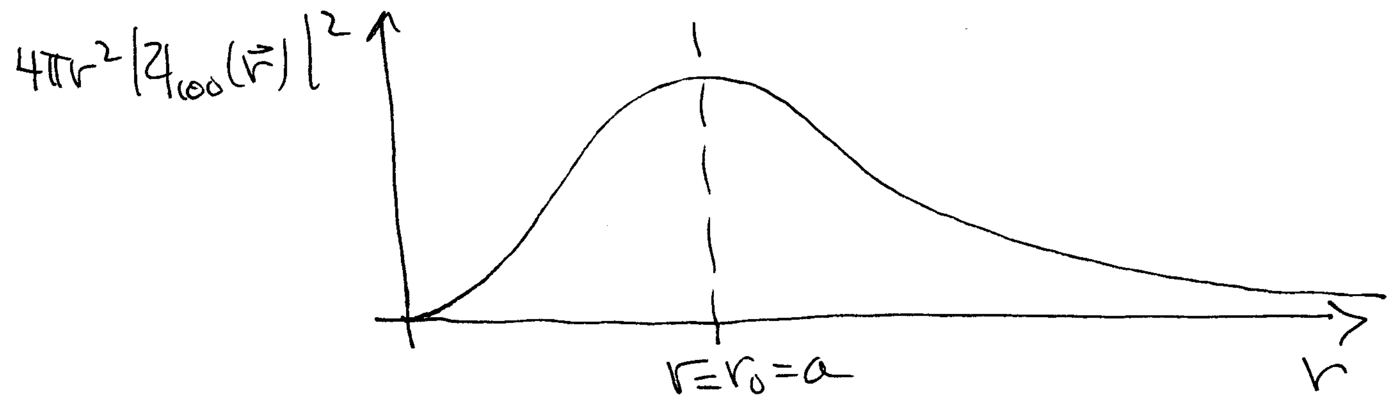
III.C) The probability density is maximized at the Bohr radius



III.D) Orbital Angular Momentum:

In classical mechanics the Hamiltonian for the central potential problem can be written as

$$H = \frac{p_r^2}{2m} + \frac{\vec{L}^2}{2mr^2} + V(r)$$

with p_r the momentum conjugate to r, $p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} = m\dot{r}$, while $\vec{L} = \vec{r} \times \vec{p}$ is the orbital angular momentum. Comparing this to the QM Hamiltonian

III.D)
$$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] + V(r)$$

we identify the radial component of the momentum squared with

$$p_r^2 = -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

and the orbital ∡ momentum squared with

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

which is just $(-\hbar^2 r^2)$ times the angular part of the Laplacian ∇^2.

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

III.D.) Further, since $\psi_{n\ell m} = R_{n\ell}(r) Y_\ell^m(\theta,\varphi)$

$$H\psi_{n\ell m}(r,\theta,\varphi) = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi_{n\ell m} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]\psi_{n\ell m}$$
$$= E_n \psi_{n\ell m}$$

$\Rightarrow Y_\ell^m(\theta,\varphi)$ are the eigenfunctions of $\vec{L}^2$

$$\vec{L}^2 Y_\ell^m(\theta,\varphi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\varphi),$$

with the (orbital $\angle$ momentum)^2 eigenvalues given by $\hbar^2\ell(\ell+1)$, $\ell = 0,1,2,\ldots$.

Of course this also just follows from the Δ equation when we separated the Schrödinger Eq.

Let's show that the spherical harmonics are indeed the eigenfunctions of $\vec{L}^2$ and L_z more carefully.

III.D) Classically $\vec{L} = \vec{r} \times \vec{p}$. Let's take this over as our definition in QM also except $\vec{p} = \frac{\hbar}{i}\vec{\nabla}$. So

$$\boxed{\vec{L} \equiv \vec{r} \times \vec{p} = \frac{\hbar}{i}\vec{r} \times \vec{\nabla}}$$

In components $(x = x_1, y = x_2, z = x_3)$

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

with ϵ_{ijk} the anti-symmetric or permutation (Levi-Civita) tensor

$$\epsilon_{ijk} = \begin{cases} +1, & (i,j,k) \text{ even permutation of } (1,2,3) \\ -1, & (i,j,k) \text{ odd } \quad " \quad " \ (1,2,3) \\ 0, & \text{otherwise (i.e. any } i,j \text{ or } k \text{ equal)} \end{cases}$$

So

$$L_1 = x_2 p_3 - x_3 p_2 = \frac{\hbar}{i}\left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2}\right)$$

$$L_2 = x_3 p_1 - x_1 p_3 = \frac{\hbar}{i}\left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3}\right)$$

$$L_3 = x_1 p_2 - x_2 p_1 = \frac{\hbar}{i}\left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1}\right)$$

[again we interchangeably use $x = x_1$, $y = x_2$, $z = x_3$ and $p_x = p_1$, $p_y = p_2$ and $p_z = p_3$.]

