Problem 4.4

Use Equations 4.27, 4.28, and 4.32, to construct Y_0^0 and Y_2^1. Check that they are normalized and orthogonal.

[TYPOS: The normalization and orthogonality conditions for the spherical harmonics in Equations 4.31 and 4.33 on pages 136 and 137, respectively, are

$$\int_0^\pi \int_0^{2\pi} |Y|^2 \sin\theta \, d\theta \, d\phi = 1 \quad \text{and} \quad \int_0^\pi \int_0^{2\pi} [Y_\ell^m(\theta,\phi)]^* \left[Y_{\ell'}^{m'}(\theta,\phi)\right] \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'}\delta_{mm'}.$$

Switch $d\theta$ and $d\phi$ in each equation, as θ represents the angle from the polar axis.]

Solution

The governing equation for the wave function is Schrödinger's equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\nabla^2\Psi + V\Psi$$

If the potential energy function is spherically symmetric $V = V(r)$, then the Laplacian operator is expanded in spherical coordinates (r, θ, ϕ), where θ is the angle from the polar axis.

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

The aim is to solve for $\Psi = \Psi(r,\theta,\phi,t)$ in all of space ($0 \le r < \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$) for $t > 0$. Since Schrödinger's equation is linear and homogeneous, the method of separation of variables can be used to solve it: Assume a product solution of the form $\Psi(r,\theta,\phi,t) = R(r)\Theta(\theta)\xi(\phi)T(t)$ and plug it into the PDE.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}[R(r)\Theta(\theta)\xi(\phi)T(t)] = -\frac{\hbar^2}{2M}\Bigg[&\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}[R(r)\Theta(\theta)\xi(\phi)T(t)]\right) \\ &+ \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}[R(r)\Theta(\theta)\xi(\phi)T(t)]\right) \\ &+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}[R(r)\Theta(\theta)\xi(\phi)T(t)]\Bigg] + V(r)[R(r)\Theta(\theta)\xi(\phi)T(t)] \end{aligned}$$

$$\begin{aligned} i\hbar R(r)\Theta(\theta)\xi(\phi)T'(t) = -\frac{\hbar^2}{2M}\Bigg[&\frac{\Theta(\theta)\xi(\phi)T(t)}{r^2}\frac{d}{dr}\left(r^2R'(r)\right) \\ &+ \frac{R(r)\xi(\phi)T(t)}{r^2\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) \\ &+ \frac{R(r)\Theta(\theta)T(t)}{r^2\sin^2\theta}\xi''(\phi)\Bigg] + V(r)[R(r)\Theta(\theta)\xi(\phi)T(t)] \end{aligned}$$

In order to separate variables, divide both sides by $R(r)\Theta(\theta)\xi(\phi)T(t)$.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2M}\left[\frac{1}{r^2R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{r^2\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{r^2\xi(\phi)\sin^2\theta}\xi''(\phi)\right] + V(r)$$

The only way a function of t can be equal to a function of r, θ, and ϕ is if both are equal to a constant.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2M}\left[\frac{1}{r^2R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{r^2\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{r^2\xi(\phi)\sin^2\theta}\xi''(\phi)\right] + V(r) = E$$

Multiply both sides by $-2Mr^2/\hbar^2$.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{\xi(\phi)\sin^2\theta}\xi''(\phi) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = 0$$

Bring the θ- and ϕ-dependent terms to the right side.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = -\frac{1}{\sin^2\theta}\left[\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)}\right]$$

The only way a function of r can be equal to a function of θ and ϕ is if both are equal to a constant.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = -\frac{1}{\sin^2\theta}\left[\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)}\right] = F$$

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

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)} = -F\sin^2\theta$$

Bring the θ-dependent terms to the left side.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta = -\frac{\xi''(\phi)}{\xi(\phi)}$$

The only way a function of θ can be equal to a function of ϕ is if both are equal to a constant.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta = -\frac{\xi''(\phi)}{\xi(\phi)} = G$$

As a result of using the method of separation of variables, Schrödinger's equation has reduced to four ODEs—one in r, one in θ, one in ϕ, and one in t.

$$\left.\begin{aligned} i\hbar\frac{T'(t)}{T(t)} &= E \\ \frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] &= F \\ \frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta &= G \\ -\frac{\xi''(\phi)}{\xi(\phi)} &= G \end{aligned}\right\}$$

The strategy is to solve the fourth eigenvalue problem first to get G, then to solve the third eigenvalue problem for F, then to solve the second eigenvalue problem for E, and then finally to solve the first eigenvalue problem to get $T(t)$.

$$\xi''(\phi) = -G\xi(\phi), \quad \xi(0) = \xi(2\pi),\ \xi'(0) = \xi'(2\pi)$$

Periodic boundary conditions are used for $\xi(\phi)$ because $\phi = 0$ and $\phi = 2\pi$ represent the same angle. The value and the slope of $\xi(\phi)$ at these angles have to be the same. Check to see if there are positive eigenvalues first: $G = \mu^2$.

$$\xi'' = -\mu^2\xi$$

The general solution can be written in terms of sine and cosine.

$$\xi(\phi) = C_1 \cos\mu\phi + C_2 \sin\mu\phi$$

Take the derivative.

$$\xi'(\phi) = \mu(-C_1 \sin\mu\phi + C_2 \cos\mu\phi)$$

Apply the boundary conditions to determine C_1 and C_2.

$$\xi(0) = C_1 = C_1 \cos 2\pi\mu + C_2 \sin 2\pi\mu = \xi(2\pi)$$

$$\xi'(0) = \mu C_2 = \mu(-C_1 \sin 2\pi\mu + C_2 \cos 2\pi\mu) = \xi'(2\pi)$$

Solve this first equation for C_1

$$C_1(1 - \cos 2\pi\mu) = C_2 \sin 2\pi\mu \quad \rightarrow \quad C_1 = C_2 \frac{\sin 2\pi\mu}{1 - \cos 2\pi\mu}$$

and then plug it into the second equation. Assume that $C_2 \neq 0$ to avoid the trivial solution.

