PHYS 250

Lecture 6.1

Schrodinger in 3D

Today

Schrodinger Equation in 3D, *xyz* version
Free Particle Solutions
Rectangular Box Solutions

Vector Calculus in Spherical Coordinates
Spherical Coordinates Laplacian Operator

Schrodinger for Spherically Symmetric Potential
Separating Spherical Schrodinger
Solving for ϕ-dependence
Solving for θ-dependence

(Wednesday we'll add the r-dependence and do spherical well and Hydrogen)

Schrodinger in *xyz*

The wavefunction has 3 space + 1 time argument: $\psi(x,t) \to \psi(x,y,z,t)$

The x-derivative becomes $\frac{\partial^2 \psi}{\partial x^2} \to \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \nabla^2 \psi$

where $\nabla^2 \psi$ is called the Laplacian operator.

The potential has 3 coordinate arguments: $V(x) \to V(x,y,z)$

Overall we have

$$i\hbar \frac{\partial}{\partial t} \psi(x,y,z,t) = \frac{-\hbar^2}{2m} \nabla^2 \psi(x,y,z,t) + V(x,y,z)\psi(x,y,z,t)$$

or in vector notation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x},t) = \frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)$$

Free Particle in *xyz*

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t)=\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x},t)+0$$

Solutions are $\psi(\vec{x},t)=\exp\left[i\left(\vec{k}\cdot\vec{x}-\omega t\right)\right]$ with $E=\frac{\vec{p}^2}{2m}=\frac{\left(\hbar\vec{k}\right)^2}{2m}=\hbar\omega$

The *k*-vector points in the direction the particle is moving.

Of course we can still superpose solutions with different k-values
to make wave packets, standing waves, etc.

Time-Independent *xyz* Schrodinger

Assume $\psi(\vec{x},t) = f(\vec{x})\cdot g(t)$, so $\frac{\partial}{\partial t}\psi = f(\vec{x})\cdot\frac{\partial}{\partial t}g(t) = f\cdot g'$ where $g' = \frac{\partial g}{\partial t}$

Also $\nabla^2\psi = \left[\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}\right]\cdot g(t) = \left[\nabla^2 f\right]\cdot g(t)$

Plug into Schrodinger: $i\hbar f\cdot g' = \frac{-\hbar^2}{2m}\left[\nabla^2 f\right]\cdot g + V(\vec{x})f\cdot g$

Divide both sides by $f\cdot g$:

$$\frac{i\hbar f\cdot g'}{f\cdot g} = \frac{-\hbar^2}{2m}\frac{\left[\nabla^2 f\right]\cdot g}{f\cdot g} + V(\vec{x})\frac{f\cdot g}{f\cdot g}$$

$$i\hbar\frac{g'(t)}{g(t)} = \frac{-\hbar^2}{2m}\frac{\nabla^2 f(\vec{x})}{f(\vec{x})} + V(\vec{x})$$

The left side doesn’t depend on $\vec{x}$, the right side doesn’t depend on *t*, so both must be equal to some constant we will call *E*.

Time-Independent *xyz* Schrodinger 2

One equation is $i\hbar \frac{1}{g}\frac{dg}{dt} = E \rightarrow \frac{dg}{g} = \frac{E}{i\hbar}dt \rightarrow \ln g = \frac{E}{i\hbar}t \rightarrow g = \exp\left[-i\frac{Et}{\hbar}\right]$

We get simple complex-exponential time-dependence

The other equation is

$$\frac{-\hbar^2}{2m}\frac{\nabla^2 f\left(\vec{x}\right)}{f\left(\vec{x}\right)} + V\left(\vec{x}\right) = E$$

$$\rightarrow \frac{-\hbar^2}{2m}\nabla^2 f\left(\vec{x}\right) + V\left(\vec{x}\right)\cdot f\left(\vec{x}\right) = E\cdot f\left(\vec{x}\right)$$

$$\rightarrow \frac{-\hbar^2}{2m}\nabla^2\psi\left(\vec{x}\right) + V\left(\vec{x}\right)\cdot\psi\left(\vec{x}\right) = E\cdot\psi\left(\vec{x}\right)$$

Just like the 1D version, except with the Laplacian, and vector $\vec{x}$ as the argument.

Particle in 3D Box

Let $V(\vec{x}) = 0$ if $0 < x < a$, and $0 < y < b$, and $0 < z < c$, otherwise $V(\vec{x}) = +\infty$

The time-independent equation is $\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) = E \cdot \psi(\vec{x})$.

This has solutions $\psi(\vec{x}) = \sin(k_x x)\cdot\sin(k_y y)\cdot\sin(k_z z)$

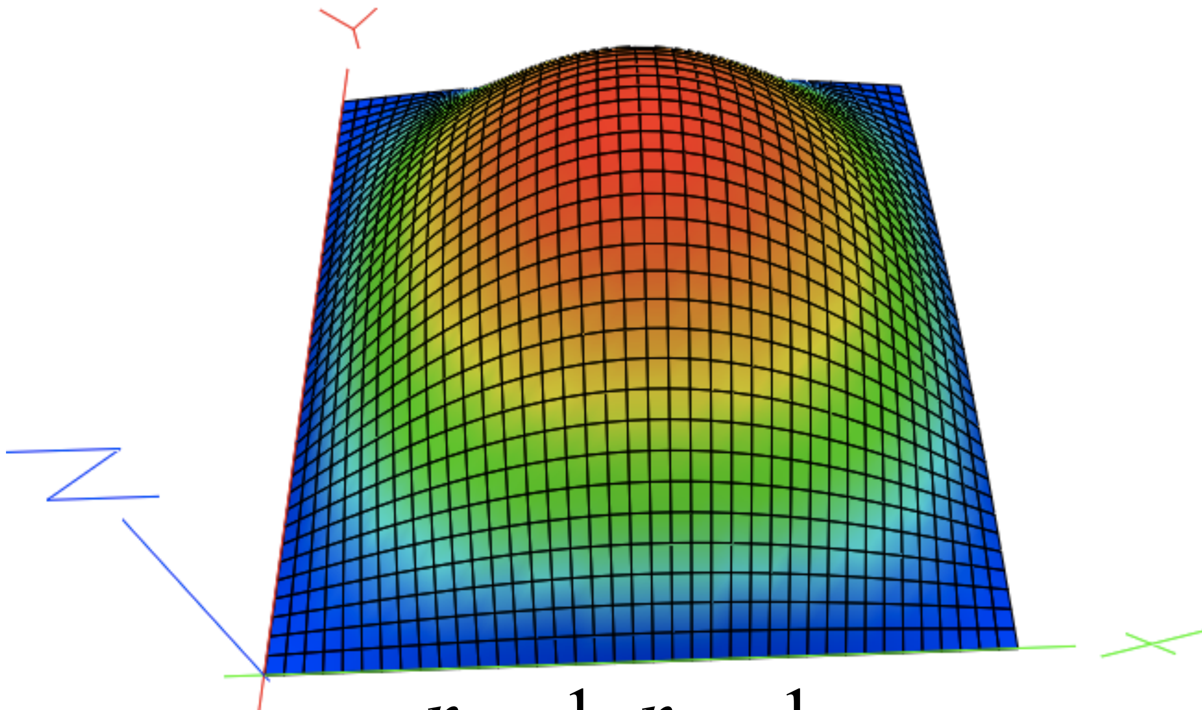
The boundary conditions are that the wavefunction must be zero at the walls.

This is automatically satisfied at $x = 0$, $y = 0$, and $z = 0$.

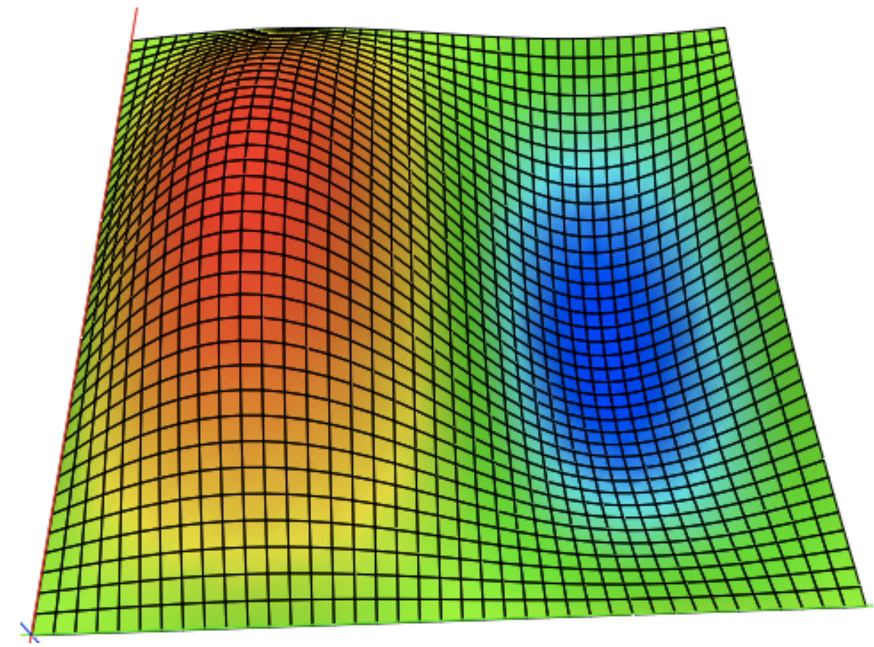
It is satisfied at $x = a$ if $k_x = \frac{n_x \pi}{a}$, at $y = b$ if $k_y = \frac{n_y \pi}{b}$, and at $z = c$ if $k_z = \frac{n_z \pi}{c}$

Note that there are 3 different n values, which don't have to be the same.

