vec{\nabla} f = r\hat{\theta} \cdot \vec{\nabla} f, \quad \frac{\partial f}{\partial \phi} = \frac{\partial \vec{r}}{\partial \phi} \cdot \vec{\nabla} f = r\sin\theta\,\hat{\phi} \cdot \nabla f$$

oh also $\hat{r} \times \hat{\theta} = \hat{\phi}$, so $\hat{r}, \hat{\theta}, \hat{\phi}$ are orthonormal:

$$\begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \end{vmatrix} = \hat{x}(-\sin^2\theta\sin\phi - \cos^2\theta\sin\phi) - \hat{y}(-\sin^2\theta\cos\phi - \cos^2\theta\cos\phi) + \hat{z}(0)$$

Anyway, because $\hat{r}$, $\hat{\theta}$, and $\hat{\phi}$ are orthonormal, we can write

$$\vec{\nabla} f = \underbrace{(\hat{r}\cdot\vec{\nabla} f)}_{=\frac{\partial f}{\partial r}}\hat{r} + \underbrace{(\hat{\theta}\cdot\vec{\nabla} f)}_{\frac{1}{r}\frac{\partial f}{\partial \theta}}\hat{\theta} + \underbrace{(\hat{\phi}\cdot\vec{\nabla} f)}_{\frac{1}{r\sin\theta}\frac{\partial f}{\partial \phi}}\hat{\phi}$$

so, $\vec{\nabla} f = \hat{r}\,\partial_r f + \frac{\hat{\theta}}{r}\partial_\theta f + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi f$

$$= \underline{\left(\hat{r}\,\partial_r + \frac{\hat{\theta}}{r}\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi\right)} f$$

which means $\vec{\nabla}$ in spherical coordinates is $\hat{r}\,\partial_r + \frac{\hat{\theta}}{r}\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi$

Thus $\langle\vec{r}|\hat{\vec{L}} = -i\hbar\,\vec{r}\times\vec{\nabla}\langle\vec{r}|$

$$= -i\hbar\,(r\hat{r})\times\left(\hat{r}\,\partial_r + \frac{\hat{\theta}}{r}\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi\right)\langle\vec{r}|$$

$\hat{r}\times\hat{r} = 0$ and we saw $\hat{r}\times\hat{\theta} = \hat{\phi}$, so:

$$\langle\vec{r}|\hat{\vec{L}} = -i\hbar\, r\left(\frac{1}{r}\hat{\phi}\,\partial_\theta - \frac{1}{r\sin\theta}\hat{\theta}\,\partial_\phi\right)\langle\vec{r}|$$

$$= -i\hbar\left(\hat{\phi}\,\partial_\theta - \frac{1}{\sin\theta}\hat{\theta}\,\partial_\phi\right)\langle\vec{r}|$$

with no dependence on $r$, as expected.

Now... $\hat{L}_z = \hat{\vec{L}}\cdot\hat{z} = -i\hbar\left(\hat{z}\cdot\hat{\phi}\,\partial_\theta - \frac{1}{\sin\theta}\hat{z}\cdot\hat{\theta}\,\partial_\phi\right)$

Remember $\hat{\theta}$ is in $z$-$y$ and $\hat{\phi}$ is in $x$-$y$, so $\hat{z}\cdot\hat{\phi} = 0$ (they're orthogonal) and $\hat{\theta}$ is $\underline{-\sin\theta\,\hat{z}} + \cos\theta\,(\hat{x}\cos\phi + \hat{y}\sin\phi)$

Thus $\hat{L}_z = -i\hbar\left(0 + \frac{\sin\theta}{\sin\theta}\partial_\phi\right) = -i\hbar\,\partial_\phi$

Similarly, $\hat{L}_x = \hat{\vec{L}}\cdot\hat{x} = -i\hbar\left(\hat{x}\cdot\hat{\phi}\,\partial_\theta - \frac{1}{\sin\theta}\hat{x}\cdot\hat{\theta}\,\partial_\phi\right)$

$$= -i\hbar\left(-\sin\phi\,\partial_\theta - \frac{\cos\theta\cos\phi}{\sin\theta}\partial_\phi\right)$$

$$= i\hbar\left(\sin\phi\,\partial_\theta + \frac{\cos\phi}{\tan\theta}\partial_\phi\right)$$

and $\hat{L}_y = \hat{\vec{L}}\cdot\hat{y}$

$$= -i\hbar\left(\cos\phi\,\partial_\theta - \frac{1}{\sin\theta}\cos\theta\sin\phi\,\partial_\phi\right)$$

$$= i\hbar\left(-\cos\phi\,\partial_\theta + \frac{\sin\phi}{\tan\theta}\partial_\phi\right)$$