$$\mu C_2 = \mu(-C_1 \sin 2\pi\mu + C_2 \cos 2\pi\mu)$$

$$C_2 = -C_1 \sin 2\pi\mu + C_2 \cos 2\pi\mu$$

$$C_1 \sin 2\pi\mu = -C_2(1 - \cos 2\pi\mu)$$

$$C_2 \frac{\sin 2\pi\mu}{1 - \cos 2\pi\mu} \sin 2\pi\mu = -C_2(1 - \cos 2\pi\mu)$$

$$\sin^2 2\pi\mu = -(1 - \cos 2\pi\mu)^2$$

$$\sin^2 2\pi\mu = -1 + 2\cos 2\pi\mu - \cos^2 2\pi\mu$$

$$(\sin^2 2\pi\mu + \cos^2 2\pi\mu) + 1 = 2\cos 2\pi\mu$$

$$2 = 2\cos 2\pi\mu$$

$$\cos 2\pi\mu = 1$$

$$2\pi\mu = 2m\pi, \quad m = 0, \pm1, \pm2, \ldots$$

$$\mu = m$$

There are positive eigenvalues $G = \mu^2 = m^2$, and the eigenfunctions associated with them are

$$\begin{aligned}\xi(\phi) &= C_1 \cos \mu\phi + C_2 \sin \mu\phi \\ &= C_1 \cos m\phi + C_2 \sin m\phi \\ &= C_1 \left(\frac{e^{im\phi} + e^{-im\phi}}{2}\right) + C_2 \left(\frac{e^{im\phi} - e^{-im\phi}}{2i}\right) \\ &= \left(\frac{C_1}{2} + \frac{C_2}{2i}\right) e^{im\phi} + \left(\frac{C_1}{2} - \frac{C_2}{2i}\right) e^{-im\phi} \\ &= C_3 e^{im\phi} + C_4 e^{-im\phi}.\end{aligned}$$

As long as m is allowed to be any nonzero integer ($m = \pm 1, \pm 2, \ldots$), the latter term can be dropped. Note that $m = 0$ leads to the zero eigenvalue.

$$\xi(\phi) = C_3 e^{im\phi}$$

Check to see if zero is an eigenvalue: $G = 0$.

$$\xi'' = 0$$

The general solution is obtained by integrating both sides twice.

$$\xi(\phi) = C_5 \phi + C_6$$

Take the derivative.

$$\xi'(\phi) = C_5$$

Apply the boundary conditions to determine C_5 and C_6.

$$\begin{aligned}\xi(0) = C_6 &= 2\pi C_5 + C_6 = \xi(2\pi) \\ \xi'(0) = C_5 &= C_5 = \xi'(2\pi)\end{aligned}$$

Solving this first equation yields $C_5 = 0$. C_6 remains arbitrary, so zero is in fact an eigenvalue. The eigenfunction associated with it is a constant.

$$\xi(\phi) = C_6$$

This can be included in the previous result by letting m be any integer.

$$\xi(\phi) = C_3 e^{im\phi}, \quad G = m^2, \quad m = 0, \pm 1, \pm 2, \ldots$$

Now check to see if there are negative eigenvalues: $G = -\gamma^2$.

$$\xi'' = \gamma^2 \xi$$

The general solution can be written in terms of hyperbolic sine and hyperbolic cosine.

$$\xi(\phi) = C_7 \cosh \gamma\phi + C_8 \sinh \gamma\phi$$

Apply the boundary conditions to determine C_7 and C_8.

$$\xi(0) = C_7 = C_7 \cosh 2\pi\gamma + C_8 \sinh 2\pi\gamma = \xi(2\pi)$$

$$\xi'(0) = \gamma C_8 = \gamma(C_7 \sinh 2\pi\gamma + C_8 \cosh 2\pi\gamma) = \xi'(2\pi)$$

Solve this first equation for C_7

$$C_7(1 - \cosh 2\pi\gamma) = C_8 \sinh 2\pi\gamma \quad \rightarrow \quad C_7 = C_8 \frac{\sinh 2\pi\gamma}{1 - \cosh 2\pi\gamma}$$

and then plug it into the second equation.

$$C_8 = C_7 \sinh 2\pi\gamma + C_8 \cosh 2\pi\gamma$$

$$C_8(1 - \cosh 2\pi\gamma) = C_7 \sinh 2\pi\gamma$$

$$C_8(1 - \cosh 2\pi\gamma) = C_8 \frac{\sinh 2\pi\gamma}{1 - \cosh 2\pi\gamma} \sinh 2\pi\gamma$$

$$C_8(1 - \cosh 2\pi\gamma)^2 = C_8 \sinh^2 2\pi\gamma$$

$$C_8(1 - 2\cosh 2\pi\gamma + \cosh^2 2\pi\gamma) = C_8 \sinh^2 2\pi\gamma$$

$$C_8[1 - 2\cosh 2\pi\gamma + (\cosh^2 2\pi\gamma - \sinh^2 2\pi\gamma)] = 0$$

$$C_8(2 - 2\cosh 2\pi\gamma) = 0$$

$$C_8(1 - \cosh 2\pi\gamma) = 0$$

$$C_8 = 0 \quad \text{or} \quad 1 = \cosh 2\pi\gamma$$

There's no nonzero value of γ that solves the second equation, so $C_8 = 0$ is necessary. This makes $C_7 = 0$, and the trivial solution is obtained. Consequently, there are no negative eigenvalues. Substitute $G = m^2$ into the ODE for $\Theta(\theta)$.

$$\frac{\sin\theta}{\Theta(\theta)} \frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta = m^2$$

Bring m^2 to the left side and multiply both sides by $\Theta(\theta)$.

$$\sin\theta \frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + (F\sin^2\theta - m^2)\Theta(\theta) = 0$$

Make the change of variables $x = \cos\theta$ and use the chain rule to find the derivative in terms of x.

$$\Theta'(\theta) = \frac{d\Theta}{d\theta} = \frac{d\Theta}{dx}\frac{dx}{d\theta} = \frac{d\Theta}{dx}(-\sin\theta)$$

Transform the ODE.

$$\sin\theta \frac{d}{d\theta}\left[\frac{d\Theta}{dx}(-\sin\theta)\sin\theta\right] + (F\sin^2\theta - m^2)\Theta(x) = 0$$

$$-\sin\theta \frac{dx}{d\theta}\frac{d}{dx}\left[\frac{d\Theta}{dx}(1-\cos^2\theta)\right] + [F(1-\cos^2\theta) - m^2]\Theta(x) = 0$$

$$-\sin\theta(-\sin\theta)\frac{d}{dx}\left[\frac{d\Theta}{dx}(1-x^2)\right] + [F(1-x^2) - m^2]\Theta(x) = 0$$

$$(1-\cos^2\theta)\left[\frac{d^2\Theta}{dx^2}(1-x^2) + \frac{d\Theta}{dx}(-2x)\right] + [F(1-x^2) - m^2]\Theta(x) = 0$$

$$(1-x^2)\left[(1-x^2)\frac{d^2\Theta}{dx^2} - 2x\frac{d\Theta}{dx}\right] + [F(1-x^2) - m^2]\Theta(x) = 0$$

$$(1-x^2)\frac{d^2\Theta}{dx^2} - 2x\frac{d\Theta}{dx} + \left(F - \frac{m^2}{1-x^2}\right)\Theta(x) = 0$$

This is the associated Legendre equation. The series solutions to this equation diverge unless $F = \ell(\ell+1)$, where $\ell = 0, 1, 2, \ldots$. In this case, the solutions (known as the associated Legendre functions) $P_\ell^m(x)$ can be written in terms of the Legendre functions $P_\ell(x)$.

