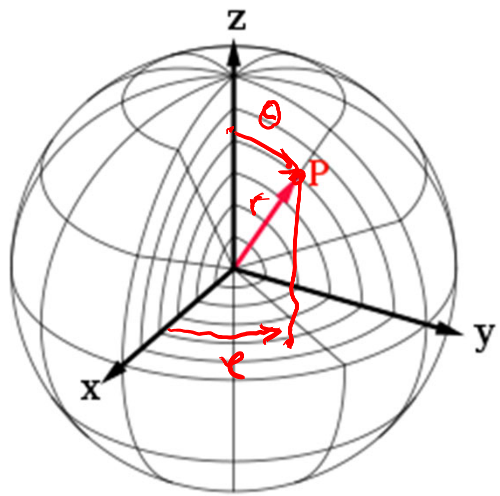
<u>Separation of variables in spherical polar coordinates</u>

We now consider the following class of PDEs:

$$\left(-\nabla^2 + f(r)\right)\psi = 0$$



The function $f(r)$ only depends on the distance from the origin.

Physics-y example: an electron around an atom obeys

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \left[V(r) - E\right]\psi = 0$$

The general form of the PDE is

$$\left(-\nabla^2 + f(r)\right)\psi = 0$$

In spherical polar coordinates, this equation is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + f(r)\psi = 0$$

Substitute a separation Ansatz:

Let $\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$

"psi" "phi"

Subbing in,

$$-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 R'\Theta\Phi\right) - \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\, R\,\Theta'\Phi\right) - \frac{1}{r^2\sin^2\theta}R\Theta\Phi'' + fR\Theta\Phi = 0.$$

Divide by $R\Theta\Phi$:

$$-\frac{1}{r^2}\frac{1}{R}\frac{\partial}{\partial r}\left(r^2R'\right) - \frac{1}{r^2\sin\theta}\frac{1}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\Theta'\right) - \frac{1}{r^2\sin^2\theta}\frac{\Phi''}{\Phi} + f = 0.$$

multiply by $-r^2\sin^2\theta$:

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2R'\right) - \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\Theta'\right) - \frac{\Phi''}{\Phi} + fr^2\sin^2\theta = 0.$$

depends only on φ

depend on (r,θ).

$$\Rightarrow -\frac{\Phi''}{\Phi} = \lambda.$$

We have found for the (r, θ) part of the equation

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\underline{\sin^2\theta} - fr^2\,\underline{\sin^2\theta} + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \lambda = 0$$

$\frac{\Phi''}{\Phi}$.

We now try to separate r and θ:

Divide by $\sin^2\theta$:

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - f(r)r^2}_{\text{depends on } r} + \underbrace{\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{\lambda}{\sin^2\theta}}_{\text{depends on } \theta} = 0.$$

$= \mp\mu$ $\qquad$ $= \pm\mu$.

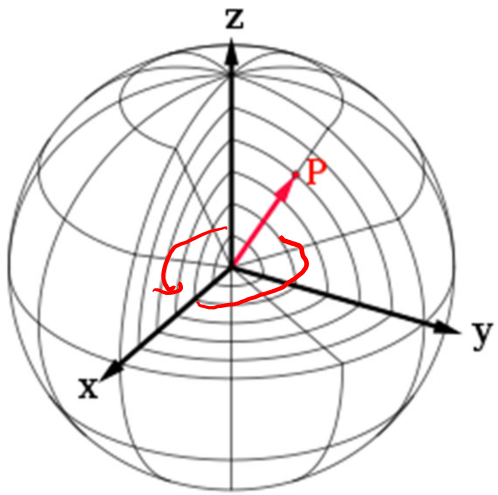
We end up with three equations:

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -\lambda$$

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{\lambda}{\sin^2\theta} = -\mu$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - f(r)r^2 = \mu$$

The problem for $\Phi(\varphi)$ is the familiar Sturm-Liouville problem:



$$\Phi'' = -\lambda\Phi$$

$$\Phi(0) = \Phi(2\pi),$$

$$\Phi'(0) = \Phi'(2\pi)$$

With solutions

$$\Phi_m(\varphi) = e^{im\varphi}$$

with $m \in \mathbb{Z}$.