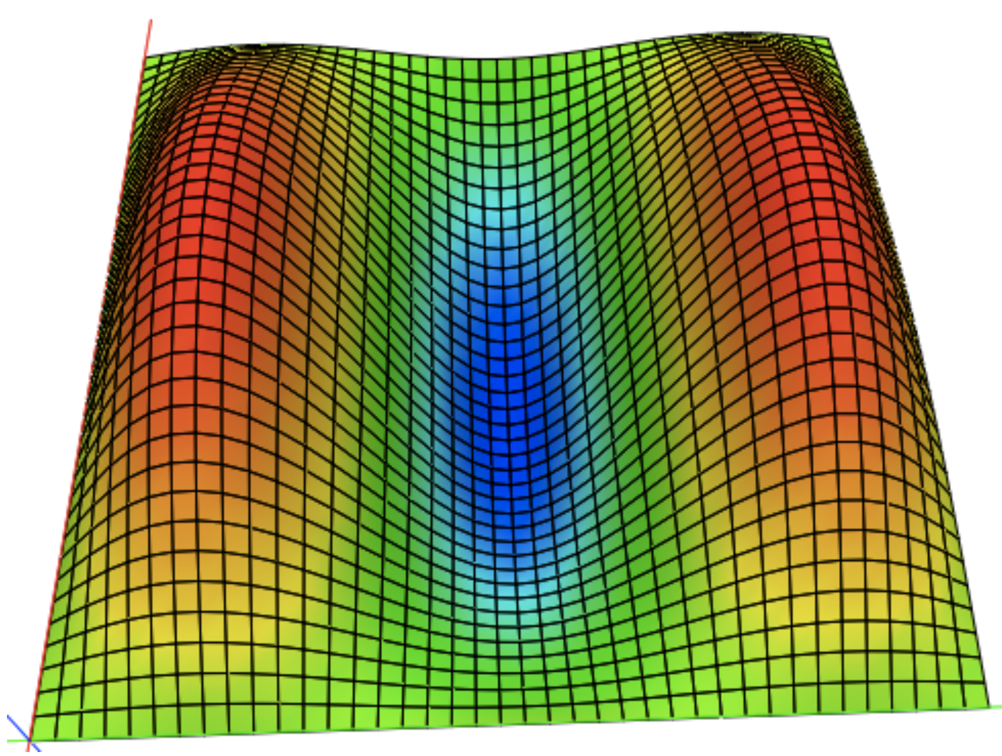
Particle in 2D Box



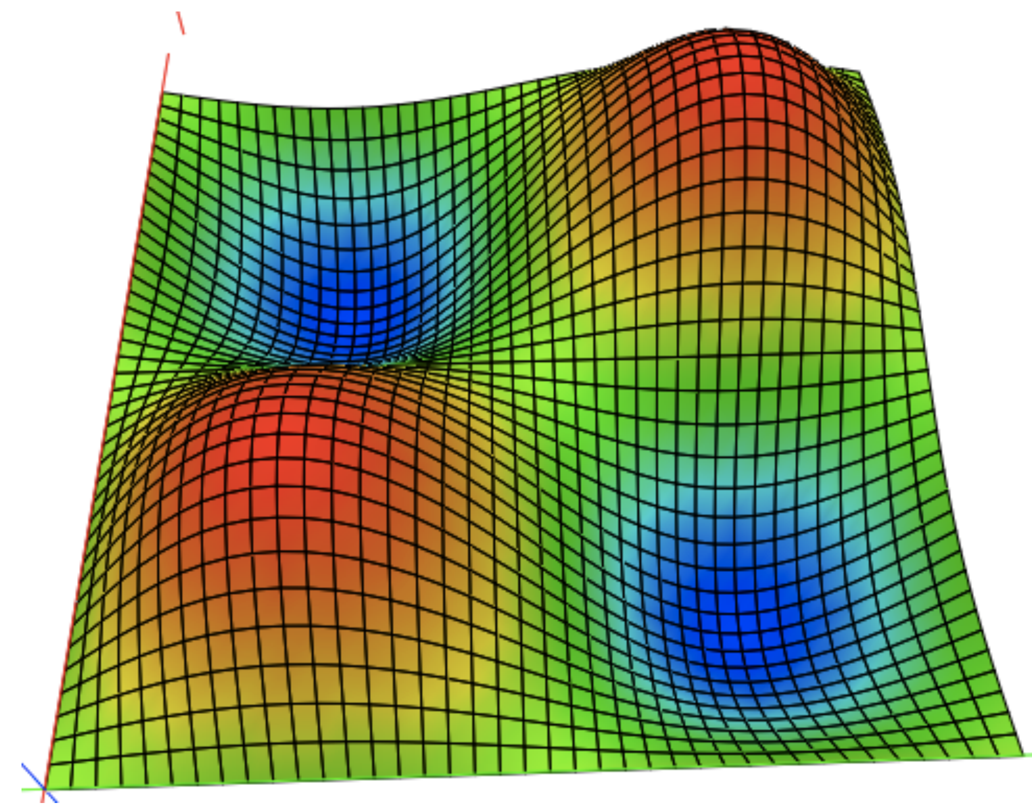
$n_x = 1,\ n_y = 1$



$n_x = 2,\ n_y = 1$

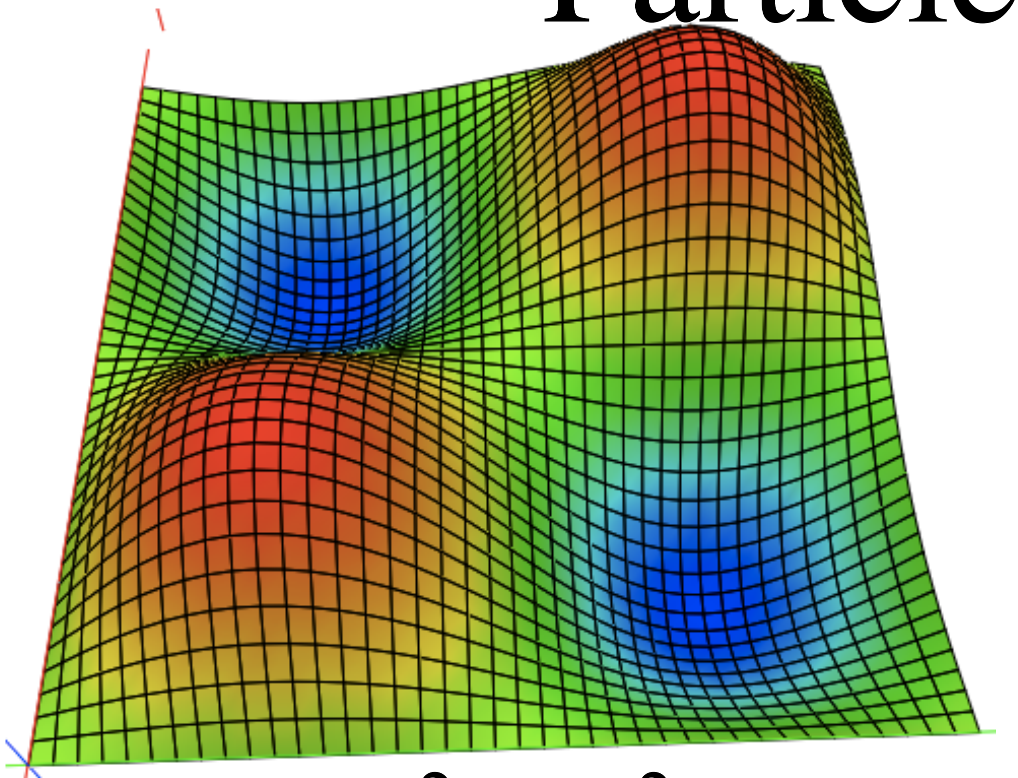


$n_x = 3,\ n_y = 1$

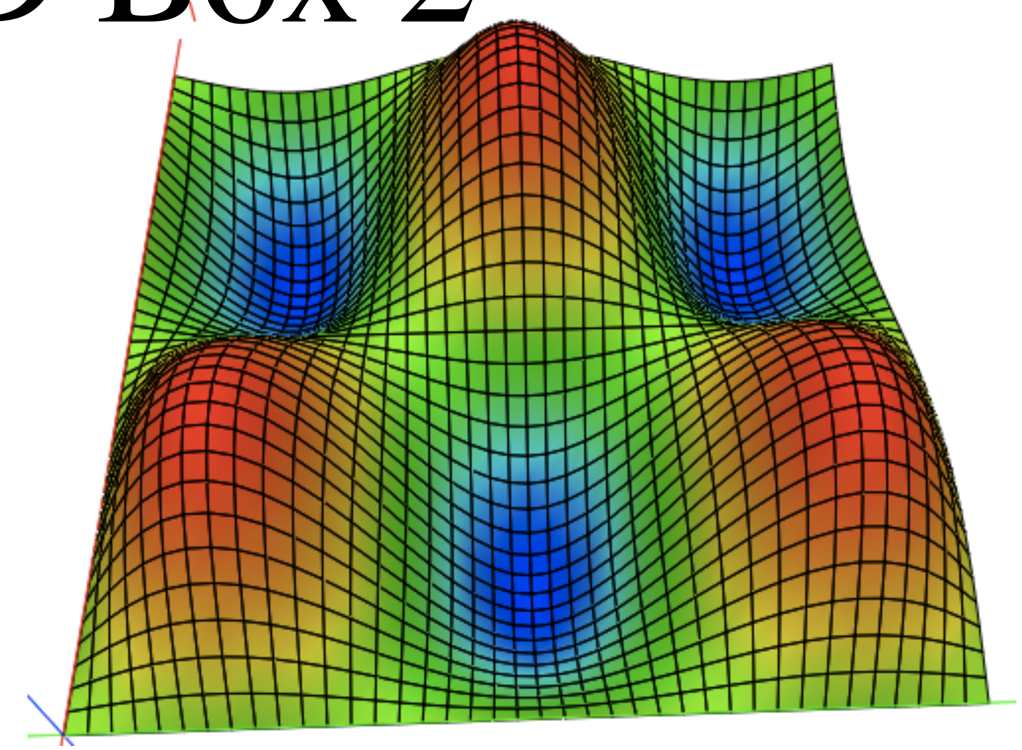


$n_x = 2,\ n_y = 2$

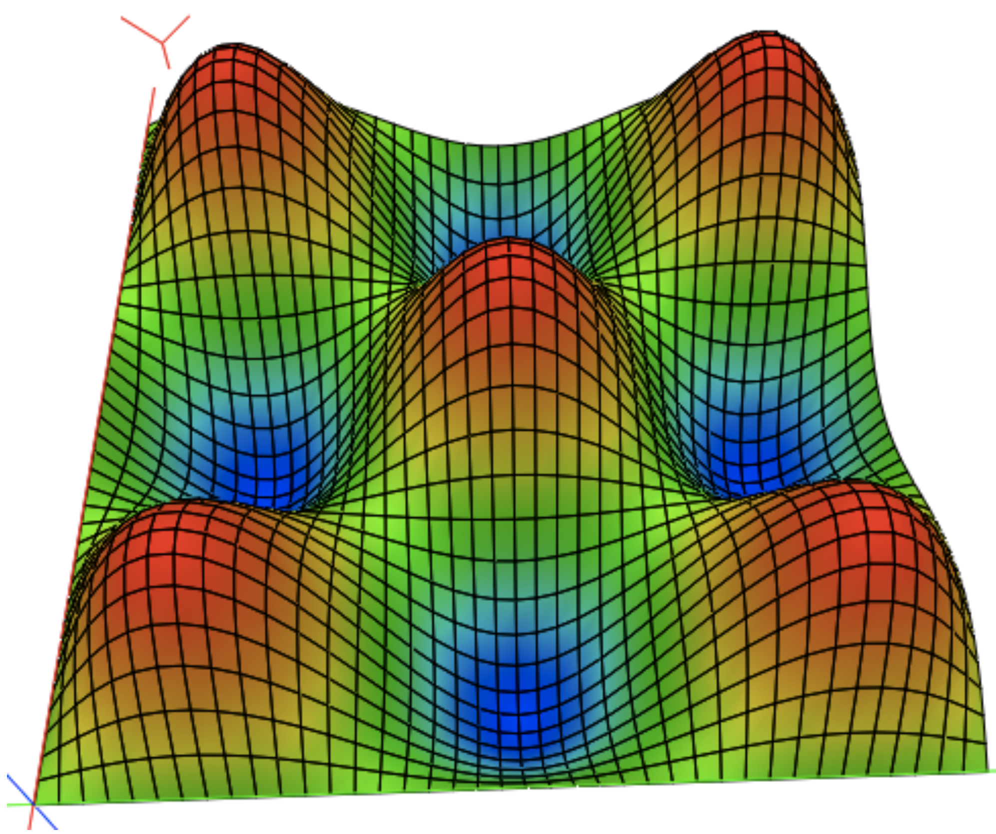
Particle in 2D Box 2



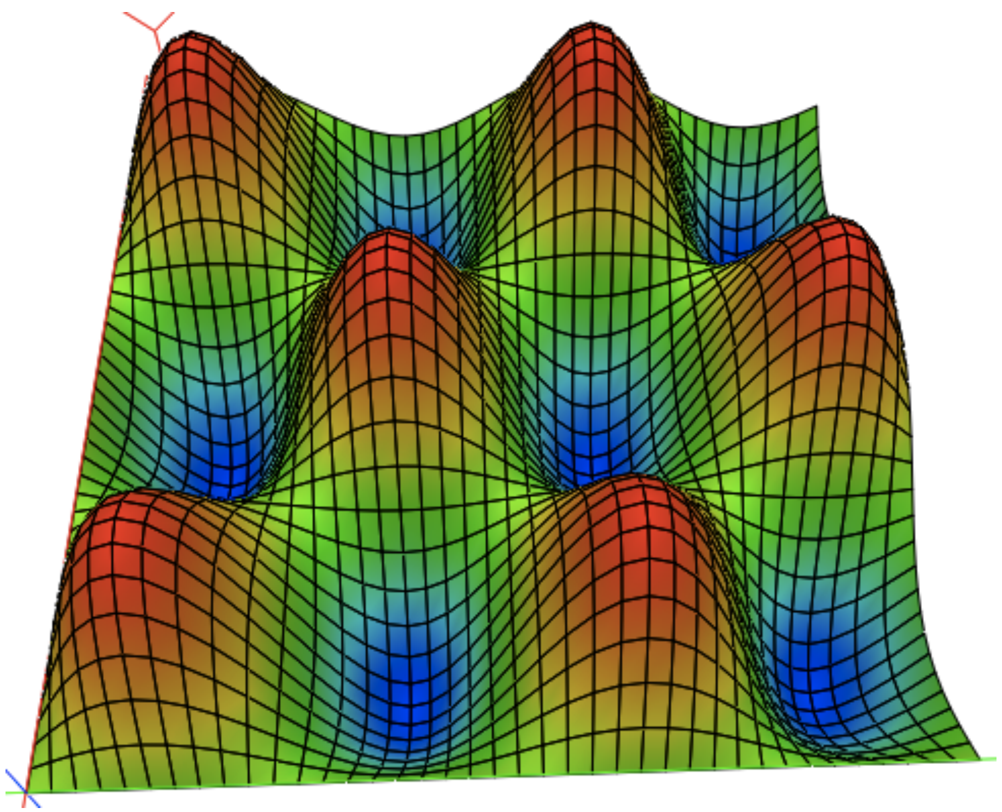
$n_x = 2, n_y = 2$



$n_x = 3,\ n_y = 2$



$n_x = 3,\ n_y = 3$



$n_x = 4,\ n_y = 3$

Particle in 3D Box 2

Writing explicitly $\psi(\vec{x}) = \sin\left(\frac{n_x\pi}{a}x\right)\cdot\sin\left(\frac{n_y\pi}{b}y\right)\cdot\sin\left(\frac{n_z\pi}{c}z\right)$, then

$$\nabla^2\psi = \left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\sin\left(\frac{n_x\pi}{a}x\right)\cdot\sin\left(\frac{n_y\pi}{b}y\right)\cdot\sin\left(\frac{n_z\pi}{c}z\right)$$

$$=\left[-\left(\frac{n_x\pi}{a}\right)^2\sin\left(\frac{n_x\pi}{a}x\right)\right]\cdot\sin\left(\frac{n_y\pi}{b}y\right)\cdot\sin\left(\frac{n_z\pi}{c}z\right)$$

$$+\sin\left(\frac{n_x\pi}{a}x\right)\cdot\left[-\left(\frac{n_y\pi}{b}\right)^2\sin\left(\frac{n_y\pi}{b}y\right)\right]\cdot\sin\left(\frac{n_z\pi}{c}z\right)$$

$$+\sin\left(\frac{n_x\pi}{a}x\right)\cdot\sin\left(\frac{n_y\pi}{b}y\right)\cdot\left[-\left(\frac{n_z\pi}{c}\right)^2\sin\left(\frac{n_z\pi}{c}z\right)\right]$$

$$=-\left[\left(\frac{n_x\pi}{a}\right)^2+\left(\frac{n_y\pi}{b}\right)^2+\left(\frac{n_z\pi}{c}\right)^2\right]\cdot\psi$$

Then $\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) = E\cdot\psi(\vec{x}) \rightarrow E = \left[\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right]\cdot\frac{\hbar^2\pi^2}{2m}$ with $n_x, n_y, n_z > 0$

Particle in Cubical Box

For the special case that $a = b = c = w$, the cubical box,

$$E_{nx,\,ny,\,nz} = \left[n_x^2 + n_y^2 + n_z^2 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2}$$

The lowest energy state is $n_x = n_y = n_z = 1$ so $E_{111} = \left[3 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2}$

The next state will have one $n = 2$ and the others 1. There are 3 ways to do it.

$$E_{211} = E_{121} = E_{112} = \left[2^2 + 1^2 + 1^2 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2} = \left[6 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2}.$$

These different wavefunctions with the same energy are called degenerate.

