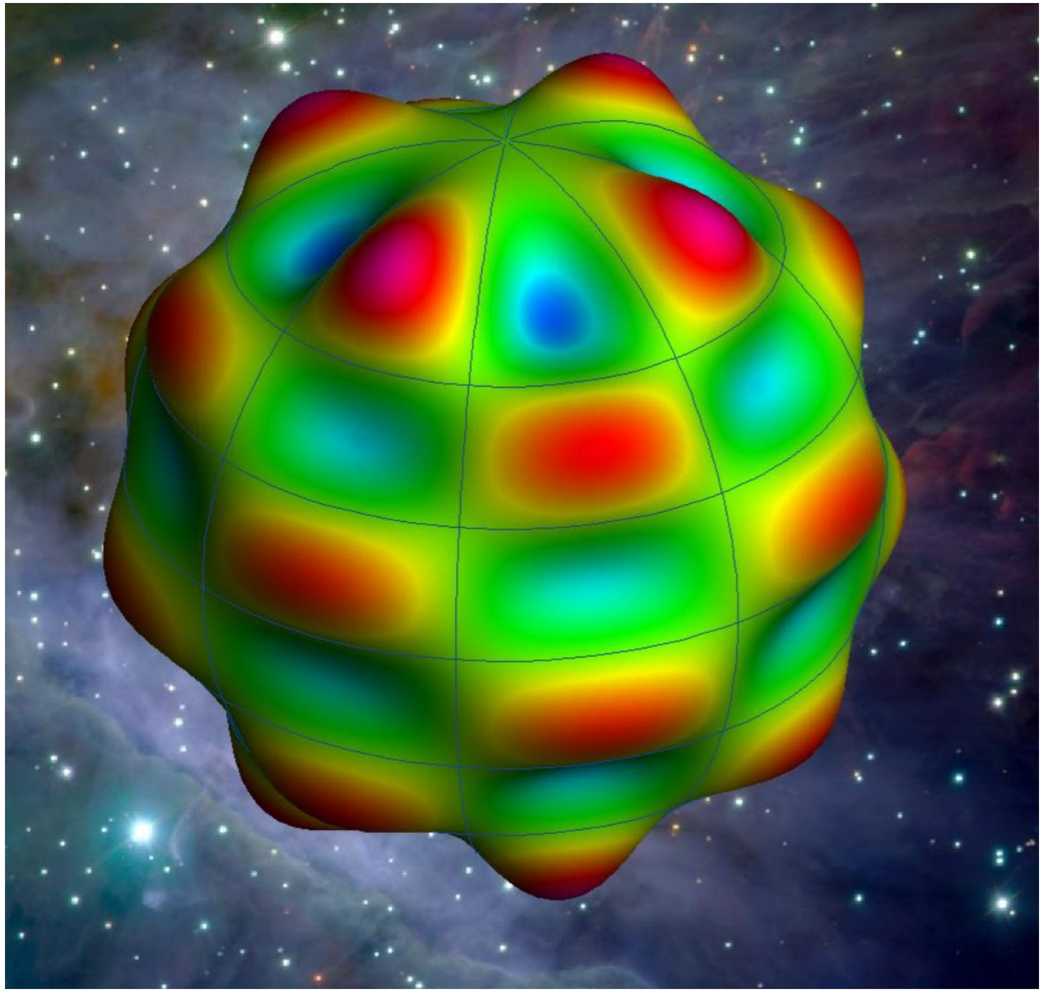
Today in Physics 237: the Schrödinger equation in 3-D

- Separation solutions in Cartesian coordinates
- Separation solution in spherical coordinates
  - Separating and solving the angular equation: spherical harmonics
  - Separating and solving the radial equation: example of the infinite spherical well ("particle in a spherical box")



Polar plot of spherical harmonic $Y_9^4(\vartheta)$, from the International Centre for Global Earth Models.