III.D.) Recall the canonical commutation relations

$$[x_i, p_j] = i\hbar\,\delta_{ij}$$

$$[x_i, x_j] = 0 = [p_i, p_j]$$

Hence the $\{L_i\}$ do not commute

$$[L_1, L_2] = \left(\frac{\hbar}{i}\right)^2 \left[x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2},\ x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3}\right]$$

$$= -\hbar^2 \left(x_2 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_2}\right)$$

$$= -\hbar^2 \left(\frac{-i}{\hbar}\right) L_3 = i\hbar L_3$$

$$\boxed{[L_1, L_2] = i\hbar L_3}$$

Likewise for the cyclic permutations of $(1,2,3)$ ex $[L_2, L_3] = i\hbar L_1$.

(Remark: This general result $[L_i, L_j] = i\hbar\,\epsilon_{ijk} L_k$ can be obtained using the important identity

$$\epsilon_{ijk}\,\epsilon_{i'j'k} = \delta_{ii'}\delta_{jj'} - \delta_{ij'}\delta_{ji'}$$

III.c) Consider

$$[L_i, L_j] = [\epsilon_{ikl}\, x_k p_l, \epsilon_{jmn}\, x_m p_n]$$

$$= \epsilon_{ikl}\,\epsilon_{jmn}\,[x_k p_l, x_m p_n]$$

Use the identity for operators

$$[A, BC] = B[A,C] + [A,B]C$$

$$\Rightarrow [x_k p_l, x_m p_n] = x_m [x_k p_l, p_n] + [x_k p_l, x_m] p_n$$

$$= x_m x_k \cancelto{0}{[p_l, p_n]} + x_m [x_k, p_n] p_l$$

$$+ x_k [p_l, x_m] p_n + \cancelto{0}{[x_k, x_m]} p_l p_n$$

$$= i\hbar \left(x_m p_l \delta_{kn} - x_k p_n \delta_{lm} \right)$$

$$\Rightarrow$$

$$[L_i, L_j] = i\hbar \left(\epsilon_{ikl}\,\epsilon_{jmk}\, x_m p_l - \epsilon_{ikl}\,\epsilon_{jln}\, x_k p_n \right)$$

(Relabeling dummy indices) $$= -i\hbar\, \epsilon_{ilk}\,\epsilon_{jmk} \left(x_m p_l - x_l p_m \right)$$

Now use THE identity

$$\epsilon_{ilk}\,\epsilon_{jmk} = \delta_{ij}\delta_{lm} - \delta_{im}\delta_{lj}$$

III D.) $[L_i, L_j] = -i\hbar\,(\delta_{ij}\, x_m p_m - x_i p_j - \delta_{ij}\, x_m p_m + x_j p_i)$

$$= i\hbar\,(x_i p_j - x_j p_i)$$

But $\epsilon_{ijk} L_k = \epsilon_{ijk}\epsilon_{klm}\, x_l p_m$

$$= (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})\, x_l p_m$$

$$= x_i p_j - x_j p_i$$

Hence $\boxed{[L_i, L_j] = i\hbar\,\epsilon_{ijk} L_k}$).

The components of $\vec{L}$ do not commute with each other! Hence they are not simultaneously diagonalizable. Heisenberg's uncertainty principle $\Rightarrow$

$$\Delta L_1\, \Delta L_2 \geq \frac{\hbar}{2}\,|L_3| \quad .$$

However $\vec{L}^2 = \vec{L}\cdot\vec{L}$ commutes with $\vec{L}$.