The next state will have two $n = 2$ and one being 1. There are 3 ways to do it.

$$E_{221} = E_{122} = E_{212} = \left[2^2 + 2^2 + 1^2 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2} = \left[9 \right] \cdot \frac{\hbar^2 \pi^2}{2mw^2}.$$

Particle in Cubical Box 2

Another state is all 3 n's being 2: $E_{222}=\left[2^2+2^2+2^2\right]\cdot\frac{\hbar^2\pi^2}{2mw^2}=\left[12\right]\cdot\frac{\hbar^2\pi^2}{2mw^2}$

There is only one way to do that.

But there is also $E_{311}=E_{131}=E_{113}=\left[3^2+1^2+1^2\right]\cdot\frac{\hbar^2\pi^2}{2mw^2}=\left[11\right]\cdot\frac{\hbar^2\pi^2}{2mw^2}$

These are slightly lower in energy than state 222.

Spherical Symmetry

The kinetic energy term $\frac{-\hbar^2}{2m}\nabla^2\psi\left(\vec{x}\right)$ doesn't depend on direction.

The Coulomb potential $V\left(r\right)=\frac{qQ}{4\pi\varepsilon_0}\frac{1}{r}$ doesn't depend on direction.

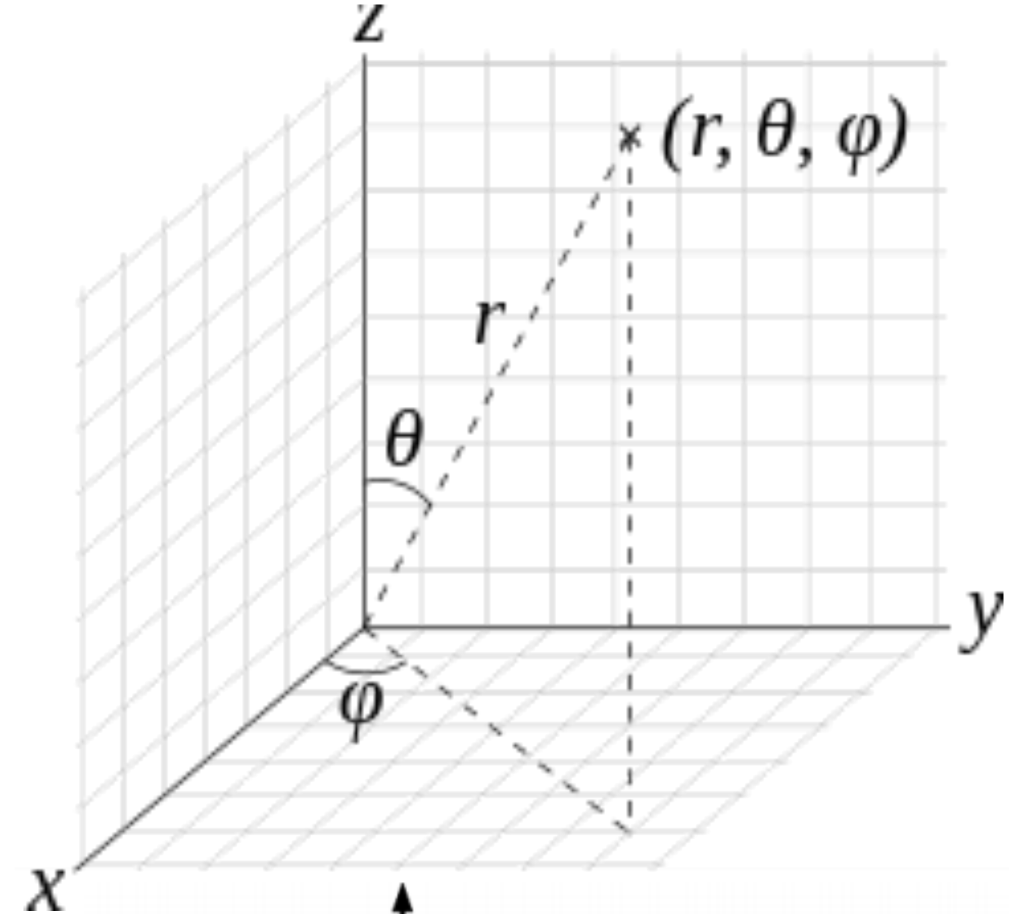
The 3D harmonic oscillator potential with all spring constants the same is $V\left(\vec{x}\right)=\frac{1}{2}\left(kx^2+ky^2+kz^2\right)=\frac{1}{2}kr^2$ and doesn't depend on direction.

Maybe we can do the separation of variables trick for spherical problems, so the potential only shows up in a radial equation.

We need to figure out $\nabla^2\psi=\vec{\nabla}\cdot\left(\vec{\nabla}\psi\right)$ in spherical coordinates.

Spherical Coordinates

This is the physics convention for spherical coordinates.
θ is measured from the +z-axis.
ϕ is the xy projection of the r vector, measured from the +x axis



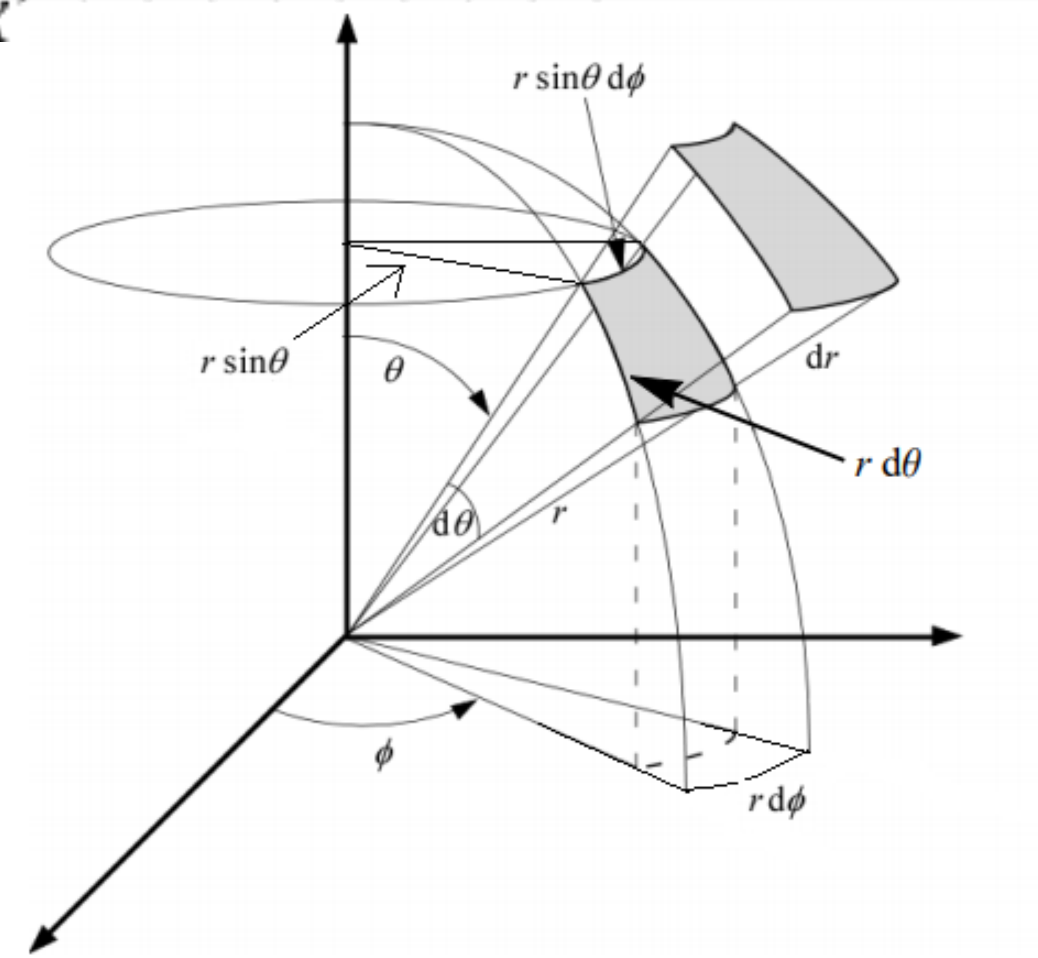
The coordinate "steps" are

$$\Delta s_r = \Delta r$$

$$\Delta s_\theta = r\Delta\theta$$

$$\Delta s_\phi = r\sin\theta\,\Delta\phi$$

The volume element looks like this:



Spherical Gradient

The spherical gradient is straightforward: just plug in the coordinate step Δ's

$$\vec{\nabla} F = \hat{r}\frac{\Delta F}{\Delta s_r} + \hat{\theta}\frac{\Delta F}{\Delta s_\theta} + \hat{\phi}\frac{\Delta F}{\Delta s_\phi}$$

$$= \hat{r}\frac{\Delta F}{\Delta r} + \hat{\theta}\frac{\Delta F}{r\Delta\theta} + \hat{\phi}\frac{\Delta F}{r\sin\theta\ \Delta\phi}$$

$$= \hat{r}\frac{\partial F}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial F}{\partial\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial F}{\partial\phi}$$

Note that the angle derivative terms have a factor of $1/r$ in them (all 3 terms have dimensions of $1/r$).

Note also that the ϕ derivative term has an extra $\dfrac{1}{\sin\theta}$ factor.

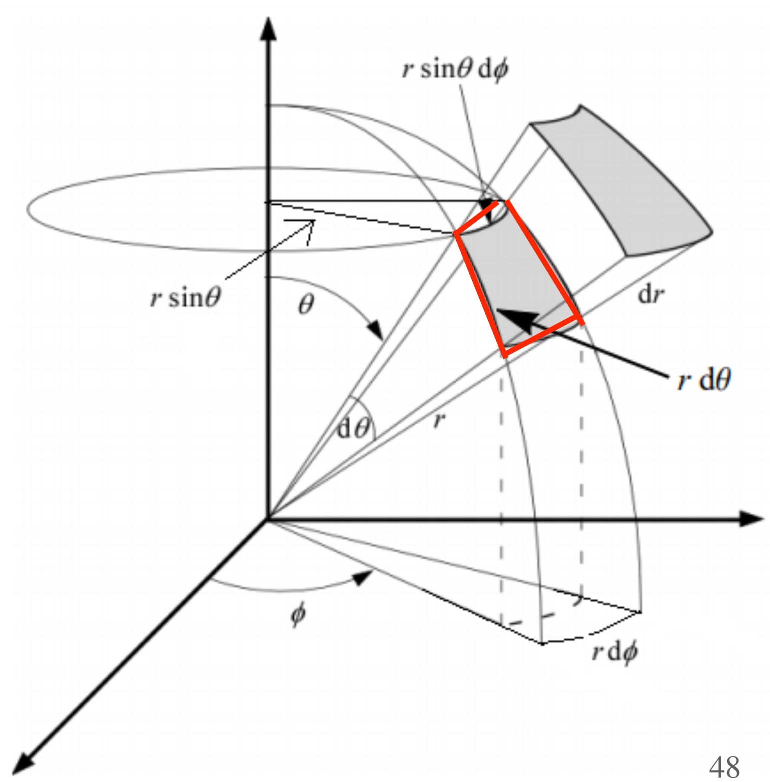
Spherical Divergence 1

The divergence can be defined as the net flux of a vector function out of a "cube," divided by the volume of the "cube."

Our vector function is written
$\vec{G}(r,\theta,\phi)=\hat{r}\cdot G_r(r,\theta,\phi)+\hat{\theta}\cdot G_\theta(r,\theta,\phi)+\hat{\phi}\cdot G_\phi(r,\theta,\phi).$
It has 3 components, in the r, θ, and ϕ directions.
The numerical values of the components can be different functions of r, θ, and ϕ.