$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z = -\hbar^2 \left( \partial_\theta^2 + \frac{1}{\tan\theta} \partial_\theta + \frac{1}{\sin^2\theta} \partial_\phi^2 \right)$

$\hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y = \hbar e^{\pm i\phi} \left( \pm \partial_\theta + i \cot\theta \, \partial_\phi \right)$

which also do not depend on $r$. $\hat{L}^2$ and $\hat{L}_z$ are self-adjoint operators on $L^2$ space of functions on the unit sphere. Because they do not depend on radial coordinates, we can write their eigen states in terms of spherical harmonics only:

$f_{k\ell m}(\vec{r}) = R_{k\ell}(r) Y_{\ell m}(\theta, \phi)$ if $f$ is only parametrically dependent on $r$. Then if we call $f$ $Y_{\ell m}(r, \theta, \phi)$ instead:

$$\hat{L}^2 Y_{\ell m}(r, \theta, \phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(r, \theta, \phi)$$
$$\hat{L}_z Y_{\ell m}(r, \theta, \phi) = \hbar m Y_{\ell m}(r, \theta, \phi)$$

and we can choose $Y_{\ell m}(\theta, \phi)$ to be orthonormal on the sphere:

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) = \delta_{\ell\ell'} \delta_{mm'}$$

hence $Y_{\ell m}(\theta, \phi)$ are spherical harmonics.

$$\hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m} = \hbar m \, Y_{\ell m}(\theta, \phi) R_{k\ell}(r)$$

$$-i\hbar \partial_\phi R(r) Y_{\ell m}(\theta, \phi) = \hbar m Y_{\ell m}(\theta, \phi) R(r)$$
$$-i\hbar \partial_\phi Y_{\ell m}(\theta, \phi) = \hbar m Y_{\ell m}(\theta, \phi)$$

$$\partial_\phi Y_{\ell m}(\theta, \phi) = im \, Y_{\ell m}(\theta, \phi)$$

which has solution $\partial_\phi \left( \ln \left( Y_{\ell m}(\theta, \phi) \right) \right) = im$

$$\ln \left( Y_{\ell m}(\theta, \phi) \right) = im\phi + C(\theta)$$

$Y_{\ell m}(\theta, 0) = e^0 e^{C(\theta)} = e^{C(\theta)} \longrightarrow Y_{\ell m}(\theta, \phi) = Y_{\ell m}(\theta, 0) e^{im\phi}$

because of the $e^{im\phi}$ term, m must be an integer, which means $\ell$ is also an integer. Since we're concerned with $-\ell, \cdots \ell$ always, $\ell \in \mathbb{N}_0$.

(This is because the ½ integers in j are introduced by intrinsic spin

If we can find $Y_{\ell m}(\theta, 0)$ for one value of $\ell, m$ we can get all the others for the same $\ell$ but a different $m$ via ladder operators. We didn't do this in class, though... Basically:

$$L_+ Y_{\ell\ell} = 0 \quad \text{(can't go any higher, } m \leq \ell\text{)}$$

$$(\partial_\theta + i\cot\theta\, \partial_\phi) Y_{\ell\ell}(\theta) e^{i\ell\phi} = 0$$

$\uparrow$ $\phi$ is fixed @ 0, so as shorthand, just $Y_{\ell\ell}(\theta)$

$$\partial_\theta \Psi_{\ell\ell}(\theta) e^{i\ell\phi} = -i\cot Y_{\ell\ell}(\theta) i\ell e^{i\ell\phi}$$

$$\Psi'_{\ell\ell}(\theta) = -i\cot Y_{\ell\ell}(\theta) i\ell = \frac{\ell}{\tan\theta} Y_{\ell\ell}(\theta)$$

which eventually yields $Y_{\ell\ell} \propto \sin^\ell\theta$, so $\underline{Y_{\ell\ell}}(\theta, \phi) = \underbrace{C_\ell \sin^\ell\theta}\, \underbrace{e^{i\ell\phi}}$

which is then $Y_{\ell\ell}(\theta, \phi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}} \sin^\ell\theta\, e^{i\ell\phi}$

after normalization (and sign convention).

Recursively, you can find $L_\pm Y_{\ell m} = \hbar\sqrt{\ell(\ell+1) \mp m(m\pm 1)}\, Y_{\ell m\pm 1}$ so:

$$Y_{\ell m}(\theta, \phi) = \sqrt{\frac{(\ell+m)!}{(2\ell)!(\ell-m)!}} \left(\frac{\hat{L}_-}{\hbar}\right)^{\ell-m} Y_{\ell\ell}(\theta, \phi)$$

The entire thing is

$$Y_{\ell m}(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} P_{\ell m}(\cos\theta) e^{im\phi} \qquad m \geq 0$$

$$Y_{\ell -m} = (-1)^m Y^*_{\ell m} \qquad \hat{\Pi} Y_{\ell m} = (-1)^\ell Y_{\ell m}$$