III.D.)

$$[\vec{L}^2, L_j] = [L_iL_i, L_j]$$

$$= L_i[L_i, L_j] + [L_i, L_j]L_i$$

$$= i\hbar\epsilon_{ijk}L_iL_k + i\hbar\epsilon_{ijk}L_kL_i$$

Change dummy i,k indicies on 2nd term

$$= i\hbar(\epsilon_{ijk} + \underbrace{\epsilon_{kji}}_{=-\epsilon_{ijk}})L_iL_k$$

$$= 0.$$

So $\boxed{[\vec{L}^2, \vec{L}] = 0}$

Hence we can determine the eigenvalues of $\vec{L}^2$ and one of the components L_i, say $L_z = L_3$, simultaneously since $[\vec{L}^2, L_3] = 0$.

Suppose $\vec{L}^2 f = \lambda f$ and $L_z f = \mu f$

we will use the algebraic approach to find λ, μ the eigenvalues

III D.) Consider the "ladder operator" technique again —

Define $L_\pm \equiv L_x \pm i L_y$

Then

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y]$$

$$= i\hbar L_y \pm i(-i\hbar) L_x$$

$$= \pm\hbar(L_x \pm i L_y) = \pm\hbar L_\pm$$

$$\Rightarrow \boxed{[L_z, L_\pm] = \pm\hbar L_\pm}$$

Still $\boxed{[\vec{L}^2, L_\pm] = 0}$

Now if f is an eigenfunction of $(\vec{L}^2, L_z)$ so is $(L_\pm f)$

$$\vec{L}^2(L_\pm f) = L_\pm \vec{L}^2 f = L_\pm \lambda f$$

$$= \lambda(L_\pm f)$$

hence $L_\pm f$ has the same $\vec{L}^2$ eigenvalue as f; λ.

III D.) Also

$$L_z(L_\pm f) = [L_z L_\pm - L_\pm L_z + L_\pm L_z] f$$

$$= \underbrace{[L_z, L_\pm]}f + L_\pm \underbrace{L_z f}$$

$$= \pm\hbar L_\pm f + L_\pm \mu f$$

$$\boxed{L_z(L_\pm f) = (\mu \pm \hbar)(L_\pm f)}$$

So $L_\pm f$ is an eigenfunction of L_z with eigenvalue $\mu \pm \hbar$. Hence

L_+ "raises" the L_z eigenvalue by $+\hbar$
L_- "lowers" " " " " $-\hbar$.

So for a given λ we obtain ladder states by applying $L_\pm$ to the eigenfunction f.

Now $\langle \vec{L}^2 \rangle_f = \langle L_x^2 + L_y^2 + L_z^2 \rangle_f$

$$= \langle L_x^2 + L_y^2 \rangle_f + \mu^2$$

Now $\langle L_{x,y}^2 \rangle_f = \int d^3r\, f^* L_{x,y}^2 f = \int d^3r\, (L_{x,y} f)^* (L_{x,y} f)$

Since $L_{x,y,z}$ are Hermitean.

III.D.) So $\langle L_{x,y}^2 \rangle = \int d^3r \, |L_{x,y} f|^2 \geq 0$

So $\langle \vec{L}^2 \rangle_f = \langle L_x^2 \rangle_f + \langle L_y^2 \rangle_f + \mu^2$

$$\boxed{\lambda^2 \geq \mu^2}$$

So $|\mu| \leq |\lambda|$

Hence we cannot raise and lower the L_z eigenvalues forever — there ~~must~~ be a state so that it is the top rung of the ladder, f_t, so that

$$L_+ f_t = 0 \,.$$

Let $\hbar l$ be the eigenvalue of L_z at this top rung.

$$L_z f_t = \hbar l f_t \;;\; \vec{L}^2 f_t = \lambda f_t$$

Now consider

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 + L_y^2 \pm i L_y L_x \mp i L_x L_y$$

$$= L_x^2 + L_y^2 \mp i \underbrace{[L_x, L_y]}_{= i\hbar L_z}$$

III.D.)

$$L_\pm L_\mp = L_x^2 + L_y^2 \pm \hbar L_z$$

$$= L_x^2 + L_y^2 + L_z^2 - L_z^2 \pm \hbar L_z$$

$$L_\pm L_\mp = \vec{L}^2 - L_z^2 \pm \hbar L_z$$

$$\Rightarrow \boxed{\vec{L}^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z}$$

So

$$\vec{L}^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t$$

but $L_+ f_t = 0$

$$= (0 + l^2\hbar^2 + \hbar^2 l) f_t$$

$$= \hbar^2 l(l+1) f_t = \lambda f_t$$

$$\Rightarrow \boxed{\lambda = \hbar^2 l(l+1)}$$

This gives λ in terms of maximum L_z eigenvalue $\hbar l$.