The flux of the r-component Φ_r through the "inner r" face is the value of the r-component times the surface area perpendicular to it:

$$\begin{aligned}\Phi_r &= G_r\cdot\Delta s_\theta\cdot\Delta s_\phi\\ &= G_r\cdot r\Delta\theta\cdot r\sin\theta\,\Delta\phi\\ &= G_r\; r^2\sin\theta\;\Delta\theta\;\Delta\phi\end{aligned}$$



Spherical Divergence 2

We want the <u>net</u> flux of the r-component out of the "cube"

$$\Delta_r \Phi_r = \Delta_r \left(G_r \cdot r\Delta\theta \cdot r\sin\theta\,\Delta\phi \right) = \Delta_r \left(G_r r^2 \sin\theta\,\Delta\theta\,\Delta\phi \right)$$

The θ and ϕ values don't change from one face to the other,
but r varies across the "cube" as well as G_r, so we should write this as

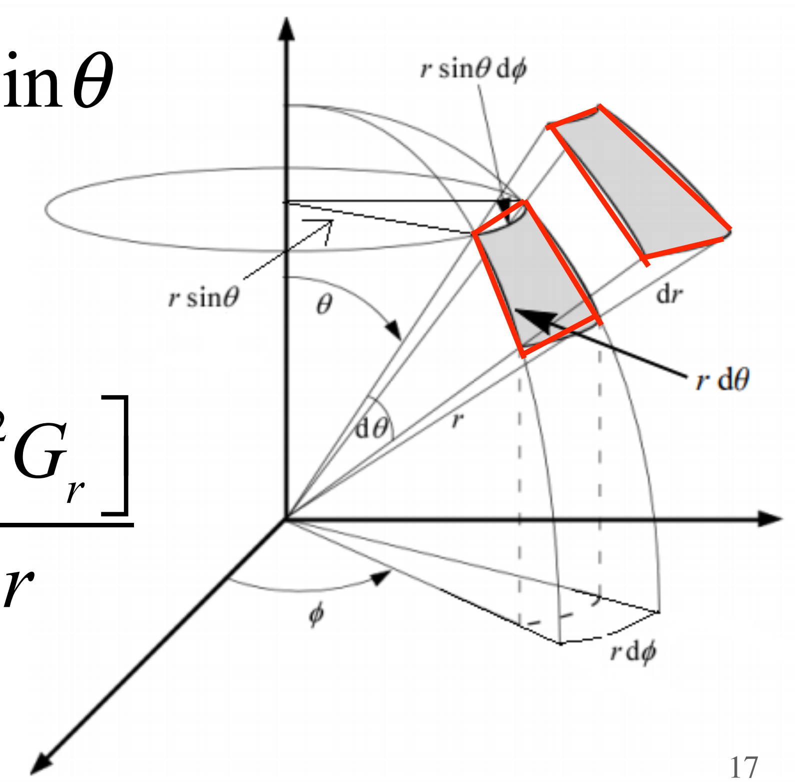
$$\Delta_r \Phi_r = \Delta_r \left[G_r r^2 \right] \sin\theta\,\Delta\theta\,\Delta\phi$$

The volume of the "cube" is

$$V = \Delta r \cdot r\Delta\theta \cdot r\sin\theta\,\Delta\phi = \Delta r \Delta\theta\,\Delta\phi \cdot r^2 \sin\theta$$

The divergence contribution is flux over volume

$$\frac{\Delta_r \Phi_r}{V} = \frac{\Delta_r \left[G_r r^2 \right] \sin\theta\,\Delta\theta\,\Delta\phi}{\Delta r \Delta\theta\,\Delta\phi \cdot r^2 \sin\theta} = \frac{1}{r^2} \frac{\partial \left[r^2 G_r \right]}{\partial r}$$



Spherical Divergence 3

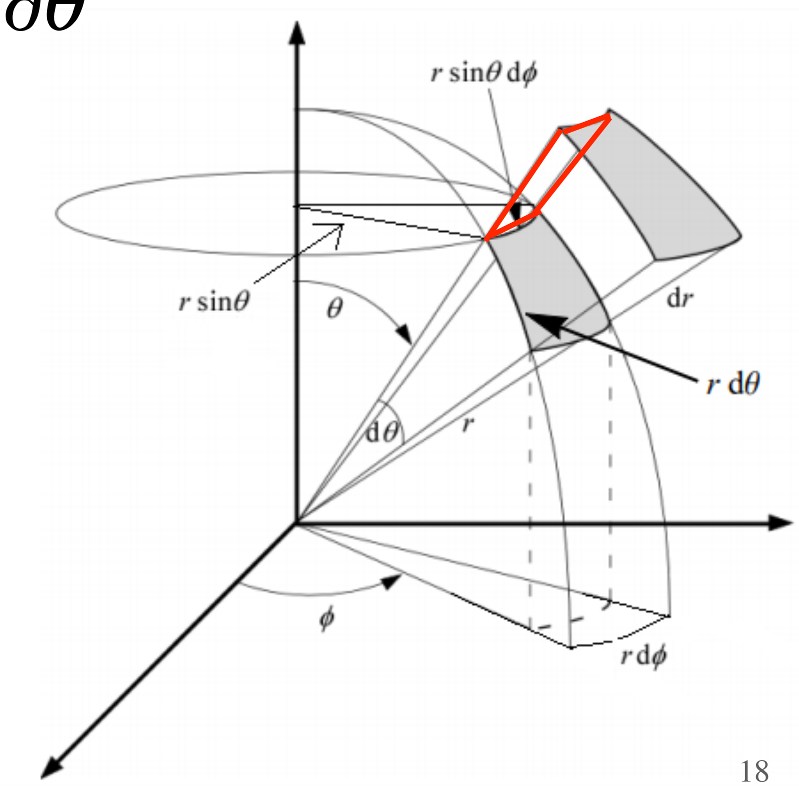
The θ-flux through the red "square" is $\Phi_\theta = G_\theta \cdot \Delta_r \cdot \Delta_\phi = G_\theta \cdot \Delta r \cdot r \sin\theta \, \Delta\phi$

We want the net θ-flux as we step in θ

$$\Delta_\theta \Phi_\theta = \Delta_\theta \left(G_\theta \cdot \Delta r \cdot r \sin\theta \, \Delta\phi \right) = \Delta_\theta \left[\sin\theta \, G_\theta \right] r \Delta r \Delta\phi$$

The volume is the same as before. The divergence contribution is

$$\frac{\Delta_\theta \Phi_\theta}{V} = \frac{\Delta_\theta \left[\sin\theta \, G_\theta \right] r \Delta r \Delta\phi}{\Delta r \Delta\theta \, \Delta\phi \cdot r^2 \sin\theta} = \frac{1}{r \sin\theta} \frac{\partial \left[\sin\theta \, G_\theta \right]}{\partial\theta}$$



Spherical Divergence 4

The ϕ-flux through the red "square" is $\Phi_\phi = G_\phi \cdot \Delta_r \cdot \Delta_\theta = G_\phi \cdot \Delta r \cdot r\,\Delta\theta$

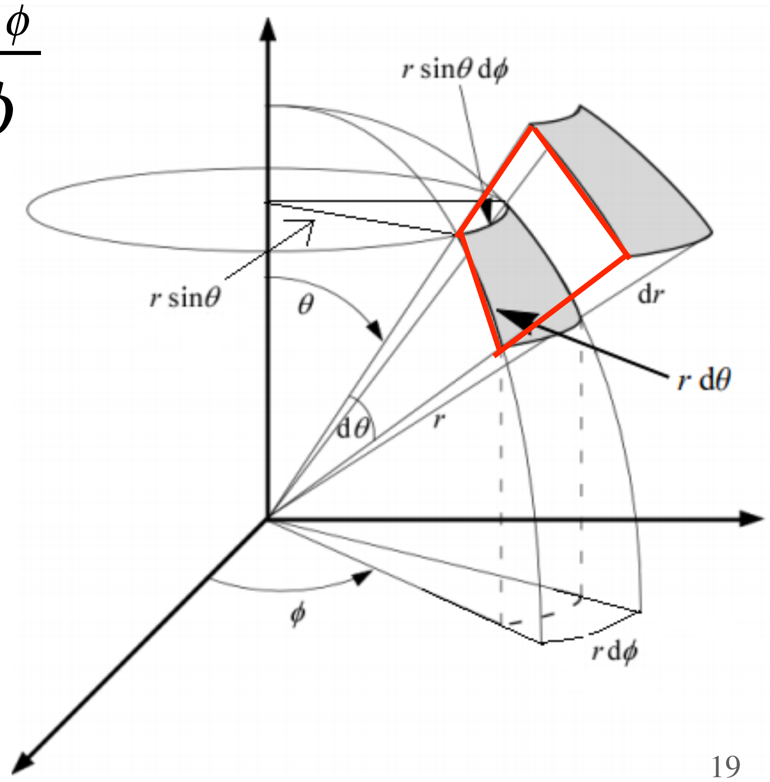
We want the net ϕ-flux as we step in ϕ

In this case, only the function changes, not the area

$$\Delta_\phi \Phi_\phi = \Delta_\phi \left(G_\phi \cdot \Delta r \cdot r \sin\theta\, \Delta\phi \right) = \Delta_\phi \left[\sin\theta\, G_\phi \right] r \Delta r \Delta\phi$$

The volume is the same as before. The divergence contribution is

$$\frac{\Delta_\phi \Phi_\phi}{V} = \frac{\Delta_\phi G_\phi\, r \Delta r \Delta\theta}{\Delta r \Delta\theta\, \Delta\phi \cdot r^2 \sin\theta} = \frac{1}{r\sin\theta} \frac{\partial G_\phi}{\partial \phi}$$



Spherical Divergence 5

The divergence is the sum of the 3 terms:

$$\vec{\nabla}\cdot\vec{G} = \frac{1}{r^2}\frac{\partial\left[r^2 G_r\right]}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial\left[\sin\theta\, G_\theta\right]}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial G_\phi}{\partial\phi}$$

Spherical Laplacian

Recall $\nabla^2 F = \vec{\nabla}\cdot\left(\vec{\nabla}F\right)$. So we plug the spherical components of $\vec{\nabla}F$ which are $\left(\vec{\nabla}F\right)_r = \dfrac{\partial F}{\partial r}$, $\left(\vec{\nabla}F\right)_\theta = \dfrac{1}{r}\dfrac{\partial F}{\partial \theta}$, $\left(\vec{\nabla}F\right)_\phi = \dfrac{1}{r\sin\theta}\dfrac{\partial F}{\partial \phi}$

into the spherical divergence $\vec{\nabla}\cdot\vec{G} = \dfrac{1}{r^2}\dfrac{\partial\left[r^2 G_r\right]}{\partial r} + \dfrac{1}{r\sin\theta}\dfrac{\partial\left[\sin\theta\, G_\theta\right]}{\partial\theta} + \dfrac{1}{r\sin\theta}\dfrac{\partial G_\phi}{\partial\phi}$

That gives

$$\nabla^2 F = \vec{\nabla}\cdot\left(\vec{\nabla}F\right) = \frac{1}{r^2}\frac{\partial\left[r^2\frac{\partial F}{\partial r}\right]}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial\left[\sin\theta\,\frac{1}{r}\frac{\partial F}{\partial\theta}\right]}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial\left[\frac{1}{r\sin\theta}\frac{\partial F}{\partial\phi}\right]}{\partial\phi}$$

We can factor some terms out of the brackets

$$\nabla^2 F = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial F}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}$$

Spherical Derivatives Summary

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

$$\vec{\nabla}\cdot\vec{G} = \frac{1}{r^2}\frac{\partial\left[r^2 G_r\right]}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial\left[\sin\theta\, G_\theta\right]}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial G_\phi}{\partial \phi}$$

$$\nabla^2 F = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial F}{\partial \theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 F}{\partial \phi^2}$$

Spherical Schrodinger

Plug the spherical Laplacian into Schrodinger with a spherical potential

$$E\psi(r,\theta,\phi) = -\frac{\hbar^2}{2M}\nabla^2\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi)$$

$$E\psi = -\frac{\hbar^2}{2M}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\} + V(r)\psi$$

Believe it or not, that's separable into $\psi(r,\theta,\phi) = F(r)G(\theta)H(\phi)$

And the $G(\theta)$ and $H(\phi)$ are the <u>same</u> (set of) functions for <u>any potential</u>, as long as it's spherical.

The $F(r)$ functions of course depend on the potential, and also have some dependence on which ones of $G(\theta)$ and $H(\phi)$ you use.