$$\begin{aligned}\Theta(x) &= C_9 P_\ell^m(x)\\ &= C_9(-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_\ell(x)\\ &= C_9\frac{(-1)^m}{2^\ell \ell!}(1-x^2)^{m/2}\frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell\end{aligned}$$

Now that the solution is known, change back to the original variable θ.

$$\Theta(\theta) = C_9 P_\ell^m(\cos\theta)$$

The product of the angular eigenfunctions is $\Theta(\theta)\xi(\phi) = C_3C_9e^{im\phi}P_\ell^m(\cos\theta)$. Use a normalization constant A for C_3C_9.

$$\Theta(\theta)\xi(\phi) = Ae^{im\phi}P_\ell^m(\cos\theta)$$

The normalization of the stationary states requires that

$$\begin{aligned}
1 = \iiint_{\text{all space}} |\Psi(r,\theta,\phi,t)|^2 \, d\mathcal{V} &= \iiint_{\text{all space}} |R(r)\Theta(\theta)\xi(\phi)T(t)|^2 \, d\mathcal{V} \\
&= \iiint_{\text{all space}} \left| R(r) A e^{im\phi} P_\ell^m(\cos\theta) e^{-iEt/\hbar} \right|^2 d\mathcal{V} \\
&= \iiint_{\text{all space}} |R(r)|^2 |A|^2 |P_\ell^m(\cos\theta)|^2 \, d\mathcal{V} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty |R(r)|^2 |A|^2 |P_\ell^m(\cos\theta)|^2 (r^2 \sin\theta \, dr \, d\phi \, d\theta) \\
&= \underbrace{\left[\int_0^\infty r^2 |R(r)|^2 \, dr \right]}_{=1} \underbrace{\left[|A|^2 \int_0^\pi \int_0^{2\pi} |P_\ell^m(\cos\theta)|^2 \sin\theta \, d\phi \, d\theta \right]}_{=1},
\end{aligned}$$

which means

$$\begin{aligned}
1 &= |A|^2 \int_0^\pi \int_0^{2\pi} |P_\ell^m(\cos\theta)|^2 \sin\theta \, d\phi \, d\theta \\
&= 2\pi |A|^2 \int_0^\pi |P_\ell^m(\cos\theta)|^2 \sin\theta \, d\theta.
\end{aligned}$$

Make the following substitution.

$$\begin{aligned}
x &= \cos\theta \\
dx &= -\sin\theta \, d\theta \quad \rightarrow \quad -dx = \sin\theta \, d\theta
\end{aligned}$$

As a result,

$$\begin{aligned}
1 &= 2\pi |A|^2 \int_{\cos 0}^{\cos\pi} |P_\ell^m(x)|^2 \, (-dx) \\
&= 2\pi |A|^2 \int_{-1}^{1} |P_\ell^m(x)|^2 \, dx \\
&= 2\pi |A|^2 \left[\frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \right].
\end{aligned}$$

The evaluation of this integral is involved and will be done in Problem 4.63. Solve for A.

$$A = \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}}.$$

The normalized angular eigenfunctions $\Theta(\theta)\xi(\phi)$ are called the spherical harmonics and are denoted by $Y_\ell^m(\theta,\phi)$.

$$Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} \, e^{im\phi} P_\ell^m(\cos\theta), \qquad \begin{cases} \ell = 0, 1, 2, \ldots \\ m = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell-1, \ell \end{cases}$$

The two spherical harmonics of interest in this problem are Y_0^0 and Y_2^1. The first one is

$$\begin{aligned} Y_0^0(\theta,\phi) = \sqrt{\frac{(1)}{4\pi}\frac{0!}{0!}}\,e^0 P_0^0(\cos\theta) &= \frac{1}{2\sqrt{\pi}}\frac{(-1)^0}{2^0 0!}\left[(1-x^2)^{0/2}\frac{d^{0+0}}{dx^{0+0}}(x^2-1)^0\right]\Bigg|_{x=\cos\theta} \\ &= \frac{1}{2\sqrt{\pi}}(1)(1)\Bigg|_{x=\cos\theta} \\ &= \frac{1}{2\sqrt{\pi}}, \end{aligned}$$

and the second one is

$$\begin{aligned} Y_2^1(\theta,\phi) &= \sqrt{\frac{[2(2)+1]}{4\pi}\frac{(2-1)!}{(2+1)!}}\,e^{i\phi}P_2^1(\cos\theta) \\ &= \sqrt{\frac{5}{4\pi}\frac{1!}{3!}}\,e^{i\phi}\left[\frac{(-1)^1}{2^2 2!}(1-x^2)^{1/2}\frac{d^{2+1}}{dx^{2+1}}(x^2-1)^2\right]\Bigg|_{x=\cos\theta} \\ &= \sqrt{\frac{5}{24\pi}}\,e^{i\phi}\left[-\frac{1}{8}(1-x^2)^{1/2}\frac{d^3}{dx^3}(x^4-2x^2+1)\right]\Bigg|_{x=\cos\theta} \\ &= \sqrt{\frac{5}{24\pi}}\,e^{i\phi}\left[-\frac{1}{8}(1-x^2)^{1/2}\frac{d^2}{dx^2}(4x^3-4x)\right]\Bigg|_{x=\cos\theta} \\ &= \sqrt{\frac{5}{24\pi}}\,e^{i\phi}\left[-\frac{1}{8}(1-x^2)^{1/2}\frac{d}{dx}(12x^2-4)\right]\Bigg|_{x=\cos\theta} \\ &= \sqrt{\frac{5}{24\pi}}\,e^{i\phi}\left[-\frac{1}{8}(1-x^2)^{1/2}(24x)\right]\Bigg|_{x=\cos\theta} \\ &= \sqrt{\frac{5}{24\pi}}\,e^{i\phi}\left(-3x\sqrt{1-x^2}\right)\Bigg|_{x=\cos\theta} \\ &= -\sqrt{\frac{45}{24\pi}}\,e^{i\phi}\cos\theta\sqrt{1-\cos^2\theta} \\ &= -\sqrt{\frac{15}{8\pi}}\,e^{i\phi}\cos\theta\sin\theta. \end{aligned}$$

The normalization of the stationary states requires that

$$\begin{aligned}
1 = \iiint_{\text{all space}} |\Psi(r,\theta,\phi,t)|^2\,d\mathcal{V} &= \iiint_{\text{all space}} |R(r)\Theta(\theta)\xi(\phi)T(t)|^2\,d\mathcal{V} \\
&= \iiint_{\text{all space}} \left|R(r)Y_\ell^m(\theta,\phi)e^{-iEt/\hbar}\right|^2 d\mathcal{V} \\
&= \iiint_{\text{all space}} |R(r)|^2\,|Y_\ell^m(\theta,\phi)|^2\,d\mathcal{V} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty |R(r)|^2\,|Y_\ell^m(\theta,\phi)|^2\,(r^2\sin\theta\,dr\,d\phi\,d\theta) \\
&= \underbrace{\left[\int_0^\infty r^2|R(r)|^2\,dr\right]}_{=1} \underbrace{\left[\int_0^\pi \int_0^{2\pi} |Y_\ell^m(\theta,\phi)|^2\sin\theta\,d\phi\,d\theta\right]}_{=1}.
\end{aligned}$$