Mutatis Mutandis, there's a lowest rung on the L_z eigenvalue ladder, I call the eigenfunction f_b.

III.D.) Where
$$L_- f_b = 0$$
Let $\hbar \underline{l}$ be the lowest L_z eigenvalue
$$L_z f_b = \hbar \underline{l}\, f_b \quad \text{and still}$$
$$\vec{L}^2 f_b = \lambda f_b.$$

So
$$\vec{L}^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b$$
since $L_- f_b = 0$
$$= (0 + \hbar^2 \underline{l}^2 - \hbar^2 \underline{l}) f_b$$
$$= \hbar^2 \underline{l}(\underline{l} - 1) f_b = \lambda f_b$$

Hence
$$\boxed{\lambda = \hbar^2 \underline{l}(\underline{l} - 1)}$$

This gives λ in terms of the lowest L_z eigenvalue $\underline{l}\hbar$.

Hence
$$\lambda = \hbar^2 l(l+1) = \hbar^2 \underline{l}(\underline{l} - 1)$$

III D.) $\Rightarrow$

$$\ell(\ell+1) = \underline{\ell}(\underline{\ell}-1)$$

Thus $$\boxed{\underline{\ell} = \ell+1 \quad \text{or} \quad \underline{\ell} = -\ell}$$

The first choice is absurd the lowest eigenvalue $\underline{\ell}$ cannot be 1 larger than the highest eigenvalue ℓ.

Hence $$\boxed{\underline{\ell} = -\ell}$$

$\lambda = \hbar^2 \ell(\ell+1)$ and the L_z eigenvalues go from $-\ell$ up to $+\ell$ in integer steps i.e.

$$\mu = m\hbar \quad \text{where}$$

$$m = \underbrace{-\ell, -\ell+1, -\ell+2, \ldots, -\ell+N = \ell}$$

There are N-rungs to go from bottom $(-\ell)$ rung to top $(\ell = -\ell+N)$.

Thus $-\ell + N = \ell \Rightarrow \ell = \frac{N}{2}$; $N = 0, 1, 2, \ldots$

$$\Rightarrow \boxed{\ell = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \ \& \ m = -\ell, -\ell+1, \ldots, \ell-1, \ell}$$

- III.D.) So

$$\vec{L}^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m$$
$$L_z f_\ell^m = m\hbar f_\ell^m$$

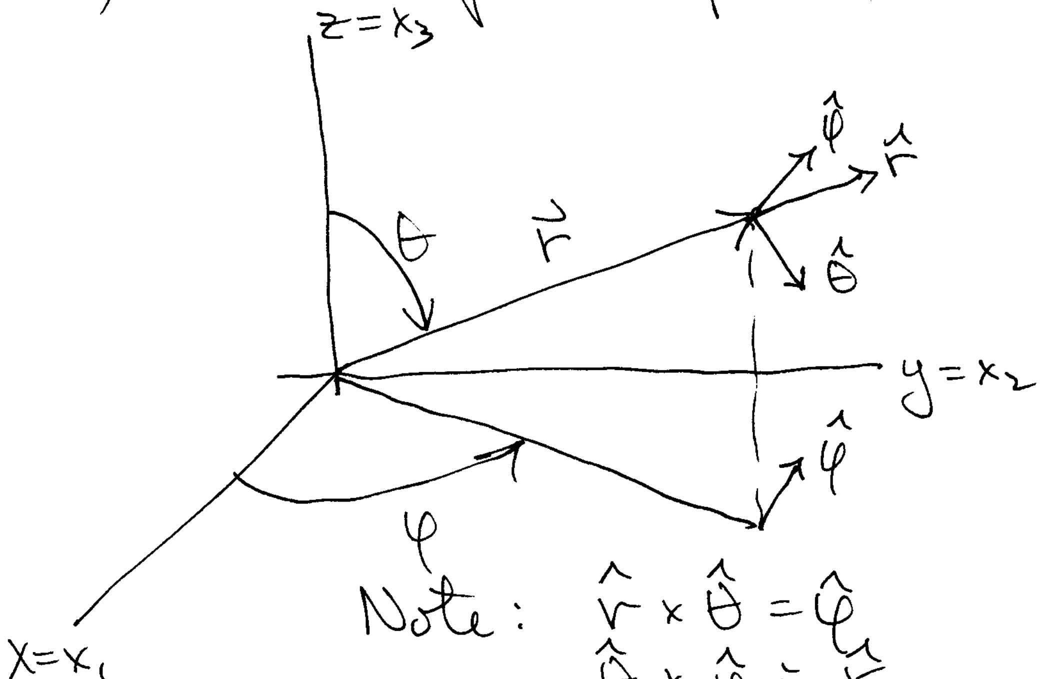
and ℓ is an integer or a half integer!