Separation 1

$$E\psi = -\frac{\hbar^2}{2M}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\} + V(r)\psi$$

Factor $1/r^2$ out of the bracket

$$E\psi = -\frac{\hbar^2}{2Mr^2}\left\{\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\} + V(r)\psi$$

Move V to the left, and multiply both sides by $\frac{2Mr^2}{\hbar^2}$

$$\frac{2Mr^2}{\hbar^2}\left[E - V(r)\right]\psi = -\left\{\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}$$

Move the term with r-dependence to the left side

$$\frac{2Mr^2}{\hbar^2}\left[E - V(r)\right]\psi + \frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] - \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

Separation 2

$$\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]\psi+\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\psi\right]=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\psi\right]-\frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2}\psi\right]$$

Assume $\psi=F(r)G(\theta)H(\phi)$, plug in, and do derivatives

$$\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]FGH+\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}FGH\right]=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}FGH\right]-\frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2}FGH\right]$$

$$\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]FGH+\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right]GH=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial G}{\partial\theta}\right]FH-\frac{1}{\sin^2\theta}\left[\frac{\partial^2 H}{\partial\phi^2}\right]FG$$

Divide by *FGH*

$$\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]+\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right]\frac{1}{F}=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial G}{\partial\theta}\right]\frac{1}{G}-\frac{1}{\sin^2\theta}\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Left side has no angles, right side has no *r*, so both sides equal a constant λ

$$\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]+\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right]\frac{1}{F}=\lambda=-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial G}{\partial\theta}\right]\frac{1}{G}-\frac{1}{\sin^2\theta}\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Separation 3

Work on the right-side equation

$$\lambda = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial G}{\partial\theta}\right]\frac{1}{G} - \frac{1}{\sin^2\theta}\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Multiply both sides by $\sin^2\theta$

$$\lambda\sin^2\theta = -\sin\theta\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial G}{\partial\theta}\right]\frac{1}{G} - \left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Put θ-dependence on the left, ϕ dependence on the right

$$\lambda\sin^2\theta + \sin\theta\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial G}{\partial\theta}\right]\frac{1}{G} = -\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Left side has no ϕ, right side has no θ, so both sides equal a constant μ

$$\lambda\sin^2\theta + \sin\theta\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial G}{\partial\theta}\right]\frac{1}{G} = \mu = -\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$$

Separation 4

Work on the right-side equation

$$\mu = -\left[\frac{\partial^2 H}{\partial \phi^2}\right]\frac{1}{H}$$

Multiply both sides by H and rearrange

$$\frac{\partial^2 H}{\partial \phi^2} = -\mu H$$

That's an easy one: $H(\phi) = \exp[im\phi]$ will work, if $\mu = m^2$.

There is also a continuity condition: $H(\phi = 0) = H(\phi = 2\pi)$.

That will be satisfied if $m = 0, \pm 1, \pm 2$, etc.

Solving for $G(\theta)$ 1

Work on the left-side equation

$$\lambda \sin^2\theta + \sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial G}{\partial\theta}\right]\frac{1}{G} = \mu = m^2$$

Move the first term to the right, and multiply by G

$$\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial G}{\partial\theta}\right] = \left[m^2 - \lambda \sin^2\theta\right]G$$

Now we plug in a guess for G, and its derivatives,
and see if there is a λ that makes it work. We know m can be any integer.

Maybe $G = \sin\theta$ could work? The double θ-derivative give back $\sin\theta$.

It's safer to try $G = \sin^M\theta$, and maybe some M value will make it work.

Solving for $G(\theta)$ 2

$G(\theta)$:	$\sin^M\theta$	First Guess
$\dfrac{\partial}{\partial\theta}$:	$M\sin^{M-1}\theta\cos\theta$	
$\times\sin\theta$:	$M\sin^M\theta\cos\theta$	
$\dfrac{\partial}{\partial\theta}$:	$M^2\sin^{M-1}\theta\cos^2\theta$	$-M\sin^{M+1}\theta$
$\times\sin\theta$:	$M^2\sin^M\theta\cos^2\theta$	$-M\sin^{M+2}\theta$
Expand:	$M^2\left(\sin^M\theta\right)\cdot\left(1-\sin^2\theta\right)$	$-M\sin^{M+2}\theta$
Collect:	$M^2\sin^M\theta$	$-\left(M^2+M\right)\sin^{M+2}\theta$

Equate: $M^2\sin^M\theta-\left(M^2+M\right)\sin^{M+2}\theta=\left(m^2-\lambda\sin^2\theta\right)\sin^M\theta$

Result: $M^2=m^2$, $\lambda=M^2+M=M\left(M+1\right)$

m must be an integer, so M must be an integer.

Negative M gives infinities at $\theta=0$ and $\theta=\pi$ so $M=\left|m\right|$

Solving for $G(\theta)$ 3

The first few solutions are

m	$G(\theta)$	$\lambda = M(M+1)$
± 4	$\sin^4\theta$	20
± 3	$\sin^3\theta$	12
± 2	$\sin^2\theta$	6
± 1	$\sin\theta$	2
0	1	0

There are also solutions with m = negative integer.
The power M of sin(θ) is still positive, just abs(m).

Next Guess

We are trying to solve $\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial G}{\partial\theta}\right] = \left[m^2 - \lambda \sin^2\theta\right]G$

We just found that $G = \sin^M\theta$ is a solution for non-negative integer M.

Maybe $G = \sin^M\theta\ \cos\theta$ could work?

Solving for $G(\theta)$ 4

$G(\theta)$: $\sin^M\theta\cos\theta$ Second Guess

$\frac{\partial}{\partial\theta}$: $M\sin^{M-1}\theta\cos^2\theta \qquad -\sin^{M+1}\theta$

$\times\sin\theta$: $M\sin^M\theta\cos^2\theta \qquad -\sin^{M+2}\theta$

$\frac{\partial}{\partial\theta}$: $M^2\sin^{M-1}\theta\cos^3\theta \quad -M\sin^{M+1}\theta\, 2\cos\theta \quad -(M+2)\sin^{M+1}\theta\cos\theta$

$\times\sin\theta$: $M^2\sin^M\theta\cos^3\theta \quad -M\sin^{M+2}\theta\, 2\cos\theta \quad -(M+2)\sin^{M+2}\theta\cos\theta$

Expand: $\begin{pmatrix} M^2\sin^M\theta\cos\theta \\ \times(1-\sin^2\theta) \end{pmatrix} \quad -M\sin^{M+2}\theta\, 2\cos\theta \quad -(M+2)\sin^{M+2}\theta\cos\theta$

Collect: $M^2\sin^M\theta\cos\theta \quad -\begin{pmatrix} M^2 + \\ 2M + \\ M+2 \end{pmatrix}\sin^{M+2}\theta\cos\theta$

Equate: $M^2\sin^M\theta\cos\theta - \begin{pmatrix} M^2 + \\ 2M + \\ M+2 \end{pmatrix}\sin^{M+2}\theta\cos\theta = \left(m^2 - \lambda\sin^2\theta\right)\sin^M\theta\cos\theta$

Result: $M^2 = m^2$, $\lambda = M^2 + 3M + 2 = (M+1)(M+2)$

Solving for $G(\theta)$ 5

m	$G(\theta)$	$\lambda = M(M+1)$
± 4	$\sin^4\theta$	20
± 3	$\sin^3\theta$	12
± 2	$\sin^2\theta$	6
± 1	$\sin\theta$	2
0	1	0

m	$G(\theta)$	$\lambda = (M+1)(M+2)$
± 4	$\sin^4\theta\cos\theta$	30
± 3	$\sin^3\theta\cos\theta$	20
± 2	$\sin^2\theta\cos\theta$	12
± 1	$\sin\theta\cos\theta$	6
0	$\cos\theta$	2

Solving for $G(\theta)$ 6

Arrange by m and λ

$m=5$						$\sin^5\theta$
$m=4$					$\sin^4\theta$	$\sin^4\theta\cos\theta$
$m=3$				$\sin^3\theta$	$\sin^3\theta\cos\theta$	
$m=2$			$\sin^2\theta$	$\sin^2\theta\cos\theta$		
$m=1$		$\sin\theta$	$\sin\theta\cos\theta$			
$m=0$	1	$\cos\theta$				
	$\lambda=0$	$\lambda=2$	$\lambda=6$	$\lambda=12$	$\lambda=20$	$\lambda=30$

Next Guess

We are trying to solve $\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial G}{\partial\theta}\right] = \left[m^2 - \lambda \sin^2\theta\right] G$

We just found that $G = \sin^M\theta \, \cos\theta$ is a solution for non-negative integer M.

We previously found that $G = \sin^M\theta$ is a solution.

Maybe $G = \sin^M\theta \, \cos^N\theta$ could work? We know it works for $N = 1$ and $N = 0$.

Solving for $G(\theta)$ 7

$G(\theta)$: $\sin^M\theta\cos^N\theta$ Third Guess

$$\frac{\partial}{\partial\theta}: \quad M\left(\sin^{M-1}\theta\cos^{N+1}\theta\right) \quad -N\left(\sin^{M+1}\theta\cos^{N-1}\theta\right)$$

$$\times\sin\theta: \quad M\left(\sin^{M}\theta\cos^{N+1}\theta\right) \quad -N\left(\sin^{M+2}\theta\cos^{N-1}\theta\right)$$

$$\frac{\partial}{\partial\theta}: \quad M\begin{pmatrix} M\sin^{M-1}\theta\cos^{N+2}\theta \\ -\sin^{M+1}\theta\, N\cos^{N}\theta \end{pmatrix} \quad -N\begin{pmatrix} (M+2)\sin^{M+1}\theta\cos^{N}\theta \\ -\sin^{M+3}\theta\,(N-1)\cos^{N-2}\theta \end{pmatrix}$$

$$\times\sin\theta: \quad M\begin{pmatrix} M\sin^{M}\theta\cos^{N+2}\theta \\ -\sin^{M+2}\theta\, N\cos^{N}\theta \end{pmatrix} \quad -N\begin{pmatrix} (M+2)\sin^{M+2}\theta\cos^{N}\theta \\ -\sin^{M+4}\theta\,(N-1)\cos^{N-2}\theta \end{pmatrix}$$

Collect: $M^2\sin^M\theta\cos^{N+2}\theta - \begin{pmatrix} MN+ \\ N(M+2) \end{pmatrix}\sin^{M+2}\theta\cos^N\theta + N(N-1)\sin^{M+4}\theta\cos^{N-2}\theta$

Solving for $G(\theta)$ 8

Collect: $M^2 \sin^M\theta \cos^{N+2}\theta - \begin{pmatrix} MN + \\ N(M+2) \end{pmatrix} \sin^{M+2}\theta\cos^N\theta + N(N-1)\sin^{M+4}\theta\cos^{N-2}\theta$

Expand: $\begin{pmatrix} M^2\sin^M\theta\cos^N\theta \\ \times(1-\sin^2\theta) \end{pmatrix} - \begin{pmatrix} MN + \\ N(M+2) \end{pmatrix} \sin^{M+2}\theta\cos^N\theta + N(N-1)\begin{pmatrix} \sin^{M+2}\theta\cos^{N-2}\theta \\ \times(1-\cos^2\theta) \end{pmatrix}$

Collect: $M^2\left[\sin^M\theta\cos^N\theta\right] - \begin{pmatrix} M^2 + \\ MN + \\ N(M+2) + \\ N(N-1) \end{pmatrix} \left[\sin^{M+2}\theta\cos^N\theta\right] + N(N-1)\left[\sin^{M+2}\theta\cos^{N-2}\theta\right]$

Simplify: $M^2\left[\sin^M\theta\cos^N\theta\right] - (M+N)(M+N+1)\left[\sin^{M+2}\theta\cos^N\theta\right] + N(N-1)\left[\sin^{M+2}\theta\cos^{N-2}\theta\right]$

Solving for $G(\theta)$ 9

Try the particular case of $N = 2$

$$M^2 \sin^M \theta \cos^N \theta - (M+N)(M+N+1)\sin^{M+2}\theta \cos^N \theta + N(N-1)\sin^{M+2}\theta \cos^{N-2}\theta$$

$$\rightarrow M^2 \sin^M \theta \cos^2 \theta - (M+2)(M+3)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta$$

$$M^2 \sin^M \theta \cos^2 \theta - (M+2)(M+3)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta = (m^2 - \lambda \sin^2\theta)\sin^M \theta \cos^2 \theta$$

$M^2 = m^2$, $\lambda = (M+2)(M+3)$ almost works, but the red term on the left doesn't match.

Next Guess

We are trying to solve $\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial G}{\partial\theta}\right] = \left[m^2 - \lambda \sin^2\theta\right] G$

We found that $G = \sin^M\theta$ is a solution for non-negative integer M.

We found that $G = \sin^M\theta \ \cos\theta$ is also a solution.

We noted that means $G = \sin^M\theta \ \cos^N\theta$ would work for $N = 1$ and $N = 0$.

But we just found that it doesn't work for $N = 2$.

Most terms have a $\cos^2\theta$ factor, but there's one term without it.

So try $G = \sin^M\theta \cdot \left(\cos^2\theta + A\right) = \sin^M\theta \ \cos^2\theta + A\sin^M\theta$
and pray that some A will make it work..

Solving for $G(\theta)$ 9

Try the particular case of $N = 2$

$$M^2 \sin^M \theta \cos^N \theta - \left(M+N\right)\left(M+N+1\right)\sin^{M+2}\theta \cos^N \theta + N\left(N-1\right)\sin^{M+2}\theta \cos^{N-2}\theta$$

$$\rightarrow M^2 \sin^M \theta \cos^2 \theta - \left(M+2\right)\left(M+3\right)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta$$

$$M^2 \sin^M \theta \cos^2 \theta - \left(M+2\right)\left(M+3\right)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta = \left(m^2 - \lambda \sin^2 \theta\right)\sin^M \theta \cos^2 \theta$$

$M^2 = m^2$, $\lambda = \left(M+2\right)\left(M+3\right)$ almost works, but the red term on the left doesn't match.