Separation solutions to the 3-D Schrödinger equation

- In 3-D, the momentum $\boldsymbol{p}$ must of course correspond to a vector operator. In Cartesian coordinates,

$$\hat{\boldsymbol{p}} = -i\hat{\boldsymbol{x}}\hbar\frac{\partial}{\partial x} - i\hat{\boldsymbol{y}}\hbar\frac{\partial}{\partial y} - i\hat{\boldsymbol{z}}\hbar\frac{\partial}{\partial z} = -i\hbar\boldsymbol{\nabla} \quad .$$

$\hat{\boldsymbol{x}}$, $\hat{\boldsymbol{y}}$, and $\hat{\boldsymbol{z}}$ are unit vectors, not operators;
$\boldsymbol{\nabla}$ is the **gradient**

- The Hamiltonian therefore corresponds to

$$\hat{H} = \frac{1}{2m}\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{p}} + V(x,y,z) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \quad ,$$

$\boldsymbol{r} = x\hat{\boldsymbol{x}} + y\hat{\boldsymbol{y}} + z\hat{\boldsymbol{z}}$;
∇^2 is the **Laplacian**

and the time-dependent Schrödinger equation becomes

$$i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) = \hat{H}\Psi(\boldsymbol{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\Psi(\boldsymbol{r},t) \quad .$$

Separation solutions to the 3-D Schrödinger equation (continued)

- The domain of spatial variables is volume in 3D, so normalization of the wavefunction involves a volume integral:

$$\int \left|\Psi(\boldsymbol{r},t)\right|^2 d\tau = \int \left|\Psi(x,y,z,t)\right|^2 dxdydz = 1 \quad .$$

- In principle, 3-D only costs extra effort of a factor of about three, because the Schrödinger equation is still separable in lots of interesting geometries.

- Time and space separate as they did before: let $\Psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})\varphi(t)$, and, as seen in Lecture 3,

$$i\hbar\psi(\boldsymbol{r})\frac{\partial}{\partial t}\varphi(t) = \varphi(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) \quad ,$$

$$i\hbar\frac{1}{\varphi(t)}\frac{\partial}{\partial t}\varphi(t) = \frac{1}{\psi(\boldsymbol{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = \text{ constant } = E \quad ,$$

$$\frac{\partial}{\partial t}\varphi(t) = -i\frac{E}{\hbar}\varphi(t) \quad , \quad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \quad .$$

Separation solutions to the 3-D Schrödinger equation (continued)

- And again the time equation is directly integrable:

$$\int \frac{d\varphi}{\varphi} = -i\frac{E}{\hbar}\int dt \quad \Rightarrow \quad \ln\varphi = -iEt/\hbar + C' \quad \Rightarrow \quad \varphi(t) = Ce^{-iEt/\hbar} \quad ,$$

  so all the effort goes into solving the time-independent equation for $\psi(\boldsymbol{r})$, usually as a boundary-value problem. For a discrete spectrum of states and energies, the general solution is still recognizable:

$$\Psi(\boldsymbol{r},t) = \sum_n c_n \psi_n(\boldsymbol{r}) e^{-iE_n t/\hbar} \quad , \quad c_n = \int_V \psi_n^*(\boldsymbol{r}) \Psi(\boldsymbol{r},0) d\tau \quad .$$

- In Cartesian coordinates, the time-independent 3-D Schrödinger equation separates into three 1-D equations just like the ones we have been solving. Let $\psi(\boldsymbol{r}) = X(x)Y(y)Z(z)$, substitute into the 3-D version, and divide through by $X(x)Y(y)Z(z)$:

$$\frac{1}{X}\frac{d^2X}{dx} + \frac{1}{Y}\frac{d^2Y}{dy} + \frac{1}{Z}\frac{d^2Z}{dz} = \frac{2mE}{\hbar^2} = k_x^2 + k_y^2 + k_z^2 \quad \Rightarrow \quad \frac{d^2X}{dx} - k_x^2 = 0 \quad \text{, etc.}$$

Separation solutions to the 3-D Schrödinger equation (continued)

- In G&S problem 4.2 on this week's assignment, you will apply all this to the 3-D version of the infinite square well: the infinite cubical well, also known as the "particle in a box."
- Since coordinates and derivatives of different coordinates are interchangeable, e.g. $x\frac{\partial}{\partial y}f(x,y)=\frac{\partial}{\partial y}xf(x,y)$, there is one uncertainty for each Cartesian coordinate:

$$\left[x,p_x\right]=\left[y,p_y\right]=\left[z,p_z\right]=i\hbar \quad ; \quad \sigma_x\sigma_{p_x}\geq\frac{\hbar}{2} \quad , \quad \sigma_y\sigma_{p_y}\geq\frac{\hbar}{2} \quad , \quad \sigma_z\sigma_{p_z}\geq\frac{\hbar}{2} \quad ;$$

  all the other combinations commute, e.g. $\left[x,p_y\right]=0$, and there is no restriction on the corresponding uncertainty products, e.g. $\sigma_x\sigma_{p_y}$ can be anything it wants.