Check that the first spherical harmonic is normalized.

$$\begin{aligned}
\int_0^\pi \int_0^{2\pi} \left|Y_0^0(\theta,\phi)\right|^2 \sin\theta\,d\phi\,d\theta &= \int_0^\pi \int_0^{2\pi} \left|\frac{1}{2\sqrt{\pi}}\right|^2 \sin\theta\,d\phi\,d\theta \\
&= \frac{1}{4\pi}\int_0^\pi \int_0^{2\pi} \sin\theta\,d\phi\,d\theta \\
&= \frac{1}{4\pi}\left(\int_0^\pi \sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right) \\
&= \frac{1}{4\pi}(2)(2\pi) \\
&= 1
\end{aligned}$$

Check that the second spherical harmonic is normalized.

$$\begin{aligned}
\int_0^\pi \int_0^{2\pi} \left|Y_2^1(\theta,\phi)\right|^2 \sin\theta\,d\phi\,d\theta &= \int_0^\pi \int_0^{2\pi} \left|-\sqrt{\frac{15}{8\pi}}\,e^{i\phi}\cos\theta\sin\theta\right|^2 \sin\theta\,d\phi\,d\theta \\
&= \frac{15}{8\pi}\int_0^\pi \int_0^{2\pi} (\cos^2\theta\sin^2\theta)\sin\theta\,d\phi\,d\theta \\
&= \frac{15}{8\pi}\left(\int_0^\pi \cos^2\theta\sin^2\theta\sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right) \\
&= \frac{15}{8\pi}\left[\int_0^\pi \cos^2\theta(1-\cos^2\theta)\sin\theta\,d\theta\right](2\pi).
\end{aligned}$$

Make the following substitution.

$$\begin{aligned}
x &= \cos\theta \\
dx &= -\sin\theta\,d\theta \quad \rightarrow \quad -dx = \sin\theta\,d\theta
\end{aligned}$$

Consequently, (note the integrand is an even function)

$$\begin{aligned}\int_0^\pi \int_0^{2\pi} \left|Y_2^1(\theta,\phi)\right|^2 \sin\theta \, d\phi \, d\theta &= \frac{15}{8\pi}\left[\int_{\cos 0}^{\cos\pi} x^2(1-x^2)(-dx)\right](2\pi) \\ &= \frac{15}{4}\int_1^{-1} x^2(1-x^2)(-dx) \\ &= \frac{15}{4}\int_{-1}^{1}(x^2-x^4)\,dx \\ &= \frac{15}{2}\int_0^1 (x^2-x^4)\,dx \\ &= \frac{15}{2}\left(\frac{1}{3}-\frac{1}{5}\right) \\ &= 1.\end{aligned}$$

Now check that the spherical harmonics are orthonormal.

$$\begin{aligned}\int_0^\pi \int_0^{2\pi} \left[Y_2^1(\theta,\phi)\right]^* \left[Y_0^0(\theta,\phi)\right] \sin\theta\,d\phi\,d\theta &= \int_0^\pi\int_0^{2\pi}\left[-\sqrt{\frac{15}{8\pi}}\,e^{i\phi}\cos\theta\sin\theta\right]^*\left[\frac{1}{2\sqrt{\pi}}\right]\sin\theta\,d\phi\,d\theta \\ &= \int_0^\pi\int_0^{2\pi}\left[-\sqrt{\frac{15}{8\pi}}\,e^{-i\phi}\cos\theta\sin\theta\right]\left[\frac{1}{2\sqrt{\pi}}\right]\sin\theta\,d\phi\,d\theta \\ &= -\frac{1}{\pi}\sqrt{\frac{15}{32}}\left(\int_0^\pi \cos\theta\sin^2\theta\,d\theta\right)\left(\int_0^{2\pi} e^{-i\phi}\,d\phi\right)\end{aligned}$$

Make the following substitution.

$$\begin{aligned} y &= \sin\theta \\ dy &= \cos\theta\,d\theta \end{aligned}$$

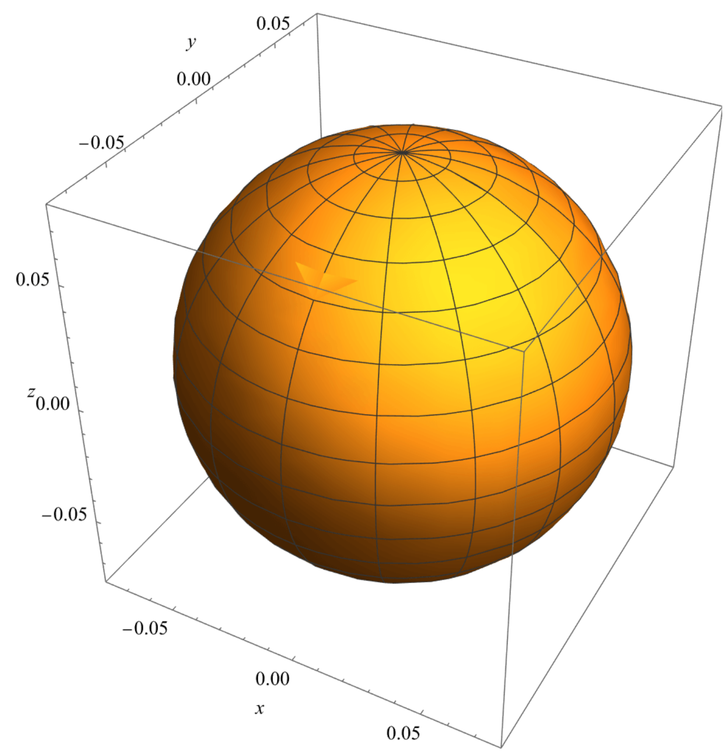
Consequently,

$$\begin{aligned}\int_0^\pi \int_0^{2\pi} \left[Y_2^1(\theta,\phi)\right]^* \left[Y_0^0(\theta,\phi)\right] \sin\theta\,d\phi\,d\theta &= -\frac{1}{\pi}\sqrt{\frac{15}{32}}\left(\int_{\sin 0}^{\sin\pi} y^2\,dy\right)\left(\int_0^{2\pi} e^{-i\phi}\,d\phi\right) \\ &= -\frac{1}{\pi}\sqrt{\frac{15}{32}}\left(\int_0^0 y^2\,dy\right)\left(\int_0^{2\pi} e^{-i\phi}\,d\phi\right) \\ &= -\frac{1}{\pi}\sqrt{\frac{15}{32}}\,(0)\left(\int_0^{2\pi} e^{-i\phi}\,d\phi\right) \\ &= 0.\end{aligned}$$

Below are plots of $|Y_\ell^m(\theta,\phi)|^2$ with $0 \le \theta \le \pi$ and $0 \le \phi \le 2\pi$ for several values of ℓ and all possible values of m.

