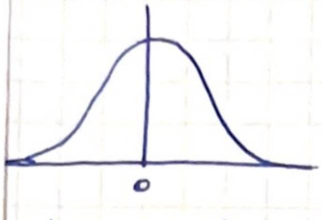
We can also now consider $\langle x \rangle$:



$$\int_{-\infty}^{\infty} \underset{\uparrow \atop \psi^*}{e^{\frac{-ax^2}{2}}} \, \underset{\uparrow \atop \hat{A}}{x} \, \underset{\uparrow \atop \psi}{e^{\frac{-ax^2}{2}}} \, dx = 0 \rightarrow$$ This makes sense as the distribution of the particle across space is symmetric.

What about $\langle p \rangle$?

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, dx = A_0^2 \int_{-\infty}^{\infty} e^{\frac{-ax^2}{2}} \left(-i\hbar \frac{d}{dx} e^{\frac{-ax^2}{2}}\right) dx = -i\hbar A_0^2 \int_{-\infty}^{\infty} e^{\frac{-ax^2}{2}} \left(axe^{\frac{-ax^2}{2}}\right) dx = -i\hbar A_0^2 \int_{-\infty}^{\infty} axe^{-ax^2}$$
$$= 0.$$

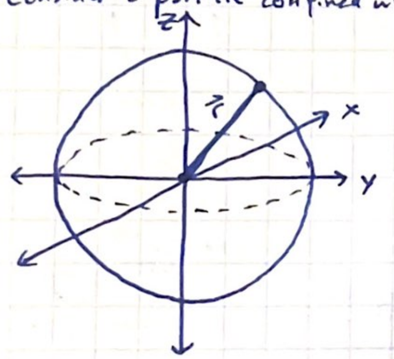
Be careful: Note that $\int_0^{\infty} x^{2m+1} e^{\frac{-ax^2}{2}} dx \neq \int_{-\infty}^{\infty} x^{2m+1} e^{-\frac{ax^2}{2}} dx$.

From Particle in a Ring to Particle in a Sphere

Recall that for a PIR, $\hat{\mathcal{H}} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$, $\hat{\mathcal{H}}\psi = E\psi$, and $-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\psi = \frac{\hbar^2}{2I} m_\ell^2 \psi$, $-\frac{d^2}{d\phi^2}\psi_{m_\ell} = m_\ell^2 \psi$

This will be useful to us later...

Consider a particle confined within a sphere with radius r:



"Particle in a sphere" - rigid rotor:

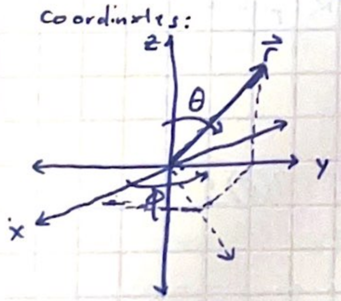
→ We can assume that $U = 0$ here since the particle independently rotates and is locked to the surface of the sphere (we assume $\frac{\partial}{\partial r} = 0$).

Recall that for 3D movement of a particle, we ~~did the conversion of~~ used the the x, y, and z compounds:

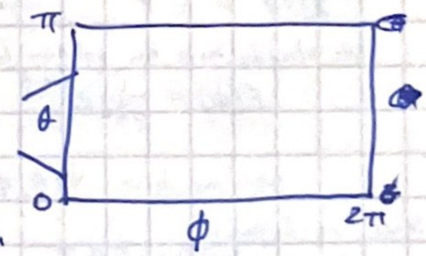
$$\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

→ Cartesian coordinates are a problem, since x, y, and z are not independent of each other.

Similar to $\{x, y\} \rightarrow \{r, \theta\}$ for polar coordinates, we now do $\{x, y, z\} \rightarrow \{r, \theta, \phi\}$ for spherical coordinates:



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



Realize that movement along the slice, with changing ϕ and constant θ, is the same as the PIR problem

→ Movement along ϕ is similar to x movement, movement along θ is similar to y movement.
→ Movement of ϕ and θ are independent of each other → 2 independent quantization effects.

To convert $\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi$ to spherical coordinates, we use the Laplacian operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$$

Which is very messy so let's clean it up accordingly for our scenario.