But try $G\left(\theta\right) = \sin^M \theta \cos^2 \theta + A\sin^M \theta$. This gives extra terms on both sides

We Already Did the Orange Term

$G(\theta)$:	$\sin^M\theta$	First Guess
$\dfrac{\partial}{\partial\theta}$:	$M\sin^{M-1}\theta\cos\theta$	
$\times\sin\theta$:	$M\sin^M\theta\cos\theta$	
$\dfrac{\partial}{\partial\theta}$:	$M^2\sin^{M-1}\theta\cos^2\theta$	$-M\sin^{M+1}\theta$
$\times\sin\theta$:	$M^2\sin^M\theta\cos^2\theta$	$-M\sin^{M+2}\theta$
Expand:	$M^2\left(\sin^M\theta\right)\cdot\left(1-\sin^2\theta\right)$	$-M\sin^{M+2}\theta$
Collect:	$M^2\sin^M\theta$	$-\left(M^2+M\right)\sin^{M+2}\theta$

Solving for $G(\theta)$ 9

Try the particular case of $N = 2$

$$M^2 \sin^M \theta \cos^N \theta - (M+N)(M+N+1)\sin^{M+2}\theta \cos^N \theta + N(N-1)\sin^{M+2}\theta \cos^{N-2}\theta$$

$$\to M^2 \sin^M \theta \cos^2 \theta - (M+2)(M+3)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta$$

$$M^2 \sin^M \theta \cos^2 \theta - (M+2)(M+3)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta = \left(m^2 - \lambda \sin^2\theta\right)\sin^M \theta \cos^2 \theta$$

$M^2 = m^2$, $\lambda = (M+2)(M+3)$ almost works, but the red term on the left doesn't match.

But try $G(\theta) = \sin^M \theta \cos^2 \theta + A \sin^M \theta$. This gives extra terms on both sides

$$\begin{pmatrix} M^2 \sin^M \theta \cos^2 \theta - (M+2)(M+3)\sin^{M+2}\theta \cos^2 \theta + 2\sin^{M+2}\theta \\ + A\left[M^2 \sin^M \theta - M(M+1)\sin^{M+2}\theta\right] \end{pmatrix} = \left(m^2 - \lambda \sin^2\theta\right)\begin{bmatrix} \sin^M \theta \cos^2 \theta \\ + A \sin^M \theta \end{bmatrix}$$

For $\sin^M \theta$ we need $AM^2 = m^2 A$. The A cancels out, and we already have $M^2 = m^2$.

For $\sin^{M+2}\theta$, we need $\left(2 - AM(M+1)\right) = -\lambda A$, so we pick A to satisfy it.

$$2 = A\left(M(M+1) - \lambda\right) \to A = \frac{2}{M^2 + M - \left(M^2 + 5M + 6\right)} = \frac{-2}{4M+6}$$

Solving for $G(\theta)$ 10

Arrange by m and λ

$m=4$					$\sin^4\theta$
$m=3$				$\sin^3\theta$	$\sin^3\theta\cos\theta$
$m=2$			$\sin^2\theta$	$\sin^2\theta\cos\theta$	$\sin^2\theta\left(\cos^2\theta-1/7\right)$
$m=1$		$\sin\theta$	$\sin\theta\cos\theta$	$\sin\theta\left(\cos^2\theta-1/5\right)$	
$m=0$	1	$\cos\theta$	$\cos^2\theta-1/3$		
	$\lambda=0$	$\lambda=2$	$\lambda=6$	$\lambda=12$	$\lambda=20$

Solving for $G(\theta)$ 11

For the $N = 3$ case

$$M^2 \sin^M \theta \cos^N \theta - (M+N)(M+N+1)\sin^{M+2}\theta \cos^N \theta + N(N-1)\sin^{M+2}\theta \cos^{N-2}\theta$$

$$\rightarrow M^2 \sin^M \theta \cos^3 \theta - (M+3)(M+4)\sin^{M+2}\theta \cos^3 \theta + 6\sin^{M+2}\theta \cos\theta$$

$$M^2 \sin^M \theta \cos^3 \theta - (M+3)(M+4)\sin^{M+2}\theta \cos^3 \theta + 6\sin^{M+2}\theta \cos\theta = (m^2 - \lambda \sin^2\theta)\sin^M \theta \cos^3 \theta$$

$M^2 = m^2, \quad \lambda = (M+3)(M+4)$ almost works, but the red term on the left doesn't match.

But try $G(\theta) = \sin^M \theta \cos^3 \theta + A\sin^M \theta \cos\theta$. This gives extra terms on both sides

We Already Did the Orange Term

$G(\theta)$: $\sin^M\theta\cos\theta$ Second Guess

$\frac{\partial}{\partial\theta}$: $M\sin^{M-1}\theta\cos^2\theta$ $-\sin^{M+1}\theta$

$\times\sin\theta$: $M\sin^M\theta\cos^2\theta$ $-\sin^{M+2}\theta$

$\frac{\partial}{\partial\theta}$: $M^2\sin^{M-1}\theta\cos^3\theta$ $-M\sin^{M+1}\theta\,2\cos\theta$ $-(M+2)\sin^{M+1}\theta\cos\theta$

$\times\sin\theta$: $M^2\sin^M\theta\cos^3\theta$ $-M\sin^{M+2}\theta\,2\cos\theta$ $-(M+2)\sin^{M+2}\theta\cos\theta$

Expand: $\begin{pmatrix} M^2\sin^M\theta\cos\theta \\ \times(1-\sin^2\theta) \end{pmatrix}$ $-M\sin^{M+2}\theta\,2\cos\theta$ $-(M+2)\sin^{M+2}\theta\cos\theta$

Collect: $M^2\sin^M\theta\cos\theta$ $-\begin{pmatrix} M^2+ \\ 2M+ \\ M+2 \end{pmatrix}\sin^{M+2}\theta\cos\theta$

Solving for $G(\theta)$ 11

For the $N = 3$ case

$$M^2 \sin^M\theta\cos^N\theta - (M+N)(M+N+1)\sin^{M+2}\theta\cos^N\theta + N(N-1)\sin^{M+2}\theta\cos^{N-2}\theta$$

$$\to M^2 \sin^M\theta\cos^3\theta - (M+3)(M+4)\sin^{M+2}\theta\cos^3\theta + 6\sin^{M+2}\theta\cos\theta$$

$$M^2 \sin^M\theta\cos^3\theta - (M+3)(M+4)\sin^{M+2}\theta\cos^3\theta + 6\sin^{M+2}\theta\cos\theta = \left(m^2 - \lambda\sin^2\theta\right)\sin^M\theta\cos^3\theta$$

$M^2 = m^2, \quad \lambda = (M+3)(M+4)$ almost works, but the red term on the left doesn't match.

But try $G(\theta) = \sin^M\theta\cos^3\theta + A\sin^M\theta\cos\theta$. This gives extra terms on both sides

$$\begin{pmatrix} M^2 \sin^M\theta\cos^3\theta - (M+3)(M+4)\sin^{M+2}\theta\cos^3\theta + 6\sin^{M+2}\theta\cos\theta \\ +A\left[M^2\sin^M\theta\cos\theta - (M+1)(M+2)\sin^{M+2}\theta\cos\theta\right] \end{pmatrix} = \left(m^2 - \lambda\sin^2\theta\right)\begin{bmatrix}\sin^M\theta\cos^3\theta \\ +A\sin^M\theta\cos\theta\end{bmatrix}$$

For $\sin^M\theta\cos\theta$ we need $AM^2 = m^2 A$. The A cancels out, and we already have $M^2 = m^2$.

For $\sin^{M+2}\theta\cos^3\theta$, we need $\left(6 - A(M+1)(M+2)\right) = -\lambda A$, so we pick A to satisfy it.

$$6 = A\left((M+1)(M+2) - \lambda\right) \to A = \frac{6}{M^2 + 3M + 2 - \left(M^2 + 7M + 12\right)} = \frac{-6}{4M + 10}$$

Solving for $G(\theta)$ 12

Arrange by m and λ

$m=4$					$\sin^4\theta$
$m=3$				$\sin^3\theta$	$\sin^3\theta\cos\theta$
$m=2$			$\sin^2\theta$	$\sin^2\theta\cos\theta$	$\sin^2\theta\left(\cos^2\theta-1/7\right)$
$m=1$		$\sin\theta$	$\sin\theta\cos\theta$	$\sin\theta\left(\cos^2\theta-1/5\right)$	
$m=0$	1	$\cos\theta$	$\cos^2\theta-1/3$		
	$\lambda=0$	$\lambda=2$	$\lambda=6$	$\lambda=12$	$\lambda=20$

Solving for $G(\theta)$ 12

Arrange by m and λ

$m=4$					$\sin^4\theta$
$m=3$				$\sin^3\theta$	$\sin^3\theta\cos\theta$
$m=2$			$\sin^2\theta$	$\sin^2\theta\cos\theta$	$\sin^2\theta\left(\cos^2\theta-1/7\right)$
$m=1$		$\sin\theta$	$\sin\theta\cos\theta$	$\sin\theta\left(\cos^2\theta-1/5\right)$	$\sin\theta\left(\cos^3\theta-3/7\cos\theta\right)$
$m=0$	1	$\cos\theta$	$\cos^2\theta-1/3$	$\cos^3\theta-3/5\cos\theta$	
	$\lambda=0$	$\lambda=2$	$\lambda=6$	$\lambda=12$	$\lambda=20$

Integer Powers

We already concluded that M in $G(\theta) = \sin^M \theta \cdot Q_{N,M}(\cos\theta)$

had to be an integer, because it was related to m from the ϕ equation,

and m has to be an integer.

M had to be positive to avoid infinities at $\theta = 0$ and $\theta = \pi$.

If N weren't an integer, the trick of adding terms with lower powers of $\cos\theta$ to deal with the extra $+2\sin^{M+2}\theta$ factor would never terminate.

Negative powers of $\cos\theta$ would give infinities at $\theta = \pi/2$ where $\cos\theta = 0$

So N must also be a positive integer.

Integer Powers

We already concluded that M in $G(\theta) = \sin^M \theta \cdot Q_{N,\,M}(\cos\theta)$ had to be an integer, because it was related to m from the ϕ equation, and m has to be an integer.

M had to be positive to avoid infinities at $\theta = 0$ and $\theta = \pi$.

If N weren't an integer, the trick of adding terms with lower powers of $\cos\theta$ to deal with the extra $+2\sin^{M+2}\theta$ factor would never terminate.

An infinite series isn't necessarily fatal, but negative powers of $\cos\theta$ would give infinities at $\theta = \pi/2$ where $\cos\theta = 0$.

So N must also be a positive integer.

Associated Legendre Functions

The λ value is always $(M+N)(M+N+1)$.

It's convenient to define $\ell = M+N$ so $\lambda = \ell(\ell+1)$.

The $G(\theta)$ we have been inventing are called the

Associated Legendre Functions $P_\ell^m(\theta)$.

The superscript m is the positive or negative m value, not a power.

They are $\sin^{|m|}\theta$ times a polynomial in $\cos\theta$ of order $\ell - |m|$,

which is the same as my N.