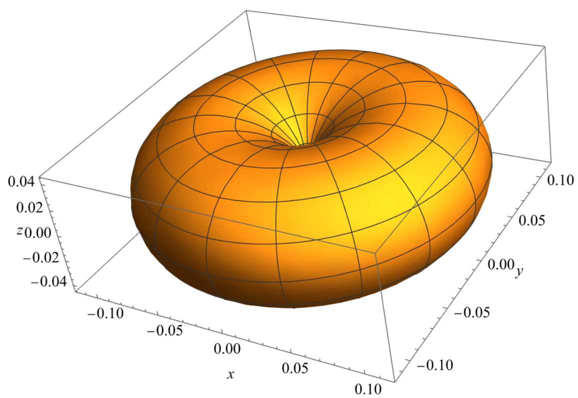
$$Y_0^0(\theta, \phi) = \frac{1}{2\sqrt{\pi}}$$

$$\left|Y_0^0(\theta, \phi)\right|^2$$

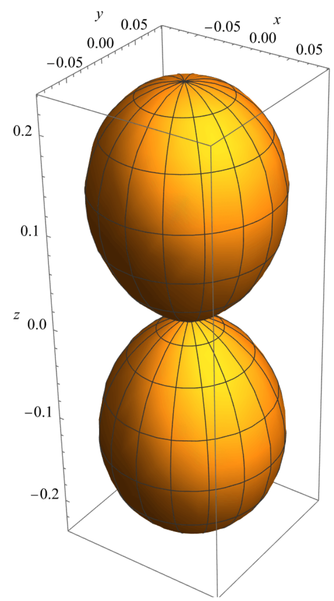


$$Y_1^{-1}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\, e^{-i\phi}\sin\theta \qquad Y_1^{0}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\cos\theta \qquad Y_1^{1}(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\, e^{i\phi}\sin\theta$$

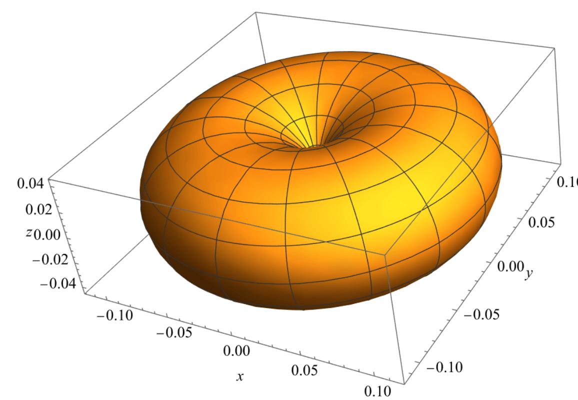
$$\left|Y_1^{-1}(\theta,\phi)\right|^2$$