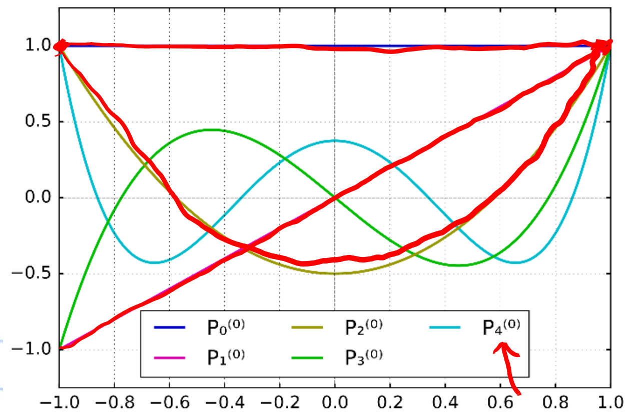
$\ldots -5, -4, -3, -2, -1, 0, 1, 2, 3, \ldots$

We write the solutions to

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\right]\Theta = -\mu\Theta$$

sub operator

$\mathcal{L}\Theta = \mu\Theta$



as

$$\Theta(\theta) = P_\ell^m(\cos\theta)$$

with

$$\mu = \ell(\ell+1)$$

$0 \le m \le \ell$

These are (complicated) functions of $\cos\theta$, called <u>Associated Legendre Polynomials</u>

$$P_0^0(x) = 1$$

$$P_1^0(x) = x$$

$$P_2^0(x) = \frac{1}{2}(3x^2 - 1)$$

$$P_1^1(x) = -(1 - x^2)^{1/2}$$

sub $P_1^0(\cos\theta) = \cos\theta$.

$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(-\sin\theta\sin\theta\right) - 0$

$= -\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin^2\theta\right) = -\frac{1}{\sin\theta}\left(2\sin\theta\cos\theta\right)$

$= -2\cos\theta$

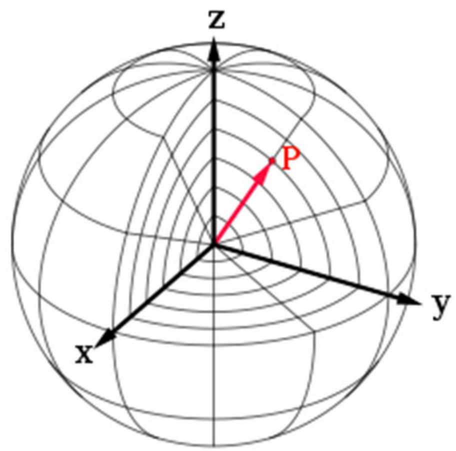
$= -(1+1)1\cos\theta = -\mu\Theta$.

These functions are "google-able" and can be easily computed.

We have found for the φ and θ dependence that

$$\Theta(\theta) = P_\ell^m(\cos\theta)$$

$$\Phi(\varphi) = e^{im\varphi}$$



It makes sense to bundle these together into a new function, called a *spherical harmonic*