- Good thing the universe isn't rectilinear on all scales, or we'd be done here.
- Fortunately many interesting situations have spherically-symmetrical potential energy.
- This doesn't, however, mean the corresponding solutions to the Schrödinger equation are spherically symmetric.

The Schrödinger equation in spherical coordinates

- Most will be familiar with spherical coordinates, in which the gradient, Laplacian, and infinitesimal element of volume are

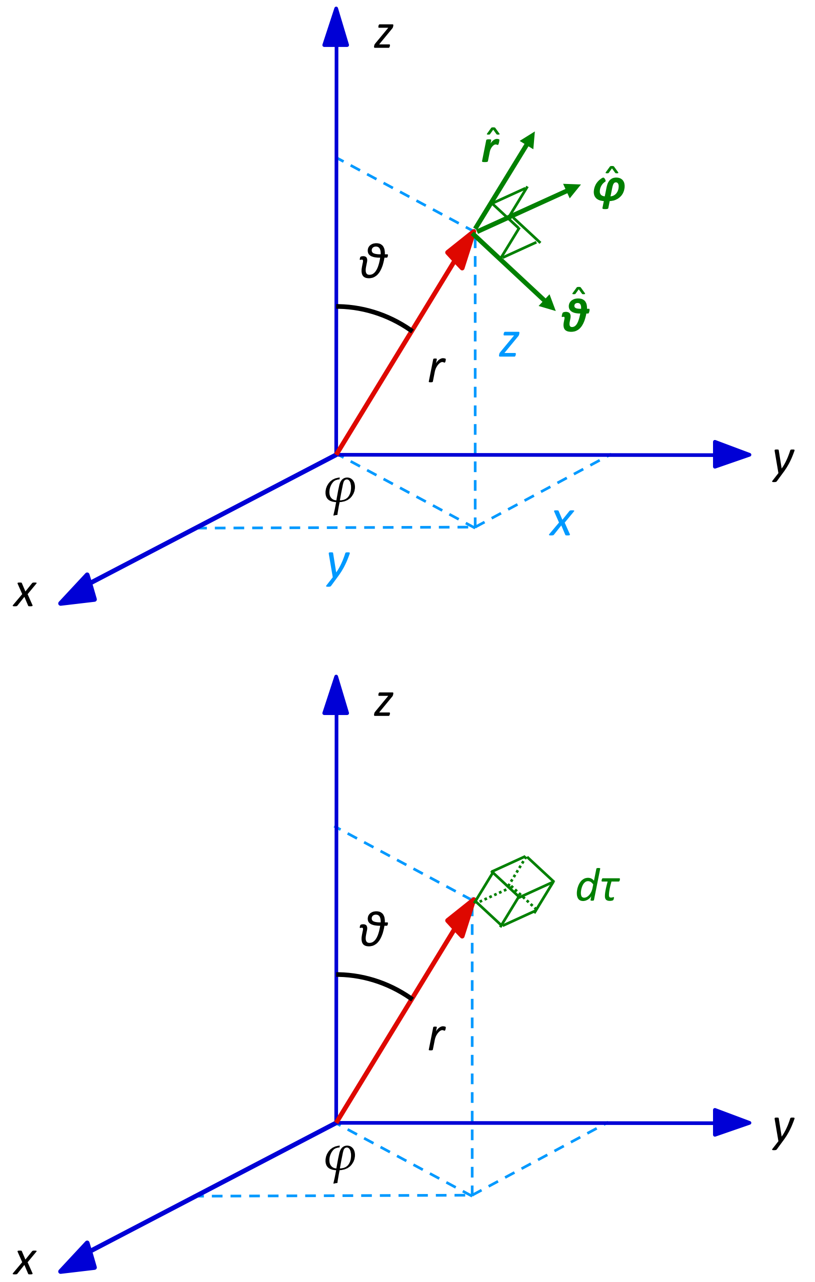
$$\boldsymbol{\nabla} = \frac{\partial}{\partial r}\hat{\boldsymbol{r}} + \frac{1}{r}\frac{\partial}{\partial \vartheta}\hat{\boldsymbol{\vartheta}} + \frac{1}{r\sin\vartheta}\frac{\partial}{\partial \varphi}\hat{\boldsymbol{\varphi}} \quad ,$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial}{\partial \vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2} \quad \text{, and}$$

$$d\tau = d\ell_r d\ell_\vartheta d\ell_\varphi = r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi \quad .$$

- You either did, or will, learn all the details in PHYS 217.