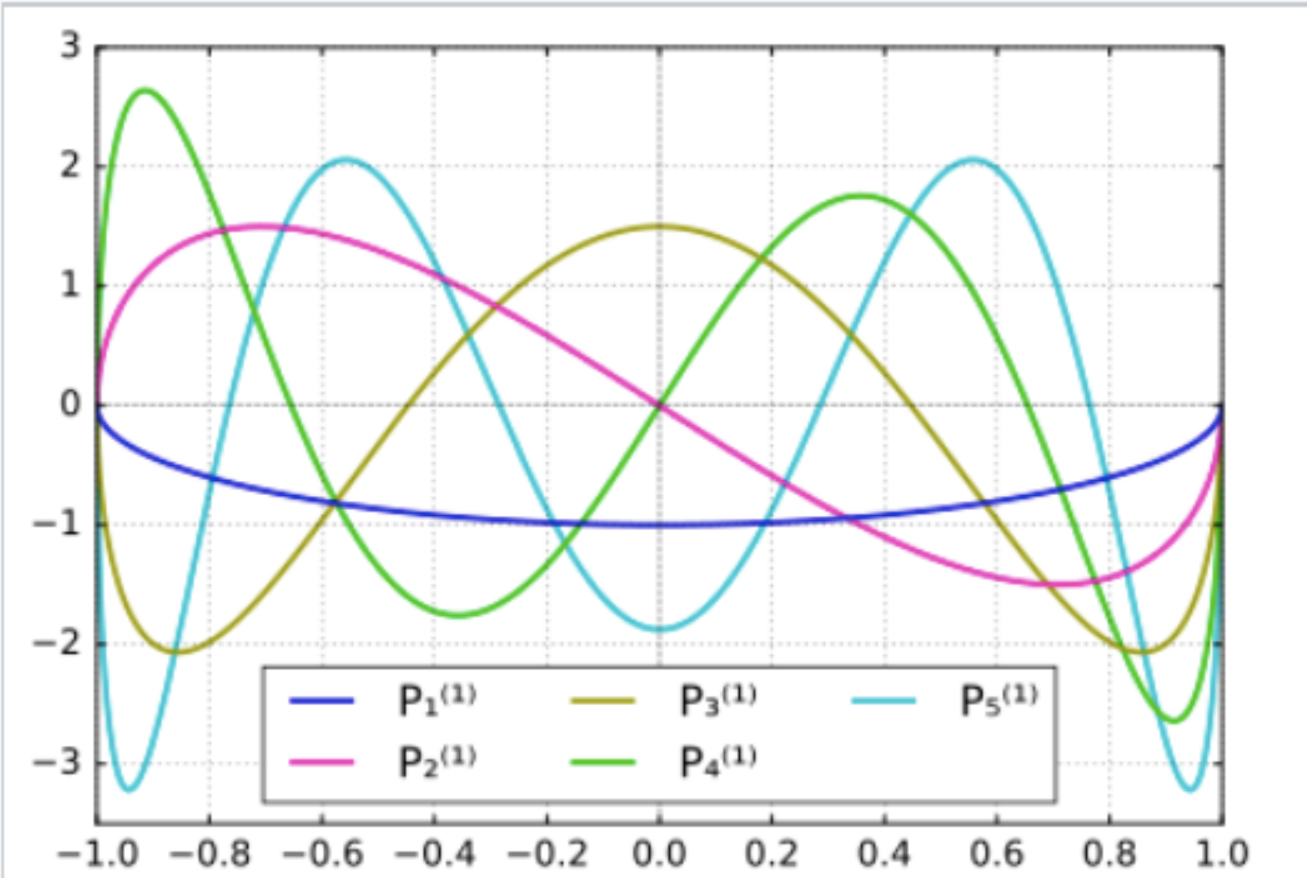
Associated Legendre Functions 2

It's conventional to normalize them so

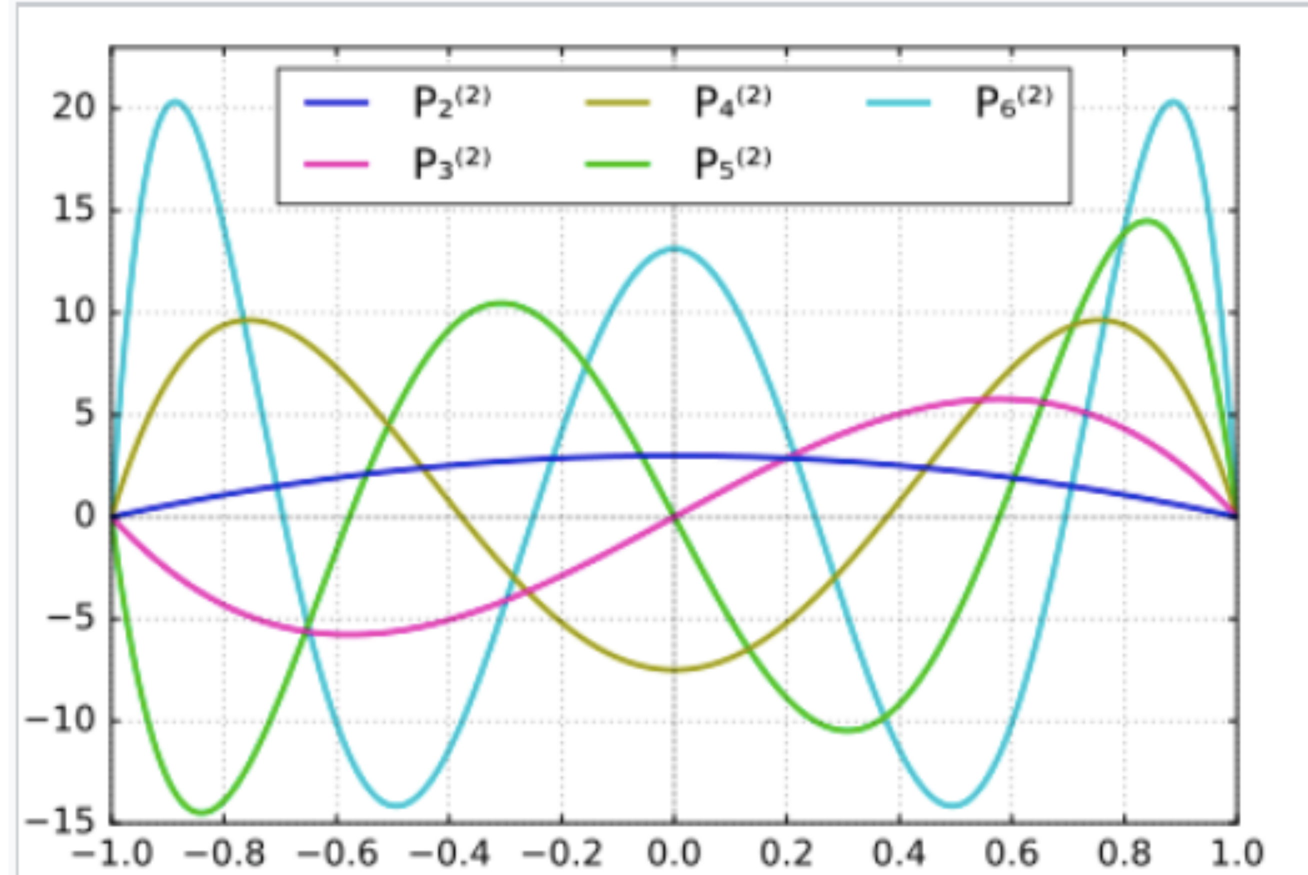
$$\int_{\theta=0}^{\theta=\pi} d(\cos\theta)\left[P_\ell^m(\theta)\right]^2 = \int_{\theta=0}^{\theta=\pi} \sin\theta\, d\theta\left[P_\ell^m(\theta)\right]^2 = 1$$

	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$
$m=4$					$105\sin^4\theta$
$m=3$				$-15\sin^3\theta$	$-105\sin^3\theta\cos\theta$
$m=2$			$3\sin^2\theta$	$15\sin^2\theta\cos\theta$	$\frac{15}{2}\sin^2\theta\left(7\cos^2\theta-1\right)$
$m=1$		$-\sin\theta$	$-3\sin\theta\cos\theta$	$-\frac{3}{2}\sin\theta\left(5\cos^2\theta-1\right)$	$-\frac{5}{2}\sin\theta\left(7\cos^3\theta-3\cos\theta\right)$
$m=0$	1	$\cos\theta$	$\frac{1}{2}\left(3\cos^2\theta-1\right)$	$\frac{1}{2}\left(5\cos^3\theta-3\cos\theta\right)$	$\frac{1}{8}\left(35\cos^4\theta-30\cos^2\theta+3\right)$

Associated Legendre Functions



Associated Legendre functions for m = 1



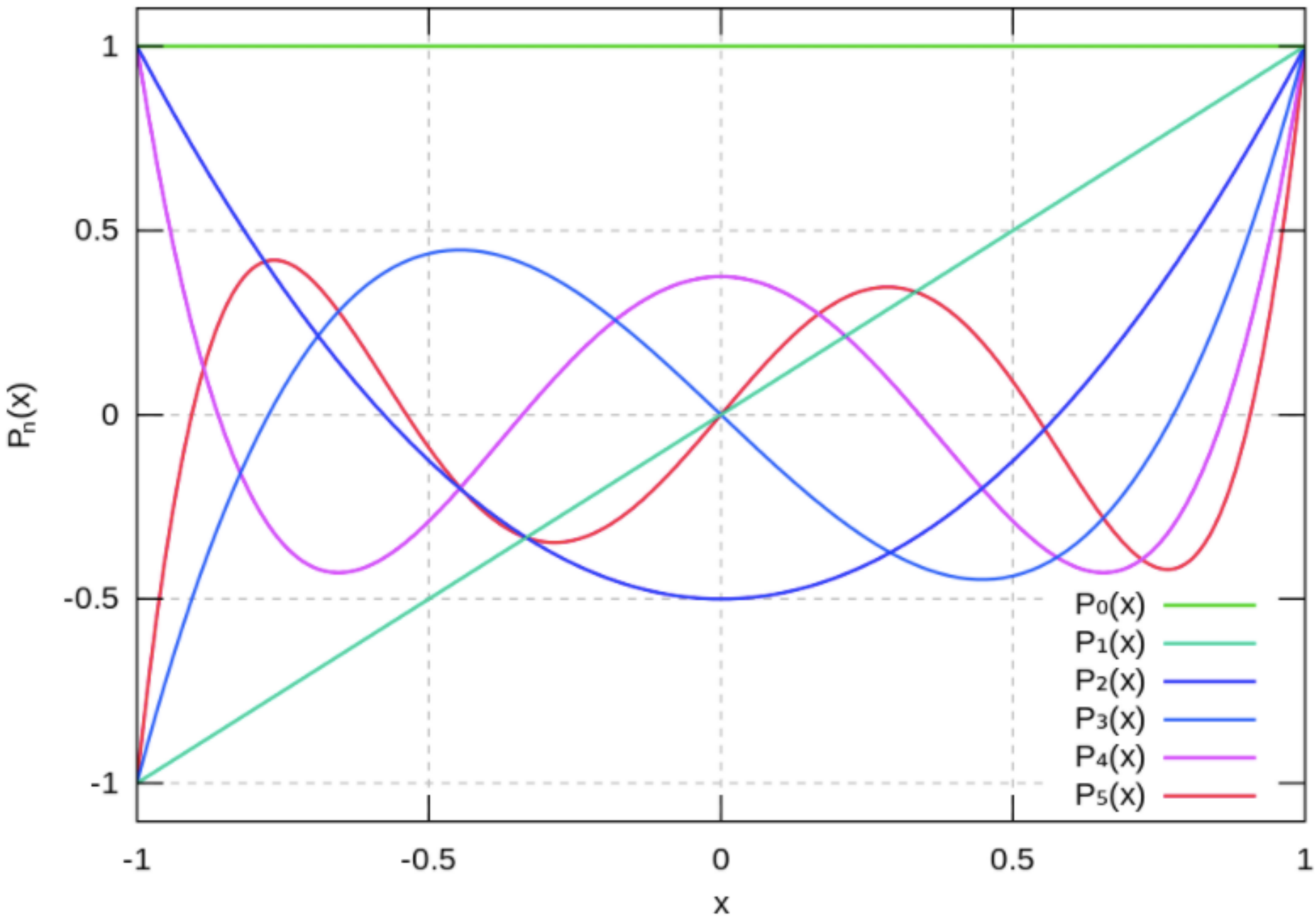
Associated Legendre functions for m = 2

Legendre Polynomials

The $m = 0$ case, which has no $\sin(\theta)$ factor, and changing from $\cos(\theta)$ to $-1 < x < 1$ are called the Legendre Polynomials $P_n(x)$

n	$P_n(x)$
0	1
1	x
2	$\frac{1}{2}\left(3x^2-1\right)$
3	$\frac{1}{2}\left(5x^3-3x\right)$
4	$\frac{1}{8}\left(35x^4-30x^2+3\right)$
5	$\frac{1}{8}\left(63x^5-70x^3+15x\right)$
6	$\frac{1}{16}\left(231x^6-315x^4+105x^2-5\right)$
7	$\frac{1}{16}\left(429x^7-693x^5+315x^3-35x\right)$
8	$\frac{1}{128}\left(6435x^8-12012x^6+6930x^4-1260x^2+35\right)$
9	$\frac{1}{128}\left(12155x^9-25740x^7+18018x^5-4620x^3+315x\right)$
10	$\frac{1}{256}\left(46189x^{10}-109395x^8+90090x^6-30030x^4+3465x^2-63\right)$

Legendre Polynomials



Spherical Harmonics

$G(\theta)\cdot H(\phi) = P_\ell^m(\theta)\cdot e^{im\phi}$ always appear together, so there is a standard name: the Spherical Harmonics $Y_\ell^m(\theta,\phi) = P_\ell^m(\theta)\cdot e^{im\phi}$

We found $H(\phi)$ and $G(\theta)$ without any knowledge of the potential. That means the Spherical Harmonics are always the same, whatever the potential.

$m=4$					$\sin^4\theta e^{4i\phi}$
$m=3$				$\sin^3\theta e^{3i\phi}$	$\sin^3\theta\cos\theta e^{3i\phi}$
$m=2$			$\sin^2\theta e^{2i\phi}$	$\sin^2\theta\cos\theta e^{2i\phi}$	$\sin^2\theta\left(7\cos^2\theta-1\right)e^{2i\phi}$
$m=1$		$\sin\theta e^{i\phi}$	$\sin\theta\cos\theta e^{i\phi}$	$\sin\theta\left(5\cos^2\theta-1\right)e^{i\phi}$	$\sin\theta\left(7\cos^3\theta-3\cos\theta\right)e^{i\phi}$
$m=0$	1	$\cos\theta$	$3\cos^2\theta-1$	$5\cos^3\theta-3\cos\theta$	$35\cos^4\theta-30\cos^2\theta+3$
	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$

This is not the standard normalization, and there are also solutions for $-m$.