$$Y_{\ell,m}(\theta,\varphi) = P_\ell^m(\cos\theta)e^{im\varphi}$$

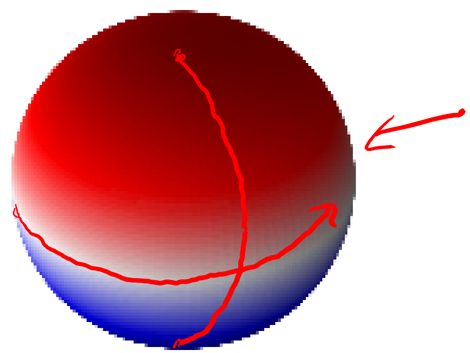
With m, ℓ integers such that

$$|m| < \ell$$

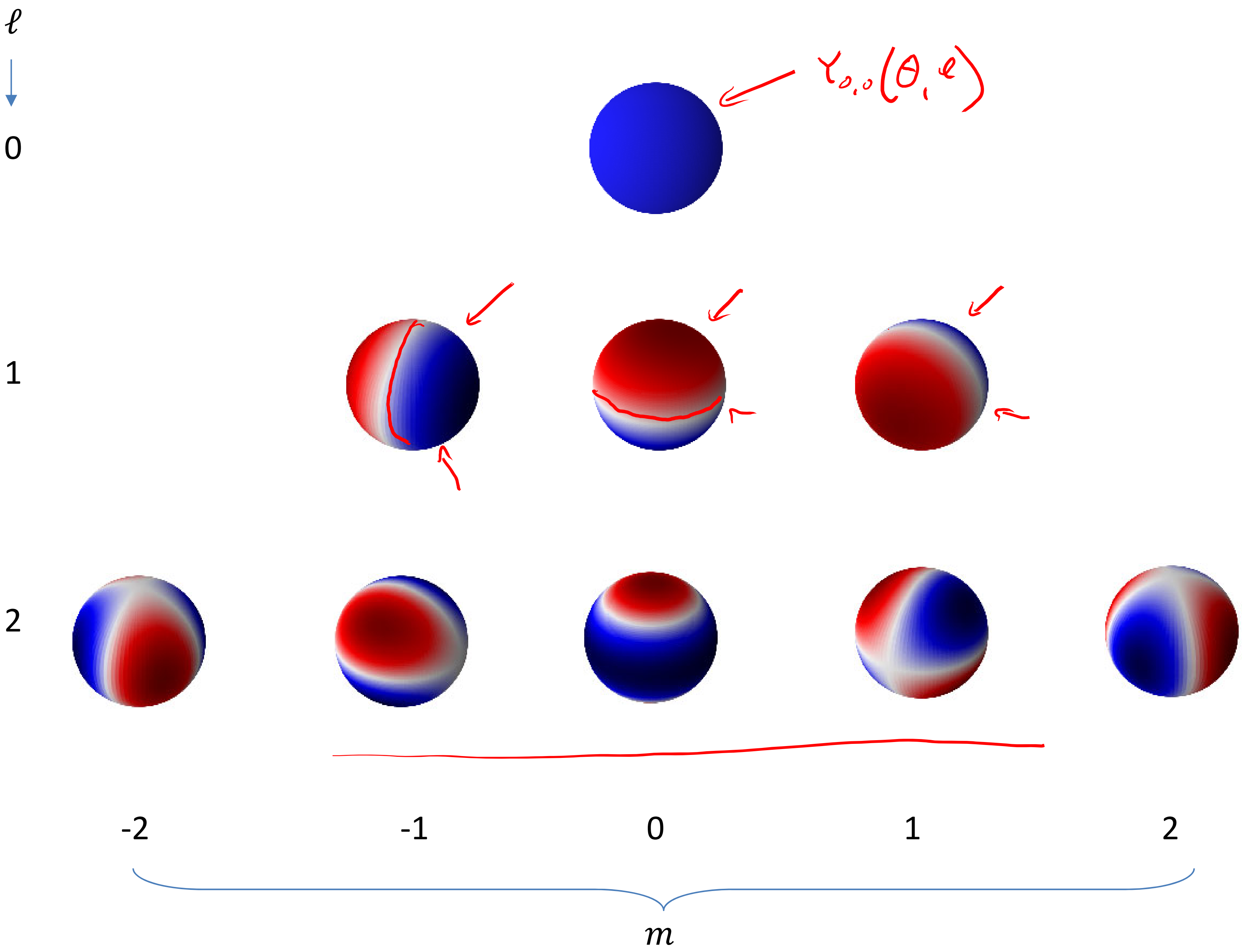
$\ell = 2$

$m = -2, -1, 0, 1, 2.$

What do these look like in 3D?