$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ while m has $2\ell+1$ values $m = -\ell, -\ell+1, \ldots, \ell-1, +\ell$.

Thus we have determined the spectrum of $\vec{L}^2$, & L_z by purely algebraic means!!

As we will see next for integer ℓ (and hence m) the eigenfunctions are the spherical harmonics Y_ℓ^m. But we also have the half-integer possible — these will correspond to spin of odd half integer $\frac{1}{2}$, $\frac{3}{2}$, ... and we will have to extend the wavefunction space to include matrixes of wavefunctions in order to realize this possibility!

III.D.) Recall spherical polar coordinates



Note: $\hat{r} \times \hat{\theta} = \hat{\varphi}$
$\hat{\theta} \times \hat{\varphi} = \hat{r}$
$\hat{\varphi} \times \hat{r} = \hat{\theta}$

In spherical polar coordinates the Cartesian coordinates are given by

$$x_1 = r \sin\theta \cos\varphi$$
$$x_2 = r \sin\theta \sin\varphi$$
$$x_3 = r \cos\theta$$

while the spherical coordinate basis vectors $(\hat{r}, \hat{\theta}, \hat{\varphi})$ are given by

III.D.)

$$\hat{r} = \sin\theta\cos\varphi\,\hat{i} + \sin\theta\sin\varphi\,\hat{j} + \cos\theta\,\hat{k}$$

$$\hat{\theta} = \cos\theta\cos\varphi\,\hat{i} + \cos\theta\sin\varphi\,\hat{j} - \sin\theta\,\hat{k}$$

$$\hat{\varphi} = -\sin\varphi\,\hat{i} + \cos\varphi\,\hat{j}$$

The gradient operator in spherical polar coordinates is

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

The orbital ∡ momentum operator then is given by

$$\vec{L} = \vec{r}\times\vec{p} = (r\hat{r})\times\left(\frac{\hbar}{i}\vec{\nabla}\right)$$

$$\boxed{\vec{L} = \frac{\hbar}{i}\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right).}$$

The Cartesian components $L_1 = \hat{i}\cdot\vec{L}$, $L_2 = \hat{j}\cdot\vec{L}$, $L_3 = \hat{k}\cdot\vec{L}$, are found in spherical polar coordinates to be

III.D.)

$$\boxed{\begin{aligned} L_x = L_1 &= \frac{\hbar}{i}\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ L_y = L_2 &= \frac{\hbar}{i}\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ L_z = L_3 &= \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \end{aligned}}$$

Directly calculating $\vec{L}$ we find

$$\boxed{\begin{aligned} \vec{L}^2 &= L_x^2 + L_y^2 + L_z^2 \\ &= -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \end{aligned}}$$

This is just as we first noticed - the angular part of the Laplacian

$$\boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\vec{L}^2}$$

Hence, just recalling page -209-

The spherical harmonics are the

III.D) normalized eigenfunctions of the $\vec{L}^2$ & L_z operators for l integer valued:

$$\vec{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi)$$

$$L_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

for $l = 0, 1, 2, \ldots$; $m = -l, -l+1, \ldots, 0, \ldots, l-1, +l$.

Hence for central potential problems the energy eigenfunctions are simultaneous eigenfunctions of $(H, \vec{L}^2, L_z)$ [thus we must have $0 = [H, \vec{L}^2] = [H, L_z] = [\vec{L}^2, L_z]$, as they do)

$$H \psi_{lm} = E \psi_{lm}$$

$$\vec{L}^2 \psi_{lm} = \hbar^2 l(l+1) \psi_{lm}$$

$$L_z \psi_{lm} = m\hbar \psi_{lm}$$