Conversion of $\Psi(x,y,z) \to \Psi(\theta,\phi)$ (Since r is constant)

since $\frac{\partial}{\partial r} = 0$

Therefore $\underbrace{\cancel{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}}_{0} + \frac{1}{r^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right) = \frac{1}{r^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$.

Applying this to $\hat{H}\Psi$, we see $-\underbrace{\frac{\hbar^2}{2\mu}\frac{1}{r^2}}_{I}\frac{1}{\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$

and $\hat{H}\Psi = E\Psi = -\frac{\hbar^2}{2I}\frac{1}{\sin^2\theta}\left(\cancel{\frac{\partial}{\partial\theta}}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\Psi = E\Psi$

$\cdot\ \frac{2I}{\hbar}$

$-\frac{1}{\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\Psi = \underbrace{\frac{2I}{\hbar^2}E}_{\beta}\Psi$, So $E = \frac{\hbar^2}{2I}\beta$

$\cdot \sin^2\theta$

$-\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\Psi = \beta\Psi\sin^2\theta$ We can rearrange this such that one side depends on θ, and the other on ϕ.

$-\frac{\partial^2}{\partial\phi^2}\Psi = \beta\Psi\sin^2\theta + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Psi$ We see that the wave function may be rewritten as: $\Psi(\theta,\phi) = \underset{T}{\Theta(\theta)}\cdot\underset{F}{\Phi(\phi)}$ (For less confusion)

$\Psi = T(\theta)\cdot F(\phi)$

$-\frac{\partial^2}{\partial\phi^2}TF = \beta TF\sin^2\theta + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)TF$

$\div\ TF$

$-\frac{\cancel{T}\frac{d^2}{d\phi^2}F}{\cancel{T}F} = \frac{\beta\sin^2\theta\ \cancel{TF} + \cancel{F}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)T}{TF}$

$-\frac{\frac{d^2}{d\phi^2}F}{F} = \beta\sin^2\theta + \frac{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)T}{T} = C$ (For simplicity's sake, and to draw and important parallel)

$\cdot F$

We end up with:

$-\frac{d^2}{d\phi^2}F = CF$ → Resembles $\boxed{-\frac{d^2}{d\phi^2}\Psi_{m_\ell} = m_\ell^2\Psi}$, from PIR problem

We already have the solution for this, that

$F(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_\ell\phi}$, as previously solved, for the P.I.R. problem.

Now we have $\Psi(\theta,\phi) = T(\theta)F(\phi) = T(\theta)\left(\frac{1}{\sqrt{2\pi}}e^{im_\ell\phi}\right)$. So what is $T(\theta)$?

Since we defined

$\beta\sin^2\theta + \frac{\sin\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}T}{T} = m_\ell^2 = C$,

$\cdot T$

$\beta\sin^2\theta\, T + \sin\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}T = m_\ell^2 T$, many solutions to this equation, depending on m_ℓ.

Therefore, to solve this equation, we need to find a combination of T and β which works.

→ There is a trivial solution to this equation. Assume $m_\ell = 0$:

$\beta\sin^2\theta + \sin\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}T = 0$, $\sin\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}T = \beta\sin^2\theta$, $\frac{d}{d\theta}\sin\frac{d}{d\theta}T = \beta\sin\theta$

If we assume T to be constant, $\frac{d}{d\theta}T = 0$, and $\beta\sin\theta = 0$. In this case $\beta = 0$ and $E = 0$.

Consider the case where $m_\ell = 0$ and T is a trig function, say, $\cos\theta$.

If $T = \cos\theta$,

$$\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\cos\theta = -\beta\sin\theta \ , \ \cancel{-\frac{d^2}{d\theta^2}\sin^2\theta \ldots}$$

$$\frac{d^2}{d\theta^2}\sin^2\theta = -\beta\sin\theta .$$

$$-\frac{d}{d\theta}\sin^2\theta = -2\sin\theta\cos\theta = -\beta\sin\theta\cos\theta$$

$\beta = 2$

These correspond to the associated Legendre Polynomials:

$m_\ell = 0$	$T =$ constant	$\beta = 0$	$E = 0$
$m_\ell = 0$	$T = \cos\theta$	$\beta = 2$	$E = \frac{\hbar^2}{2I}\cdot 2$
$m_\ell = \pm 1$	$T = \pm\sin\theta$	$\beta = 2$	
$m_\ell = 0$	$T = 3\cos^2\theta - 1$	$\beta = 6$	$E = \frac{\hbar^2}{2I}\cdot 6$
$m_\ell = \pm 1$	$T = \pm\cos\theta\sin\theta$	$\beta = 6$	
$m_\ell \pm 2$	$T = \sin^2\theta$	$\beta = 6$	

E

$E = \frac{\hbar^2}{2I}\cdot 6$, $\ell = 2$

$E = \frac{\hbar^2}{2I}\cdot 2$, $\ell = 1$

$E = 0$, $\ell = 0$

Note that the Legendre Polynomials are related to the orbitals of electrons!

We can use this newly solved $T(\theta)$ in conjunction with $F(\phi)$ to find the spherical harmonics, which correspond to the wave function.

Note the pattern of β, where β: 0, 2, 6, 12, ...

$$\boxed{E = \frac{\hbar^2}{2I}\ell(\ell+1)}$$

where $\ell = 0, 1, 2, \ldots$

What does all of this imply?

→ Particles can only move discretely in rotation, due to 2 quantum numbers, m_ℓ and ℓ:

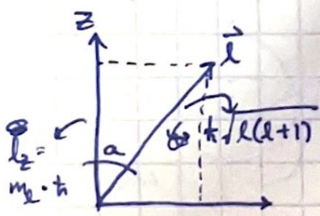
$E = K = \frac{\vec{\ell}^2}{2I}$ ← Angular momentum, NOT quantum number ℓ. , and $\vec{\ell} = I\vec{\omega}$.

For K, $\hat{\mathcal{H}} = \frac{\vec{\ell}^2}{2\mu r^2}$. The eigenvalues can be solved relating $\frac{\hbar^2}{2\mu}(\ell(\ell+1))$

$$\left(\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\phi^2}\right)\right)$$

$$\vec{\ell} = \hbar^2\ell(\ell+1)$$
$$|\vec{\ell}| = \sqrt{\hbar^2(\ell+1)\ell}$$
$$|\vec{\ell}| = \hbar\sqrt{\ell(\ell+1)}$$

Visually:



The eigenvalues are therefore:

- $\ell_z = \hbar m_\ell$
- $\hat{\ell}_z = -i\hbar\frac{d}{d\phi}$

For angle a, we can solve through:

$\ell_z = |\vec{\ell}|\cos a$:

$$\cos a = \frac{m_\ell\cdot\cancel{\hbar}}{\cancel{\hbar}\sqrt{\ell(\ell+1)}} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

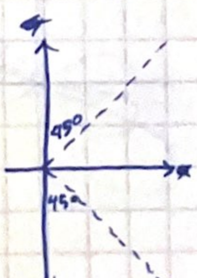
Only discrete combinations of its projections: Only fixed orientation in space.

Consider the case that $m_\ell = 0$:

$$\cos a = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} = 0 \ , \ a = \frac{\pi}{2}$$

Consider the case that $\ell = 1$, $m_\ell = \pm 1$:

$$\cos a = \pm\frac{1}{\sqrt{2}} \ , \ a = \frac{\pi}{4}$$



We see that $\vec{\ell}$ can only be pointing at 45° intervals, quantized to these ranges. Can this momentum face along the side? NO

Since $\cos a = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$, $\cos a$ is maximized when $\ell = m_\ell$:

$$\cos a = \frac{\ell}{\sqrt{\ell(\ell+1)}} = \sqrt{\frac{\ell}{\ell+1}} < 1.$$

Therefore the vector of momentum can only point upwards, or downwards, but never sideways.

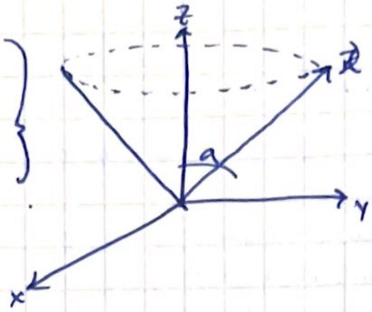
"Quantization of Space"

Since $\vec{l}_z = |\vec{l}| \cos a$,

$|\vec{l}| = \hbar\sqrt{l(l+1)}$, meaning that the length of angular momentum is also quantized.