$m = 0, \ell = 1$



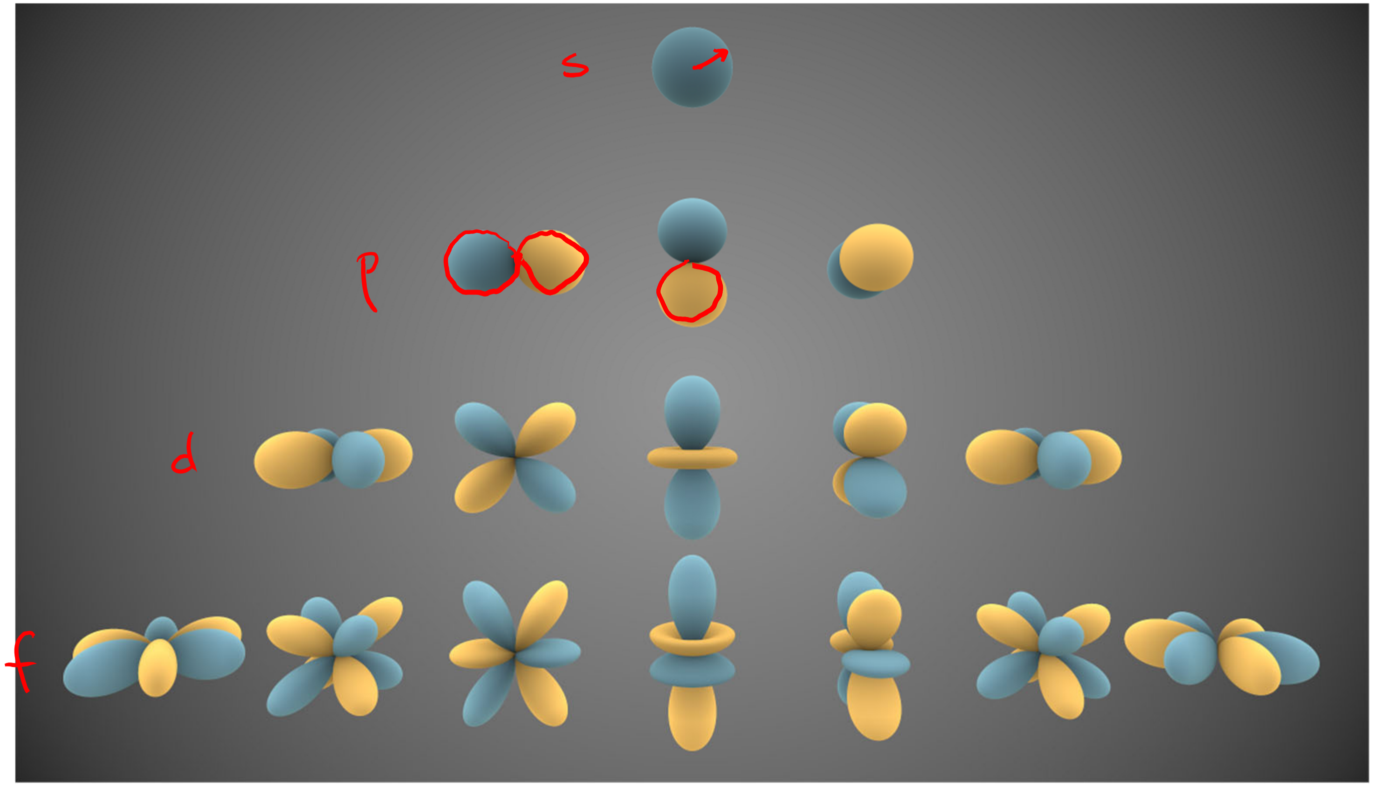
ℓ
0
1
2
$Y_{0,0}(\theta, \varphi)$
-2
-1
0
1
2
m

$l=0$

$l=1$

$l=2$

$l=3$



From Wikipedia:
“Spherical harmonics”

We end up with three equations:

$$\frac{1}{\Phi}\frac{\partial \Phi}{\partial \varphi} = -\cancel{\mu}\, m^2$$

$$\frac{1}{\Theta \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Theta}{\partial \theta}\right) - \frac{\lambda}{\sin^2\theta} = -\cancel{\mu}\, l(l+1)$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) - f(r) r^2 = \cancel{\mu}\, l(l+1)$$

What about the problem for R? We had

$$\boxed{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - f(r)r^2 - \ell(\ell+1) = 0}$$

The solution now depends on $f(r)$, which depends on the problem we are trying to solve.

Start with Laplace's equation:

$\nabla^2\psi = 0$

$f(r) = 0$

$-\nabla^2\psi + \cancel{f\psi} = 0.$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \ell(\ell+1)R = 0.$$

Try

$R = r^m$

$r^2R' = m r^{m-1} r^2$

$= m r^{m+1}$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) = \frac{\partial}{\partial r}\left(m r^{m+1}\right) = m(m+1)r^m.$$

Sub in to the D.E:

$m(m+1)r^m - \ell(\ell+1)r^m = 0.$

$[\underbrace{m(m+1) - \ell(\ell+1)}]r^m = 0.$

when $m = \ell$ this is satisfied.

Also works when

$m = -\ell-1$

check:

$[(-\ell-1)(-\ell) - \ell(\ell+1)]r^m =$

$[\underbrace{\ell(\ell+1) - \ell(\ell+1)}_{=0}]r^m = 0$ ✓

$$m = \begin{cases}\ell \\ -(\ell+1).\end{cases}$$

The general solution is then

$$\Psi(r,\theta,\varphi) = \sum_{l=-\infty}^{\infty} \sum_{m=-l}^{+l} \underbrace{\left[A_{lm} r^{l} + B_{lm} r^{-(l+1)} \right]}_{R(r)} \underbrace{Y_{l,m}(\theta,\varphi)}_{P_l^m(\cos\theta)\, e^{im\theta}}.$$

Schrödinger's equation for the hydrogen atom

Separation of variables in spherical polar coordinates

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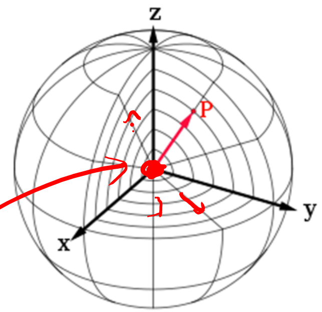
The function $f(r)$ only depends on the distance from the origin.