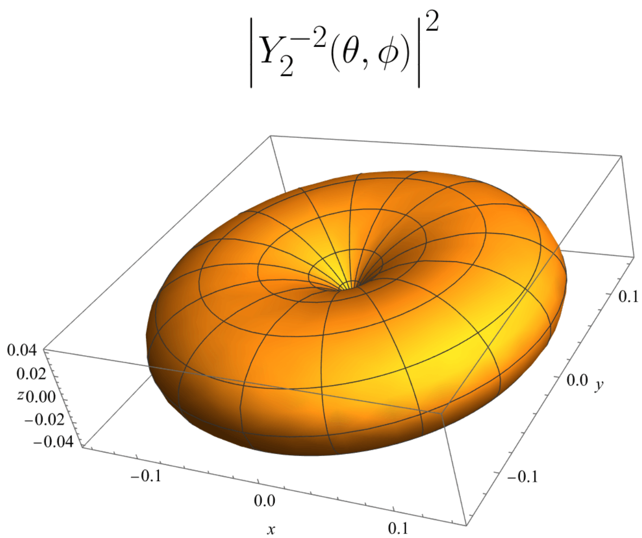
$$\left|Y_1^{0}(\theta,\phi)\right|^2$$

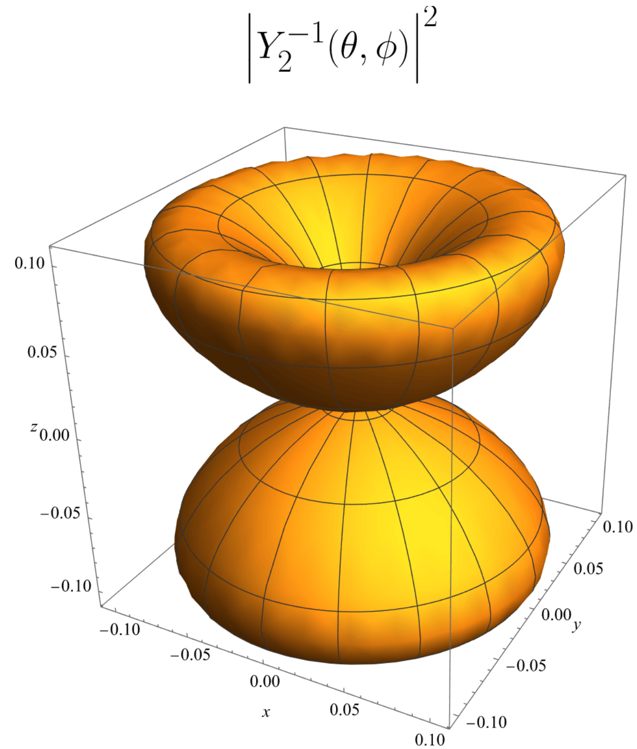


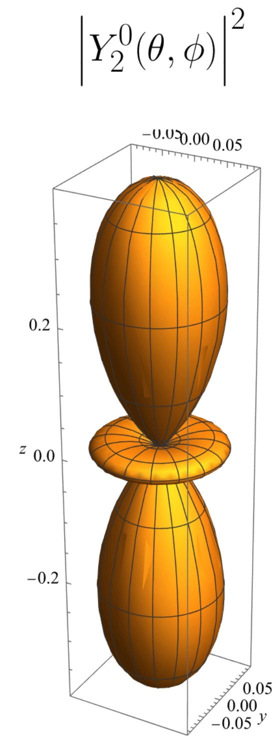
$$\left|Y_1^{1}(\theta,\phi)\right|^2$$



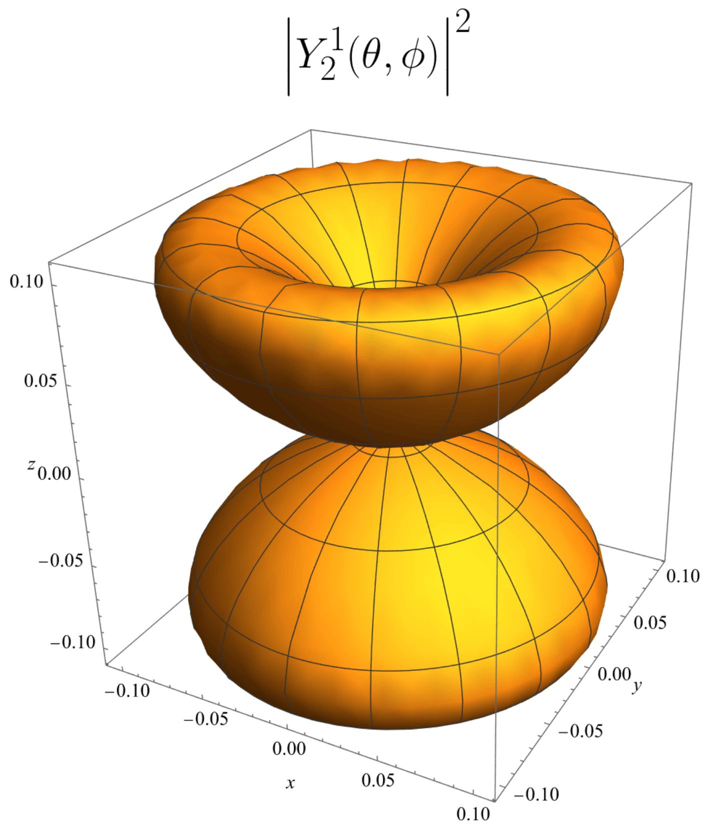
$$Y_2^{-2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\,e^{-2i\phi}\sin^2\theta \qquad Y_2^{-1}(\theta,\phi)=\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,e^{-i\phi}\cos\theta\sin\theta \qquad Y_2^{0}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3\cos^2\theta-1)$$



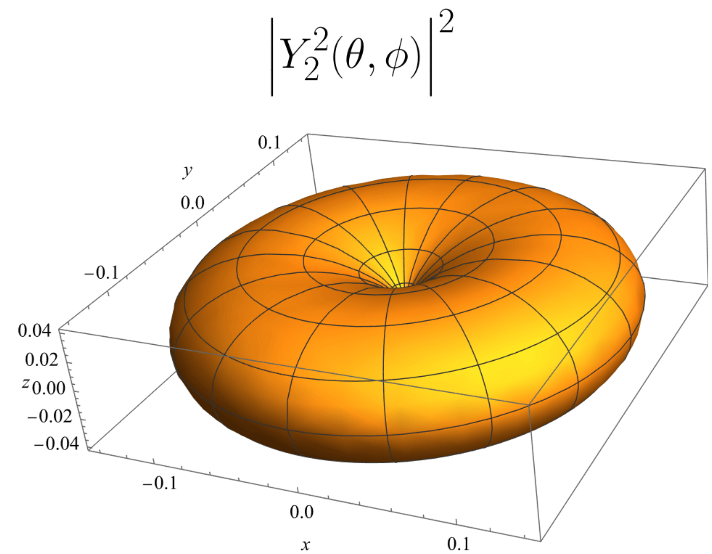




$$Y_2^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,e^{i\phi}\cos\theta\sin\theta$$

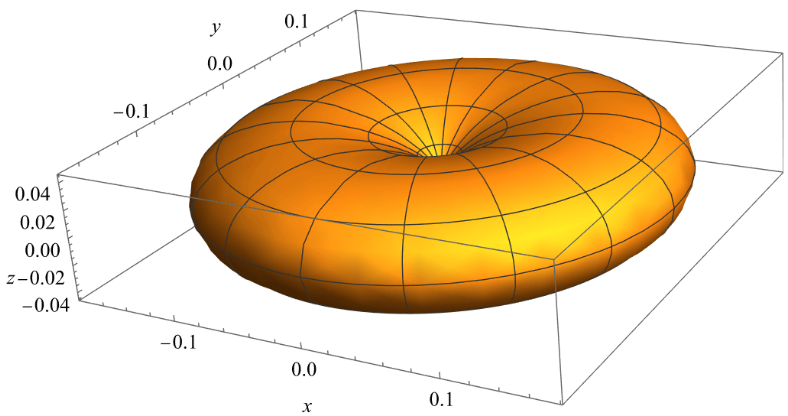


$$Y_2^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,e^{2i\phi}\sin^2\theta$$



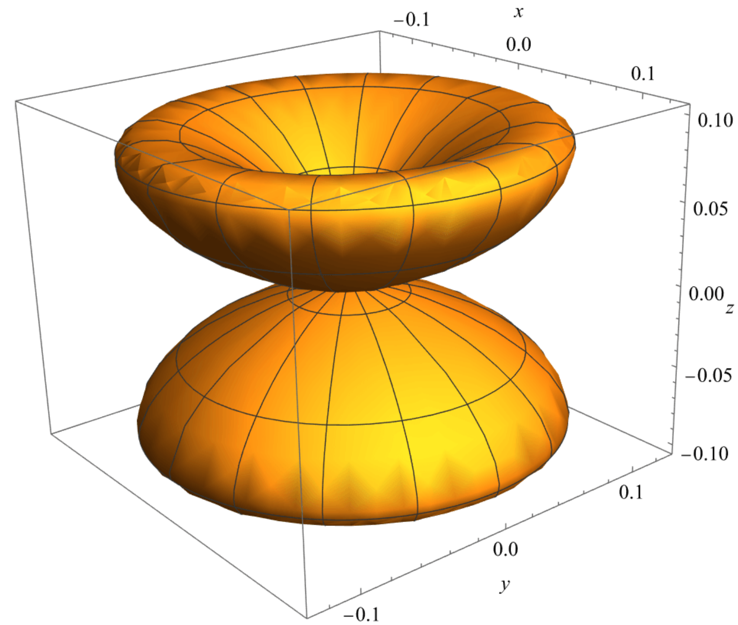
$$Y_3^{-3}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{35}{\pi}}\,e^{-3i\phi}\sin^3\theta$$

$$\left|Y_3^{-3}(\theta,\phi)\right|^2$$



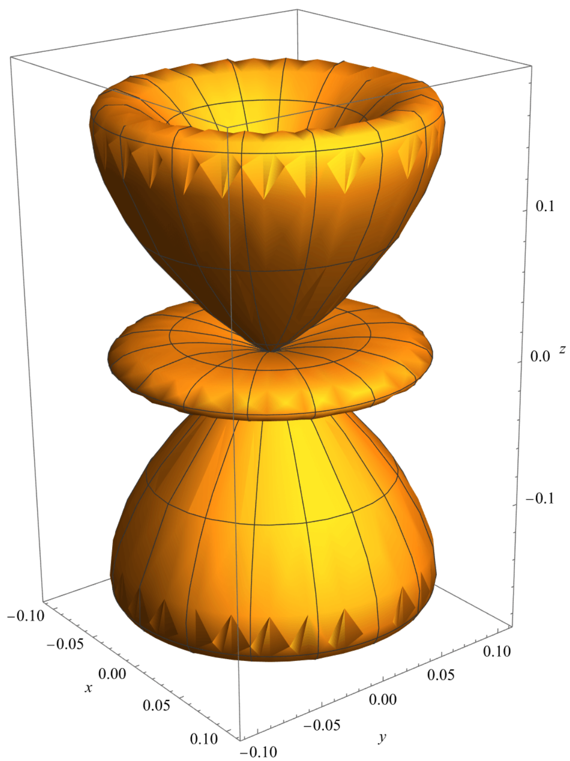
$$Y_3^{-2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\,e^{-2i\phi}\cos\theta\sin^2\theta$$