- Since we won't be *adding* vectors in this class for a while, we'll just give you these formulas for now and start using them.



The Schrödinger equation in spherical coordinates (continued)

- The time-independent Schrödinger equation:

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}+V(\boldsymbol{r})\right]\psi(\boldsymbol{r})=E\psi(\boldsymbol{r}) \quad .$$

- Suppose that the potential energy is **independent of the angular coordinates**: $V(\boldsymbol{r})=V(r)$,
- … and use a solution of the form $\psi(\boldsymbol{r})=R(r)Y(\vartheta,\varphi)$:

$$\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{R}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{R}{r^2\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}-RY\frac{2m}{\hbar^2}V(r)=-\frac{2mE}{\hbar^2}RY$$

$$\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2mr^2}{\hbar^2}(V-E)\right]+\frac{1}{Y}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right]=0$$

The Schrödinger equation in spherical coordinates (continued)

- Endowed with foresight, we choose a separation constant of the form $\ell(\ell+1)$:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}(E-V)=\ell(\ell+1)\quad,\quad \frac{1}{Y}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right]=-\ell(\ell+1)\quad .$$

- From here we consider the radial and angular equations separately, angular first:

$$\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{\partial^2}{\partial\varphi^2}\right]Y(\vartheta,\varphi)=-\ell(\ell+1)\sin^2\vartheta\, Y(\vartheta,\varphi)\quad .$$

  which is starting to look familiar to victims of PHYS 217; it will indeed lead to Legendre polynomials, and worse.

- In electrodynamics we usually proceed for a while with the solution assumed to be independent of the azimuthal coordinate φ. Not this time, though.

Separating the angular equation

- Suppose the angular equation's solution has the form $Y(\vartheta,\varphi)=\Theta(\vartheta)\Phi(\varphi)$. Substitute this in, divide through by $\Theta(\vartheta)\Phi(\varphi)$, and choose m^2 to be the separation constant (**not to be confused with the quantum's mass *m*!!**):

$$\left[\frac{1}{\Theta}\sin\vartheta\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)+\ell(\ell+1)\sin^2\vartheta\right]+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=0=m^2-m^2 \quad ;$$

$$\left[\sin\vartheta\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)+\ell(\ell+1)\sin^2\vartheta-m^2\right]\Theta=0 \quad , \quad \frac{d^2\Phi}{d\varphi^2}+m^2\Phi=0 \quad .$$

- The **azimuthal** equation is the harmonic-oscillator equation yet again. We will find it more convenient to use complex exponentials in its solution, rather than sines and cosines:

$$\Phi(\varphi)=Ae^{im\varphi}+Be^{-im\varphi}$$

Let m range from $-\infty$ to $+\infty$ so only one of these terms is necessary;

$$=Ae^{im\varphi}\doteq\boxed{e^{im\varphi}} \quad ,$$

absorbing the constant A into the ϑ equation.

Separating the angular equation (continued)

- The complex exponential is a periodic function just like the sines and cosines, so *m* must be an integer:

$$\Phi(\varphi)=\Phi(\varphi+2\pi) \;\Rightarrow\; e^{im\varphi}=e^{im\varphi}e^{2\pi im} \;\Rightarrow\; e^{2\pi im}=1 \;\Rightarrow\; \boxed{m=0,\pm1,\pm2,\ldots}$$

- This leaves us with the **polar** equation:

$$\left[\sin\vartheta\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d}{d\vartheta}\right)+\ell(\ell+1)\sin^2\vartheta-m^2\right]\Theta=0 \quad ,$$

which is not quite Legendre's equation, but close. Its solutions are called the **associated Legendre functions,** $P_\ell^m(x)$:

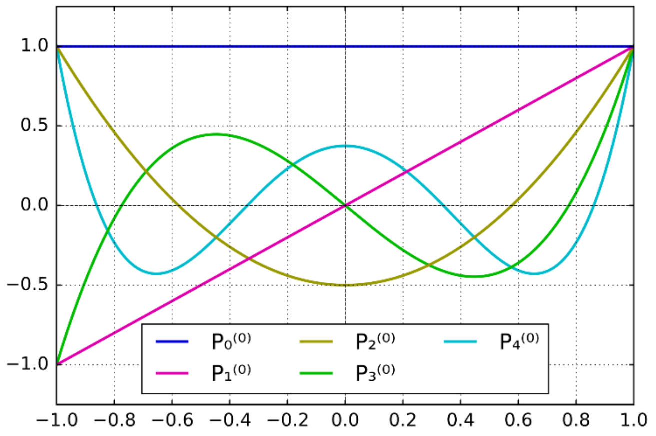
$$\boxed{\Theta(\vartheta)=AP_\ell^m(\cos\vartheta) \quad , \quad P_\ell^m(x)=(-1)^m\left(1-x^2\right)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x) \quad ,}$$

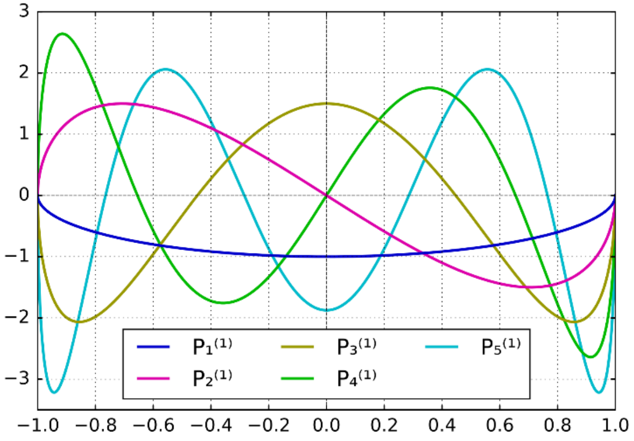
Separating the angular equation (continued)

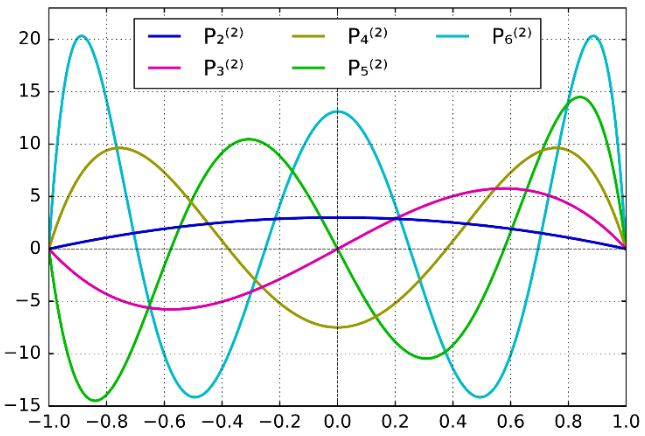
where the $P_\ell(x)$ are the somewhat-more-familiar **Legendre polynomials**:

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell \left(x^2 - 1\right)^\ell \quad , \quad \ell \geq 0 \quad .$$

- All the properties of these special functions are developed in MATH 281; the Legendre polynomials are discussed in detail in PHYS 217. You will get practice with some of their properties in G&S problems 4.6 and 4.8 on this week's assignment. Here's what the $P_\ell^m(x)$ look like for m = 0, 1, and 2 (Geek3, Wikimedia Commons):







Separating the angular equation (continued)

- In the definition of $P_\ell^m(x)$ the mth derivative is undefined if $m > \ell$, which restricts m:

$$m = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell \quad .$$

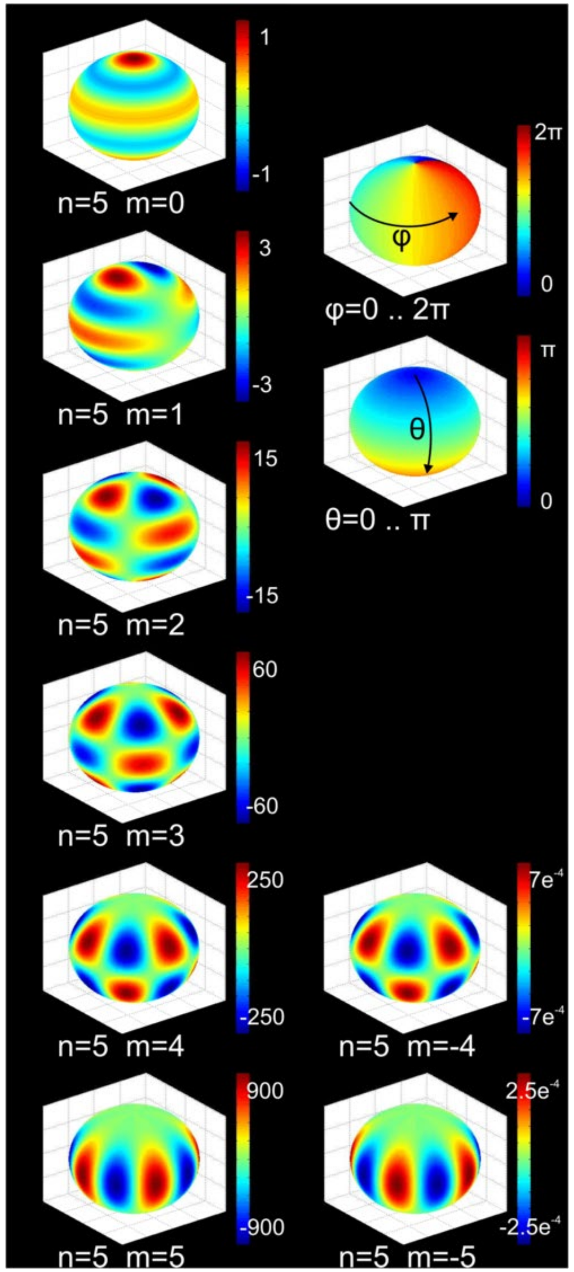
- The products of the polar and azimuthal solutions are called the **spherical harmonics**:

$$Y_\ell^m(\vartheta,\varphi) = \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} e^{im\varphi} P_\ell^m(\cos\vartheta) \quad .$$

- It is convenient to normalize $Y_\ell^m(\vartheta,\varphi)$ independently of the radial solution; that's what the terms under the square root do. And they are orthonormal:

$$\int_0^\pi d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi \left[Y_\ell^m(\vartheta,\varphi)\right]^* \left[Y_{\ell'}^{m'}(\vartheta,\varphi)\right] = \delta_{\ell\ell'}\delta_{mm'} \quad .$$

- See here for a very nice space-filling, interactive tool to visualize spherical harmonics; the static display at right is from Wikimedia Commons.



The radial equation

- Which leaves us with the radial equation: $\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)R = \ell(\ell+1)R$, in which we will immediately change variables:

$$u(r) = rR(r) \quad \Rightarrow \quad R = \frac{u}{r} \quad , \quad \frac{dR}{dr} = \frac{dR}{du}\frac{du}{dr} = \frac{1}{r^2}\left(r\frac{du}{dr} - u\right) \quad , \quad \frac{d}{dr}r^2\frac{dR}{dr} = r\frac{d^2u}{du^2} \quad ;$$

- We are left with

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \quad .$$

- Compare to the 1-D time-independent Schrödinger equation (Lecture 3, p. 4): the only difference is the addition of the **centrifugal term**, $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$, to the potential energy *V*.
- All the Schrödinger-equation solutions for spherically-symmetric *V* have a multiplicative factor of $Y_\ell^m(\vartheta,\varphi)$; we can leave this for each problem's end, and concentrate for a while on solving the radial equation for a variety of *V*(*r*)s.

"Particle in a spherical box"

G&S example 4.1. Consider the infinite spherical well: $V(r)=\begin{cases} 0 & r\le a \quad , \\ \infty & r>a \quad . \end{cases}$ Find the wavefunctions and allowed energies.

- Outside the well, the wavefunction must be zero, just like the original 1-D infinite square well. Inside, after the usual abbreviation $k=\sqrt{2mE}/\hbar$, we have

$$\frac{d^2u}{dr^2}=\left[\frac{\ell(\ell+1)}{r^2}-k^2\right]u \quad , \quad u(a)=0 \quad .$$

- Easily solved if $\ell=0$ as it's just the 1-D case; easy to solve if k = 0, as victims of ASTR 111 and ASTR 142 know. Too bad we have to use another special function if neither is zero, but at least that special function turns out to have many uses in physics. And the $\ell=0$ case is illuminating here:
  - For $\ell=0$, we get (Lecture 4) $u(r)=A\sin kr+B\cos kr$. This is OK for u, but we must remember that $R(r)=u(r)/r$, so to keep it from blowing up at the origin we must have B = 0.
  - With the boundary condition at r = a, we have, just as before, $0=\sin ka, ka=N\pi$, and $E_{N,\ell=0}=\dfrac{N^2\pi^2\hbar^2}{2ma^2}$.