$\underline{P_{\ell m}}(u) = \sqrt{(1-u^2)^m}\, \frac{d^m P_\ell(u)}{du^m}$ $\quad m \geq 0$ are <u>Associated Legendre Polynomials.</u>

$$P_{\ell -m}(u) = (-1)^m \frac{(\ell-m)!}{(\ell+m)!} P_{\ell m}(u)$$

and,

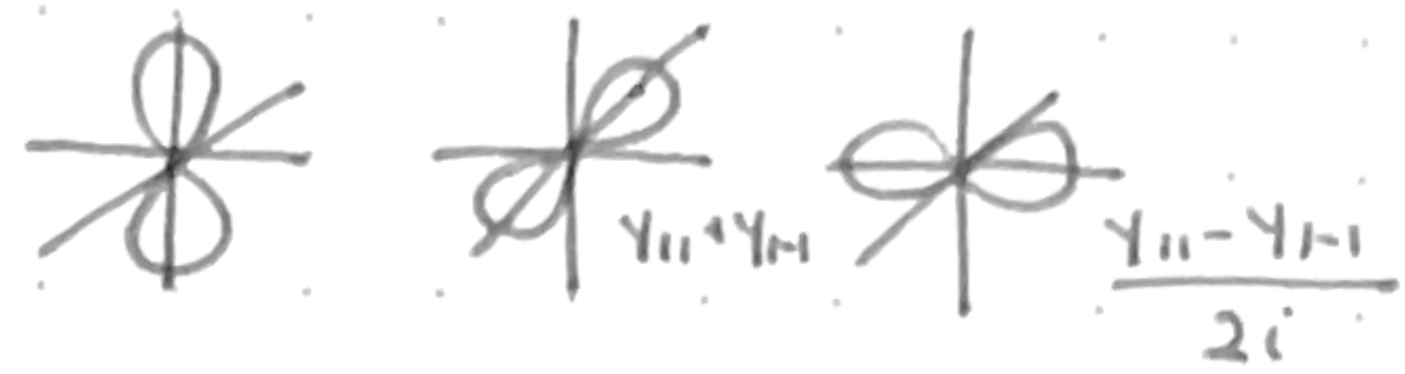
$P_\ell(u) = \frac{(-1)^\ell}{2^\ell \ell!} \frac{d^\ell}{du^\ell}(1-u^2)^\ell$ are <u>Legendre Polynomials</u>

normalized so that $P_\ell(1) = 1$

$$Y_{\ell 0}(\theta, \phi) = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta), \quad Y_{00} = \sqrt{\frac{1}{4\pi}}$$

$Y_{1m}(\vec{r})$ has $Y_{11} \propto \frac{x+iy}{r}$, $Y_{10}\ \frac{z}{r}$, $Y_{1-1} \propto \frac{x-iy}{r}$, generally:

$$Y_{\ell m} \propto \sum_{ijk}^{\ell = i+j+k} \frac{x^i y^j z^k}{r^\ell} C_{ijk}$$




## APPLICATION OF SPHERICAL HARMONICS: CENTRAL POTENTIALS

e.g. Particle in spherical box / confined to spherical shell, Quantum dots, Hydrogenic atoms ($H$, $He^+$, $Li^{2+}$), Isotropic harmonic oscillator

one particle in 3D:

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{V}(r)$$, note $r$ = dist from origin, invariant under rotation (scalar)

$\mu$ ↑ reduced mass of particle

$\hat{H}$ is a scalar! So $[\hat{H}, \hat{L}_i] = 0$ and $[\hat{H}, \hat{L}^2] = 0$ We can separate angular & radial contributions again, for KE, and we want to find:

$$\hat{H}\,|\psi_{n\ell m}\rangle = E_{n\ell}\,|\psi_{n\ell m}\rangle$$
$$\hat{L}^2\,|\psi_{n\ell m}\rangle = \hbar\,\ell(\ell+1)\,|\psi_{n\ell m}\rangle$$
$$\hat{L}_z\,|\psi_{n\ell m}\rangle = \hbar m\,|\psi_{n\ell m}\rangle$$

where $\psi_{n\ell m}(\vec{r}) = \langle \hat{r} | \psi_{n\ell m}\rangle = \underbrace{R_{n\ell}(r)}_{\text{need to find}}\ \underbrace{Y_{\ell m}(\theta,\phi)}_{\text{we know the sph. harmonics already}}$

To find $R_{n\ell}(r)$: rewrite $\hat{p}$ (and KE)

$$\hat{L}^2 = \sum_i \hat{L}_i \hat{L}_i = \underbrace{(\varepsilon_{ijk}\hat{x}_j\hat{p}_k)(\varepsilon_{i\ell m}\hat{x}_\ell\hat{p}_m)}_{\text{because } \hat{L}_i\hat{L}_i}$$ summation implied...