Can we know $\vec{l}_x$, $\vec{l}_y$, and $\vec{l}_z$ with arbitrary precision? - No:

$$\left.\begin{aligned} [\hat{l}_x, \hat{l}_y] &= i\hbar\hat{l}_z \neq 0 \\ [\hat{l}_z, \hat{l}_x] &= i\hbar\hat{l}_y \neq 0 \\ [\hat{l}_y, \hat{l}_z] &= i\hbar\hat{l}_x \neq 0 \\ [\hat{l}_z, \hat{l}_y] &= -i\hbar\hat{l}_x \neq 0 \end{aligned}\right\}$$



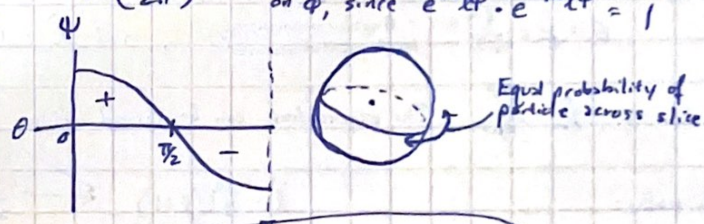
This means that the vector for $|\vec{l}|$ could be anywhere along the side of the cone formed, since l_x and l_y cannot be known at the same time as l_z.

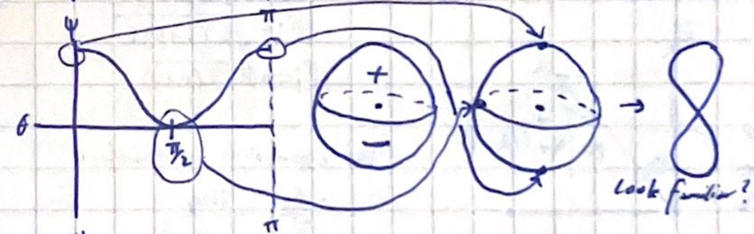
Consider also that since $\cos a = \frac{m_l}{\sqrt{l(l+1)}}$, The vector cannot be along the z-axis.
If we knew that $\vec{l}$ is along the z-axis, we would also know that $\vec{l}_x$ and $\vec{l}_y = 0$, which violates what the previous statement about uncertainties has shown.

Consider the spherical harmonic $Y(\theta, \phi) = T(\theta) \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$, where $Y(\theta,\phi)$ and $T(\theta)$ both depend m_l and l quantum numbers. What is $P(\phi)$? → First, change to probability

$$|Y(\theta,\phi)|^2 = T^2 \left| \frac{e^{im_l\phi}}{\sqrt{2\pi}} \right|^2 = T^2\left(\frac{1}{2\pi}\right)$$ → Note that there should be no dependence on ϕ, since $e^{im_l\phi} \cdot e^{-im_l\phi} = 1$

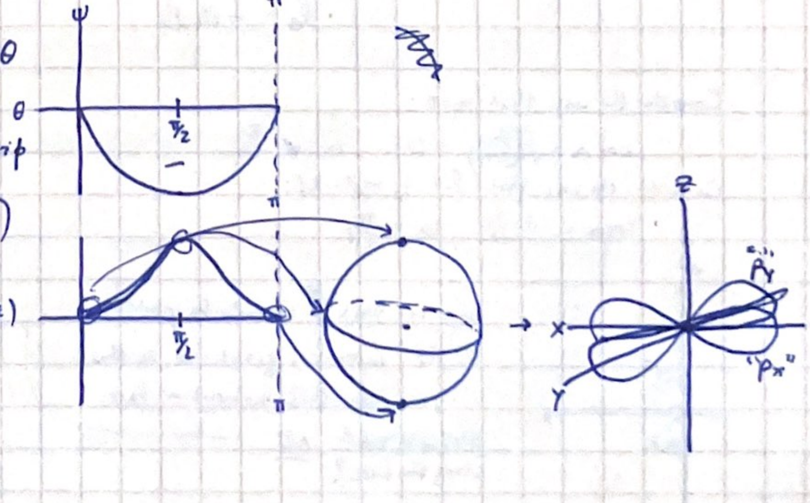
When $l=0$, $m_l = 0$, T_{00} = constant
$l=1$, $m_l=0$, $T_{10} \propto \cos\theta$