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Physics-y example: an electron around an atom obeys

$$-\frac{\hbar^2}{2m}\nabla^2\psi + [V(r) - E]\,\psi = 0$$

Re-arrange:

$$\Big[-\nabla^2 + \underbrace{\frac{2m}{\hbar^2}\big[V(r) - E\big]}_{f(r)}\Big]\psi = 0.$$

$$\vec{E} = -\nabla V$$

$V(r)$ is the electric potential (see Week 7)

$$V(r) = -\frac{q^2}{4\pi\epsilon_0}\frac{1}{r}$$

So we want to solve

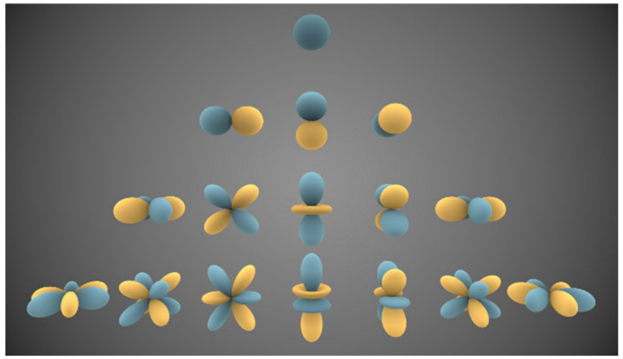
$$\Big(-\nabla^2 + \frac{2m}{\hbar^2}\Big(-\frac{q^2}{4\pi\epsilon_0}\frac{1}{r} - E\Big)\Big)\psi = 0$$

$$H\psi = E\psi$$

Choose the function

$$f(r) = -\frac{2m}{\hbar^2}\left(E - \frac{q^2}{4\pi\varepsilon_0 r}\right)$$

$$= -E' - \frac{k}{r}$$



and try to solve for the $\ell = 0$ case:

$R(r)$

$$\frac{1}{r^2}\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + E' + \frac{k}{r} = 0$$

Let $R(r) = e^{-\alpha r}$

$$r^2\frac{\partial R}{\partial r} = \underbrace{-\alpha e^{-\alpha r} r^2}$$

So

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) = -\alpha e^{-\alpha r}2r + r^2\alpha^2 e^{-\alpha r}.$$

Sub into

$$\Rightarrow \frac{1}{r^2}\underbrace{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)} + \left(E' + \frac{k}{r}\right)R = 0.$$

$$\Rightarrow \frac{1}{r^2}\left[-2\alpha r e^{-\alpha r} + r^2\alpha^2 e^{-\alpha r}\right] + \left(E' + \frac{k}{r}\right)e^{-\alpha r} = 0$$

$$\left(-\frac{2\alpha}{r} + \alpha^2\right)e^{-\alpha r} + E'e^{-\alpha r} + \frac{k}{r}e^{-\alpha r} = 0$$

$$e^{-\alpha r}\left[\underbrace{\frac{1}{r}(-2\alpha + k)} + \underbrace{\left(E' + \alpha^2\right)}\right] = 0.$$

This will be satisfied if

$$\alpha = \frac{k}{2} = \frac{mq^2}{\underline{4\pi\varepsilon_0\hbar^2}} = \frac{1}{(\text{radius of atom})}$$

The complete solution is

$$\psi(r,\theta,\varphi) = A\,R(r)\,Y_{0,0}(\theta,\varphi)$$

$$= A\,e^{-\alpha r}\,\underbrace{P_0^0(\cos\theta)}\,e^{i0\theta}.$$

$$\longrightarrow \quad P_0^0(x) = 1$$

$$= A\,e^{-\alpha r}.$$

$$H\psi = E\psi$$

$$E' = -\alpha^2$$

$$E = \frac{\hbar^2}{2m}E' = -\frac{\hbar^2}{2m}\alpha^2.$$