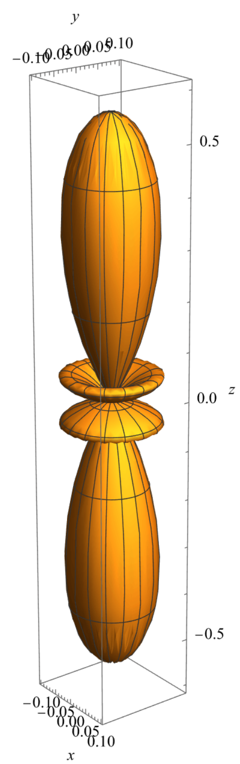
$$\left|Y_3^{-2}(\theta,\phi)\right|^2$$

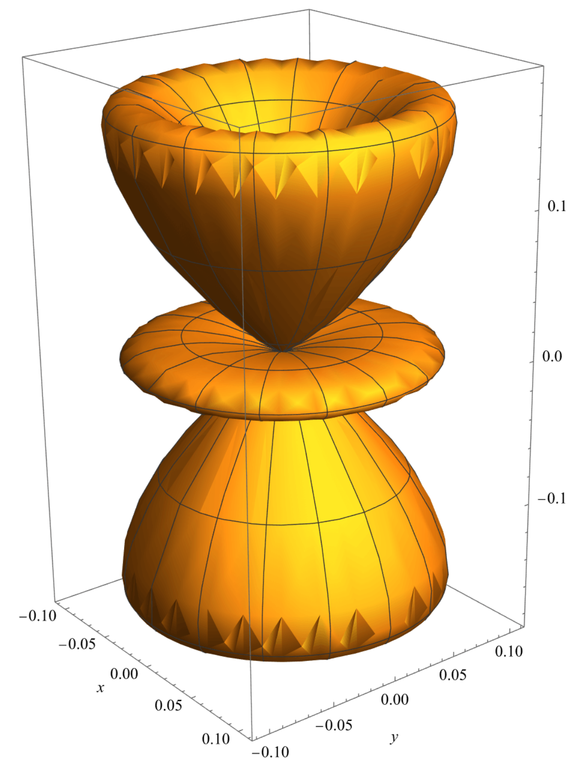


$$Y_3^{-1}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{21}{\pi}}\,e^{-i\phi}(5\cos^2\theta-1)\sin\theta \qquad Y_3^{0}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{7}{\pi}}\,(5\cos^2\theta-3)\cos\theta \qquad Y_3^{1}(\theta,\phi)=-\frac{1}{8}\sqrt{\frac{21}{\pi}}\,e^{i\phi}(5\cos^2\theta-1)\sin\theta$$

$$\left|Y_3^{-1}(\theta,\phi)\right|^2 \qquad \left|Y_3^{0}(\theta,\phi)\right|^2 \qquad \left|Y_3^{1}(\theta,\phi)\right|^2$$



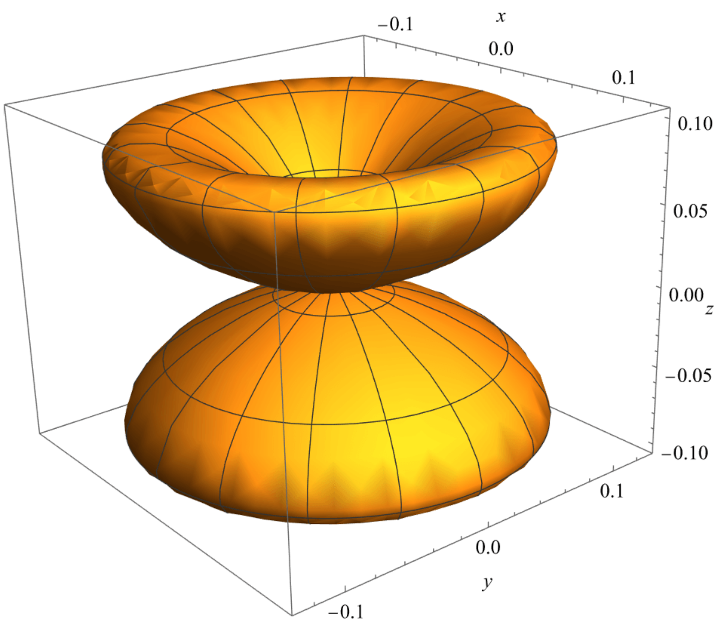




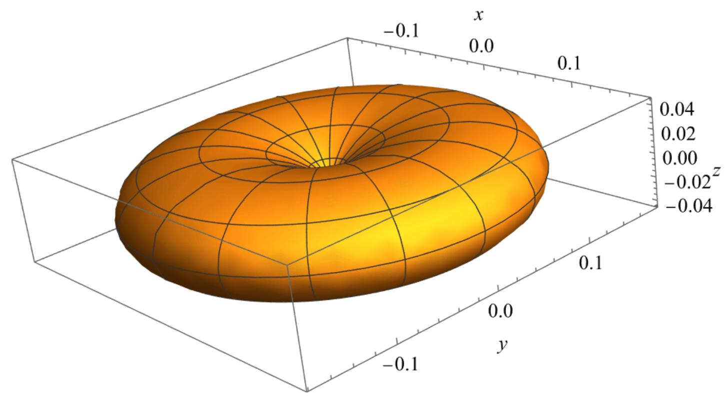
$$Y_3^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\, e^{2i\phi}\cos\theta\sin^2\theta$$

$$Y_3^3(\theta,\phi) = -\frac{1}{8}\sqrt{\frac{35}{\pi}}\, e^{3i\phi}\sin^3\theta$$

$$\left|Y_3^2(\theta,\phi)\right|^2$$



$$\left|Y_3^3(\theta,\phi)\right|^2$$



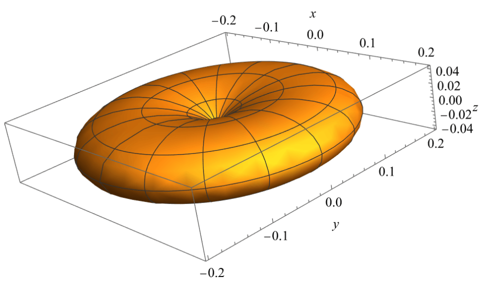
Special thanks to Spider on Ko-fi.com for correcting the formulas on this page.