Normalized Spherical Harmonics

	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$
$m=4$					$+\sqrt{\frac{315}{512\pi}}\sin^4\theta\, e^{4i\phi}$
$m=3$				$-\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{3i\phi}$	$-\sqrt{\frac{315}{64\pi}}\sin^3\theta\cos\theta\, e^{3i\phi}$
$m=2$			$+\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi}$	$+\sqrt{\frac{35}{64\pi}}\sin^2\theta\cos\theta\, e^{2i\phi}$	$+\sqrt{\frac{45}{128\pi}}\sin^2\theta\left(7\cos^2\theta-1\right)e^{2i\phi}$
$m=1$		$-\sqrt{\frac{3}{4\pi}}\sin\theta\, e^{i\phi}$	$-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$	$-\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{i\phi}$	$-\sqrt{\frac{45}{64\pi}}\sin\theta\left(7\cos^3\theta-3\cos\theta\right)e^{i\phi}$
$m=0$	$\sqrt{\frac{1}{4\pi}}$	$+\sqrt{\frac{3}{4\pi}}\cos\theta$	$+\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$	$+\sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta-3\cos\theta\right)$	$+\sqrt{\frac{9}{256\pi}}\left(35\cos^4\theta-30\cos^2\theta+3\right)$
$m=-1$		$+\sqrt{\frac{3}{4\pi}}\sin\theta\, e^{-i\phi}$	$+\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{-i\phi}$	$+\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{-i\phi}$	$+\sqrt{\frac{45}{64\pi}}\sin\theta\left(7\cos^3\theta-3\cos\theta\right)e^{-i\phi}$
$m=-2$			$+\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{-2i\phi}$	$+\sqrt{\frac{35}{64\pi}}\sin^2\theta\cos\theta\, e^{-2i\phi}$	$+\sqrt{\frac{45}{128\pi}}\sin^2\theta\left(7\cos^2\theta-1\right)e^{-2i\phi}$
$m=-3$				$+\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{-3i\phi}$	$+\sqrt{\frac{315}{64\pi}}\sin^3\theta\cos\theta\, e^{-3i\phi}$
$m=-4$					$+\sqrt{\frac{315}{512\pi}}\sin^4\theta\, e^{-4i\phi}$

Patterns and Jargon

The ℓ values go from 0 to infinity.

For each ℓ value, the m values go from $-\ell$ to $+\ell$
For $\ell = 0$ there is only $m = 0$.
For $\ell = 1$ there is $m = -1, 0$ and $+1$.
For $\ell = 2$ there is $m = -2, -1, 0\ +1$, and $+2$.

The ℓ value is the the power of $\sin\theta$ plus the highest power of $\cos\theta$.

The power of $\sin\theta$ is $|m|$.

The m value is the integer appearing in $e^{im\phi}$.

$\ell = 0$ are called S-states or S-wave states.
$\ell = 1$ are called P-states or P-wave states.
$\ell = 2$ are called D-states or D-wave states.
$\ell = 3$ are called F-states or F-wave states.

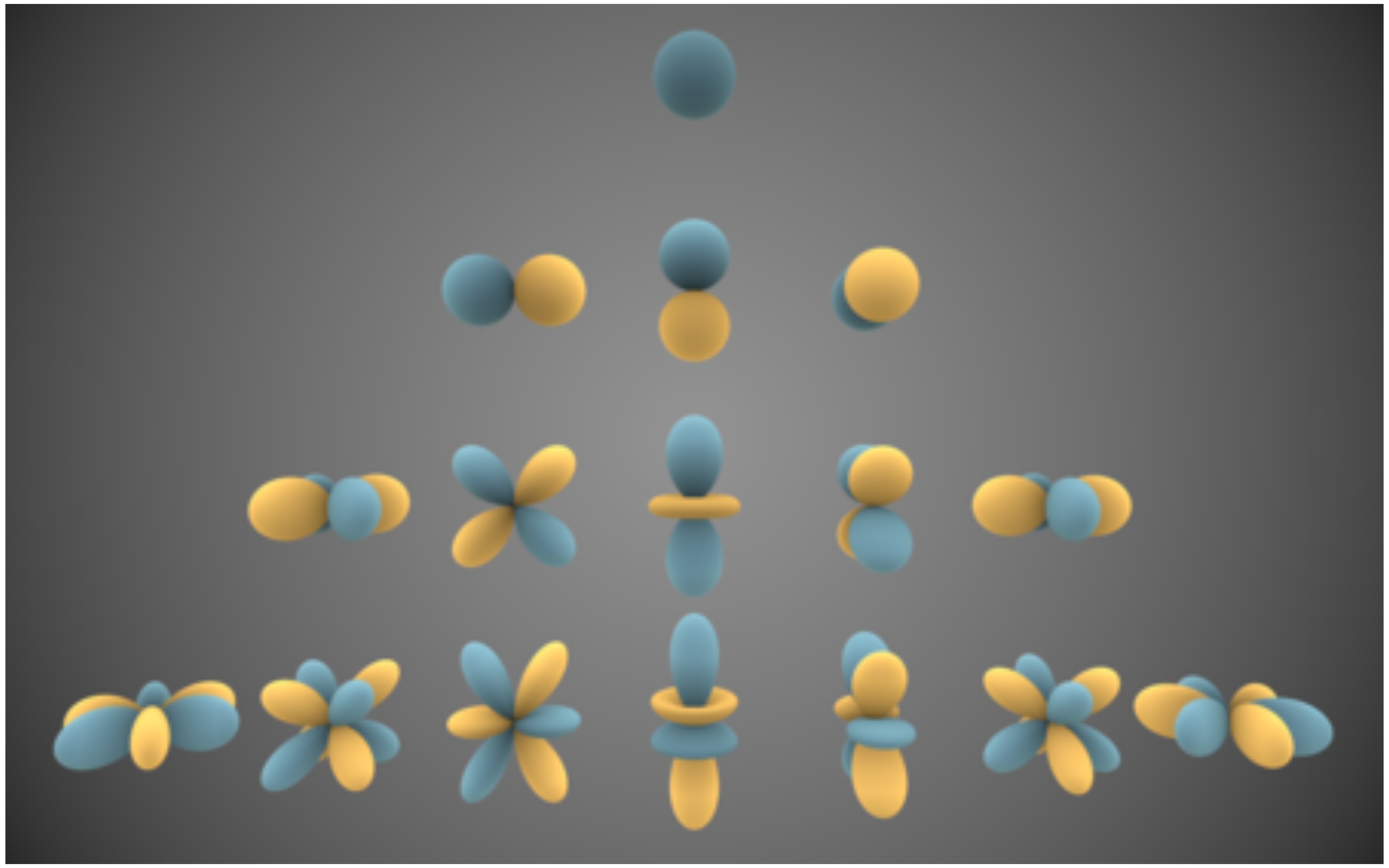
Visualizing the Spherical Harmonics

The Spherical Harmonics "exist" on the surface of a sphere.

The angular equations didn't have any explicit i's, so there are real solutions, which are way easier to visualize. We get them by

$$\frac{e^{im\phi}+e^{-im\phi}}{2}=\cos m\phi \text{ and } \frac{e^{im\phi}-e^{-im\phi}}{2i}=\sin m\phi$$

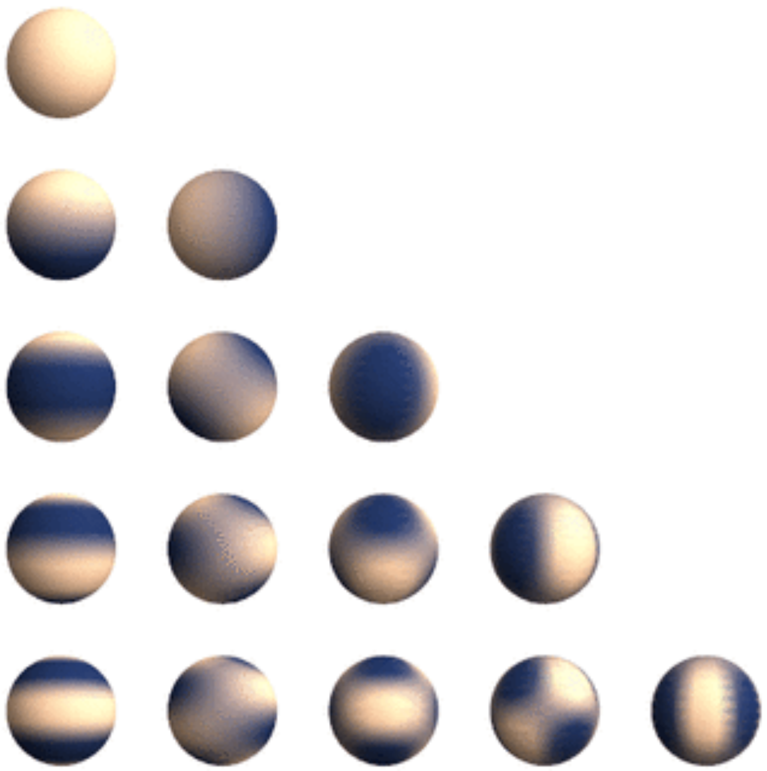
We can then represent the value as a radial distance, with blue for positive and yellow for negative.



Visualizing the Spherical Harmonics 2

That 3D picture is pretty standard, but I don't like it much, because it's the radial solution that determines how far the particle is from the origin, not the Spherical Harmonic.

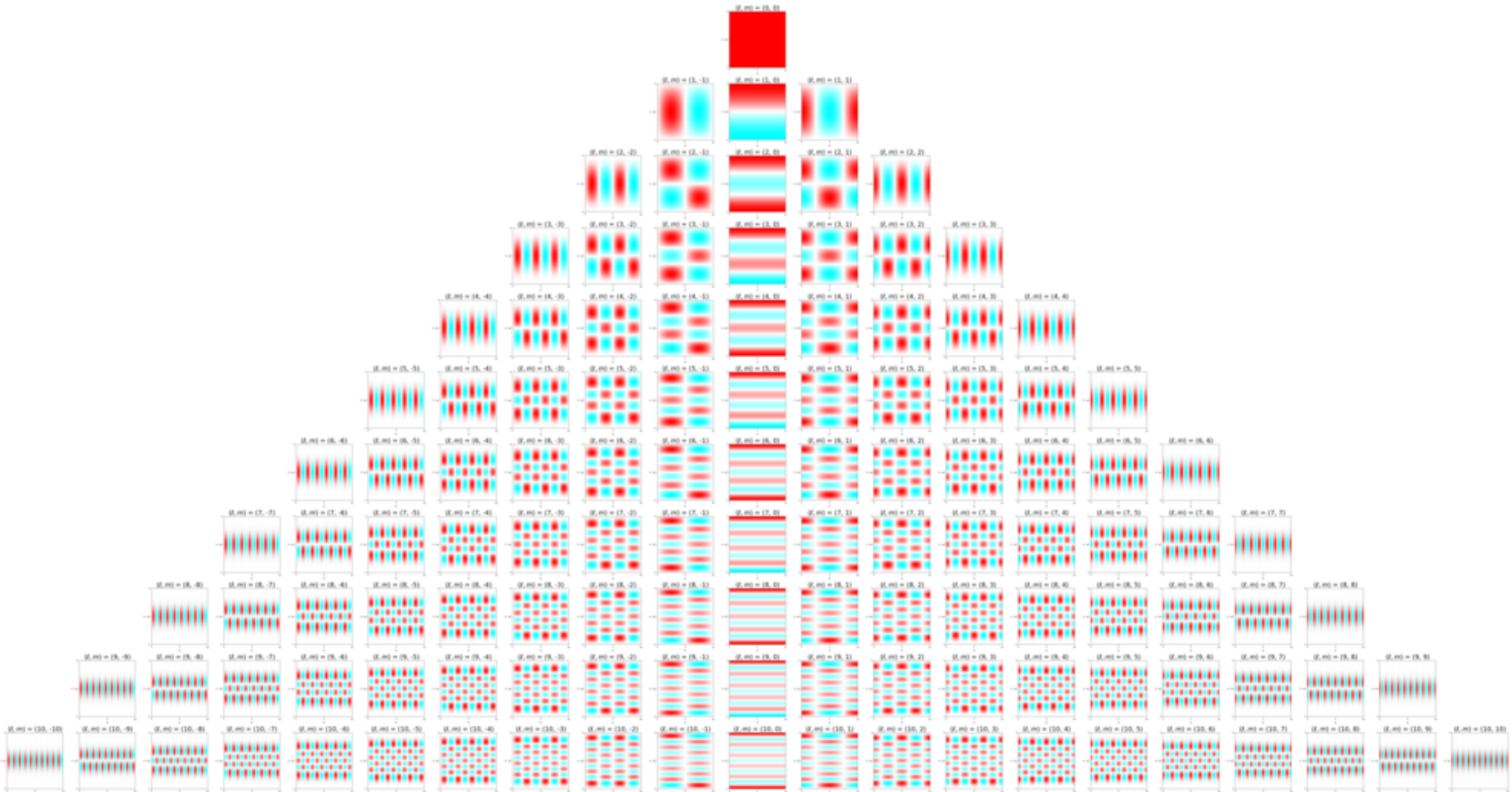
A better picture is to paint a sphere with the positive and negative real values.



You have to rotate the spheres to see everything. If you click the .gif version in the Canvas Module, you will see the animation. Or you can just go to Wikipedia where I got it.

Visualizing the Spherical Harmonics 3

I think the best visualization is to use red and blue to represent positive and negative real values, and plot vs θ and ϕ, so you can see everything at once.



Observations

The $m = 0$ harmonics, the middle column, define bands of "latitude," independent of "longitude."

The "maximum $|m|$" or "$|m| = \ell$" harmonics, the diagonal edges, define bands of "longitude" that are increasingly focused near the "equator."

The harmonics in between make "checkerboards"
with fewer "bands" in latitude and more bands in "longitude"
as you move away from the center.

For Next Time

Homework 5 is due tonight at midnight.

Homework 6 will be posted Tuesday, due Sunday night.

Wednesday the last lecture. We'll solve the radial Schrodinger equation for the energies and radial wavefunctions. Particularly for hydrogen.

There will be a tutorial worksheet on Friday, and office hours.