(collapse $\varepsilon$'s) $= (\delta_{j\ell}\delta_{km} - \delta_{jm}\delta_{k\ell})\,\hat{x}_j\hat{p}_k\hat{x}_\ell\hat{p}_m$

(only non-zero if indices match) $= \hat{x}_j \underline{\hat{p}_k \hat{x}_j} \hat{p}_k - \hat{x}_j\hat{p}_k\hat{x}_k\hat{p}_j$

$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$, so $\hat{p}_k\hat{x}_j = \hat{x}_j\hat{p}_k - i\hbar\delta_{jk}$ and $\sum_k \hat{p}_k\hat{x}_k = \sum_k \hat{x}_k\hat{p}_k - i\hbar\underbrace{\delta_{kk}}_{=1}$ ↑ 3 poss.

$$= \underbrace{\hat{x}_j\hat{x}_j}_{\hat{r}^2}\underbrace{\hat{p}_k\hat{p}_k}_{\hat{p}^2} - i\hbar\,\underline{\underline{\hat{x}_j\hat{p}_j}} - \hat{x}_j\hat{x}_k\hat{p}_k\hat{p}_j + \underline{\underline{3i\hbar\,\hat{x}_j\hat{p}_j}}$$

$$-\hat{x}_k\hat{p}_k\hat{x}_j\hat{p}_j - i\hbar\,\hat{x}_k\hat{p}_k$$

So ... $\hat{L}^2 = \hat{r}^2\hat{p}^2 + 2i\hbar\,\hat{x}_j\hat{p}_j - \hat{x}_k\hat{x}_j\hat{p}_k\hat{p}_j$

$$= \hat{r}^2\hat{p}^2 + i\hbar\,\vec{r}\cdot\vec{p} - (\vec{r}\cdot\vec{p})^2$$

and $\hat{p}^2 = \frac{1}{r^2}\left((\vec{r}\cdot\vec{p})^2 - i\hbar\,\vec{r}\cdot\vec{p} + \hat{L}^2\right)$

$$= \frac{1}{r^2}\left(\hat{L}^2 - \hbar^2 r\partial_r r\partial_r - \hbar^2 r\partial_r\right) \quad \text{using } \vec{r}\cdot\vec{p} = -i\hbar r\partial_r$$

$$= \frac{1}{r^2}\left(\hat{L}^2 - \hbar^2 r\partial_r (r\partial_r + 1)\right)$$

$(r\partial_r + 1)f = r\partial_r f + f = \partial_r(rf)$

$$= \frac{1}{r^2}\left(\hat{L}^2 - \hbar^2 r\underbrace{\partial_r(\partial_r r}\right)$$

$$= \frac{1}{r^2}\left(\hat{L}^2 - \hbar^2 r\partial_r^2 r\right)$$

Thus the entire Hamiltonian is $\hat{H} = \frac{1}{2\mu r^2}\left(\hat{L}^2 - \hbar^2 r\partial_r^2 r\right) + V(r))$

$$\hat{H}\left(R_{n\ell}(r)Y_{\ell m}(\theta,\phi)\right) = E_{n\ell} R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$$

$$\left(\frac{1}{2\mu r^2}\left(\underline{\underline{\hat{L}^2}} - \hbar^2 r\partial_r^2 r\right) + V(r)\right)R_{n\ell}(r) = E_{n\ell} R_{n\ell}$$

$$\left(\frac{1}{2\mu r^2}\left(\hbar^2 \ell(\ell+1) - \hbar^2 r\partial_r^2 r\right) + V(r)\right)R_{n\ell} = E_{n\ell} R_{n\ell}$$

$$\left(\frac{\hbar^2}{2\mu r^2}\left(\underbrace{\ell(\ell+1)}_{\text{angular KE}} - \underbrace{r\partial_r^2 r}_{\text{radial KE}}\right) + V(r)\right)R_{n\ell} = E_{n\ell} R_{n\ell} \quad \text{(The Radial Equation.)}$$

which has non-constant coefficients. Using $u_\ell(r) = r R_{n\ell}(r)$

$$\left(-\frac{\hbar^2}{2\mu}\partial_r^2 + V(r) + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right) r R_{n\ell} = E\, r R_{n\ell}$$

$$-\frac{\hbar^2}{2\mu}u_\ell''(r) + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}u_\ell(r) + V(r)u_\ell(r) = E\,u_\ell(r)$$

Which is the reduced radial equation. $V_{eff}(r) \equiv V(r) + \underbrace{\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{\text{centrifugal}}$ or the effective radial potential, makes:

$$-\frac{\hbar^2}{2\mu}u_\ell'' + V_{eff}\,u_\ell = E\,u_\ell$$