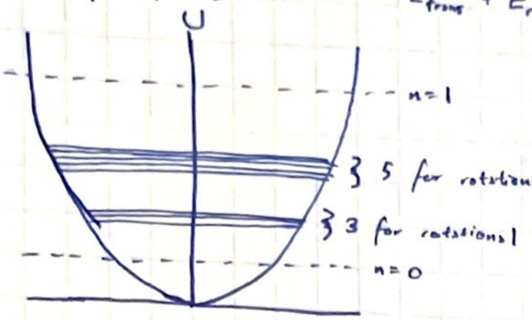


When $l=1$, $m_l = \pm 1$, $T_{1,\pm1} \propto -\sin\theta$
Linear combination of $m_l=+1$ and $m_l=-1$.

$$\frac{-Y_{1,+1} + Y_{1,-1}}{\sqrt{2}} = \sin\theta e^{i\phi} + \sin\theta e^{-i\phi}$$
$$\hookrightarrow \sin\theta\left(e^{i\phi} + e^{-i\phi}\right)$$
$$= \sin\theta(\cos\phi)$$
(We ignore the constant)



Comparing energies: $\sum E = E_{trans} + E_{rot} + E_{vib}$, where $E_{tr} << E_{rot} << E_{vib}$.



$E_{vibr} = h\nu(n + 1/2)$, $E_{rot} = \frac{\hbar^2}{2I} l(l+1)$

The Hydrogen Atom

The hydrogen atom contains two particles: e^- and p^+ which are not bound to each other.

$m_{e^-} = 9.1 \times 10^{-31}$ kg $\approx \frac{1}{2000}(m_{p^+})$

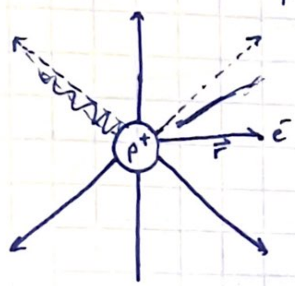
$m_{p^+} = 1.7 \times 10^{-27}$ kg

$$U = -\frac{e^2}{r}\underbrace{\left(\frac{1}{4\pi\varepsilon_0}\right)}_{\text{Permittivity of Free Space (A constant)}}$$

Center of mass calculation: $R_{com} = \frac{\vec{r}_{p^+}m_{p^+} + \vec{r}_{e^-}m_{e^-}}{m_{p^+}} \approx \vec{r}_p$

↳ All of the mass is practically centered on the proton.

Reduced mass: $\frac{m_{p^+}(m_{e^-})}{m_{p^+} + m_{e^-}} \approx m_{e^-} = \mu = m$



The potential energy of this system does not depend on orientation – "central potential."

$$U = -\frac{1}{4\pi\varepsilon_0}\left(\frac{e^2}{r}\right), \text{ where } r = \sqrt{x^2+y^2+z^2}$$

Since cartesian coordinates are not convenient, we swap $\{x, y, z\} \rightarrow \{r, \theta, \phi\}$

→ The potential does not change along the sphere, however, movement along layers of a sphere, $\frac{\partial}{\partial r}$, depends on the potential. The total hamiltonian can be expressed as:

$$\hat{\mathcal{H}} = \hat{K} + \hat{U} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}, \text{ where } m = m_{e^-}$$

We can express this more explicitly using $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2}{2mr^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$

Recall that $\hat{K} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{equals 0 for particle in a sphere, but cannot = 0 for hydrogen atom model.}} - \frac{\hbar^2}{2mr^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$

We can calculate the energies of the hydrogen atom by using Schrödinger's time independent equation:

$\hat{\mathcal{H}}\psi = E\psi$,

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) - \frac{\hbar^2}{2mr^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi \cdot \frac{r^2}{4\pi\varepsilon_0}\frac{e^2}{r}\psi = E\psi$$

We can use some tricks to make sure only one side depends on r and one side on ϕ, θ.