"Particle in a spherical box" (continued)

- But for $\ell > 0$ the general solution is $u(r) = Ar\, j_\ell(kr) + Brn_\ell(kr)$, where $j_\ell(x)$ and $n_\ell(x)$ are the **spherical Bessel function** and the **spherical Neumann function**, respectively, both of the **first kind**, both of order ℓ:

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x} \quad , \quad n_\ell(x) = -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x} \quad .$$

- For small x – that is, in first order approximation, $\sin x/x \cong 1 \xrightarrow[x=0]{} 1$, while $\cos x/x \cong 1/x \xrightarrow[x=0]{} \infty$. So just as for the $\ell = 0$ case, we must have $B = 0$; we will have no further use for the spherical Neumann function.

- From the boundary condition $R(a) = u(a)/a = 0$, we get $j_\ell(ka) = 0$.
  - Unfortunately the **zeroes** – the values of x which make $j_\ell(x) = 0$ – do not come out evenly spaced or simply expressed, fortunately they are easy to compute numerically. Let's call the zeroes $\beta_{N\ell}$.

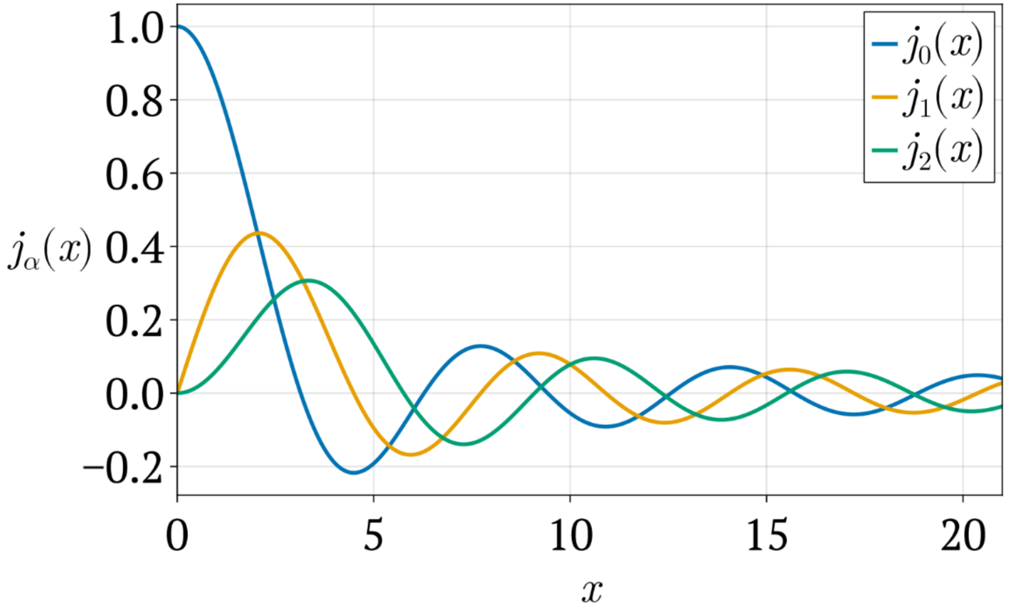
"Particle in a spherical box" (continued)

- Then $k = \frac{1}{a}\beta_{N\ell} \Rightarrow \boxed{E_{N\ell} = \frac{\hbar^2}{2ma^2}\beta_{N\ell}^2}$.

- Finally, the wavefunction is

$$\boxed{\psi_{n\ell m}(r,\vartheta,\varphi) = A_{n\ell}\, j_\ell\left(\beta_{N\ell}\frac{r}{a}\right) Y_\ell^m(\vartheta,\varphi) \quad ,}$$

where n = 1,2,3,… is called the principal quantum number, and the constant A is determined by normalization.



$\beta_{N\ell}$	ℓ = 0	1	2	3
N = 0	3.1416 (π)	6.2832	9.4248	12.5664
1	4.4934	7.7253	10.9041	14.0662
2	5.7635	9.0950	12.3229	15.5146
3	6.9879	10.4171	13.6980	16.9236

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