$$Y_4^{-4}(\theta,\phi)=\frac{3}{16}\sqrt{\frac{35}{2\pi}}\,e^{-4i\phi}\sin^4\theta$$

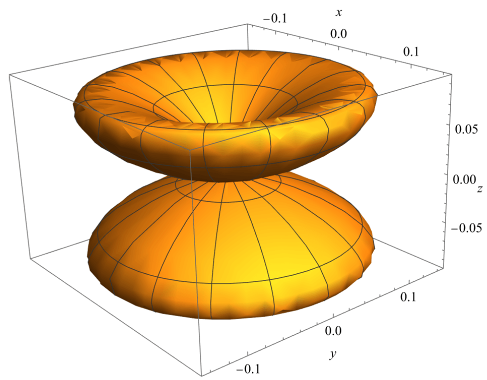
$$Y_4^{-3}(\theta,\phi)=\frac{3}{8}\sqrt{\frac{35}{\pi}}\,e^{-3i\phi}\cos\theta\sin^3\theta$$

$$Y_4^{-2}(\theta,\phi)=\frac{3}{8}\sqrt{\frac{5}{2\pi}}\,e^{-2i\phi}(7\cos^2\theta-1)\sin^2\theta$$

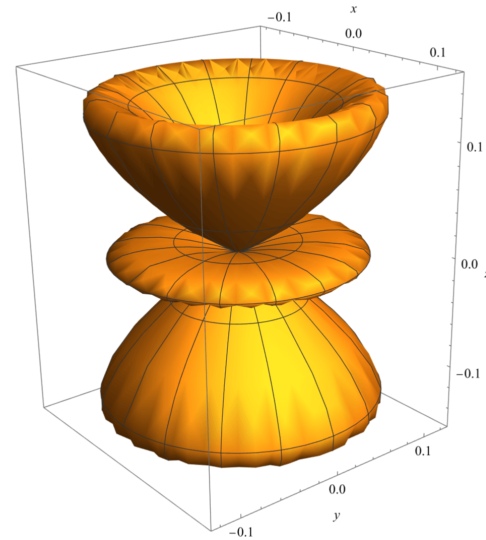
$$\left|Y_4^{-4}(\theta,\phi)\right|^2$$



$$\left|Y_4^{-3}(\theta,\phi)\right|^2$$

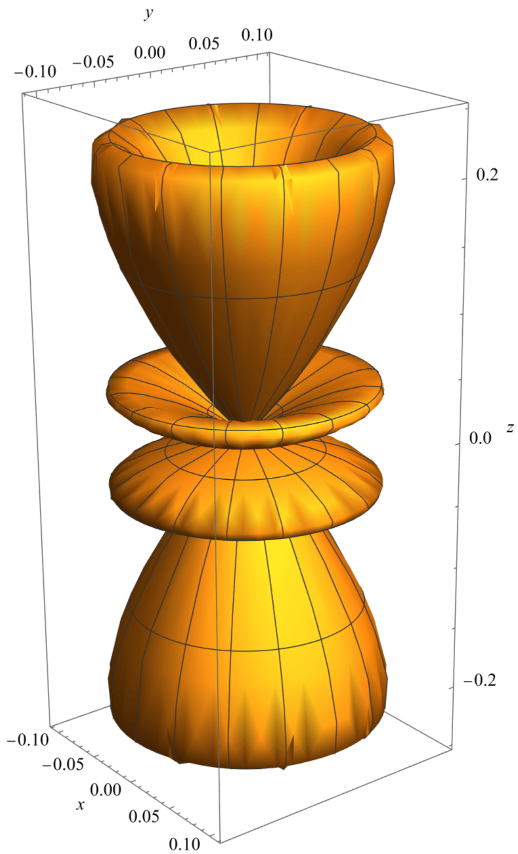


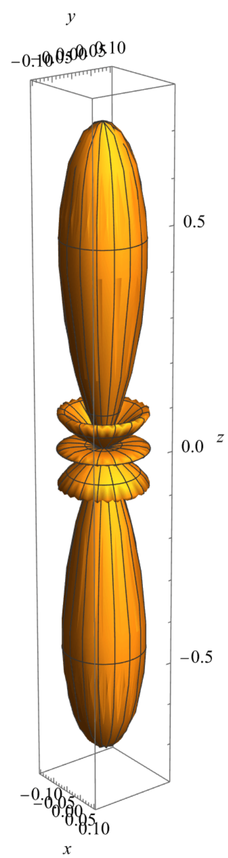
$$\left|Y_4^{-2}(\theta,\phi)\right|^2$$

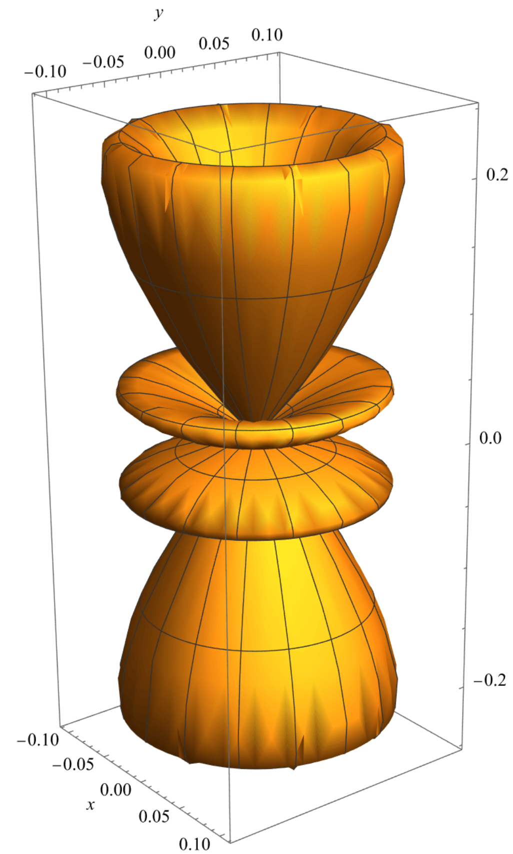


$$Y_4^{-1}(\theta,\phi) = \frac{3}{8}\sqrt{\frac{5}{\pi}}\,e^{-i\phi}\cos\theta\sin\theta(7\cos^2\theta - 3) \qquad Y_4^0(\theta,\phi) = \frac{3}{16\sqrt{\pi}}(35\cos^4\theta - 30\cos^2\theta + 3) \qquad Y_4^1(\theta,\phi) = -\frac{3}{8}\sqrt{\frac{5}{\pi}}\,e^{i\phi}\cos\theta\sin\theta(7\cos^2\theta - 3)$$

$$\left|Y_4^{-1}(\theta,\phi)\right|^2 \qquad \left|Y_4^{0}(\theta,\phi)\right|^2 \qquad \left|Y_4^{1}(\theta,\phi)\right|^2$$

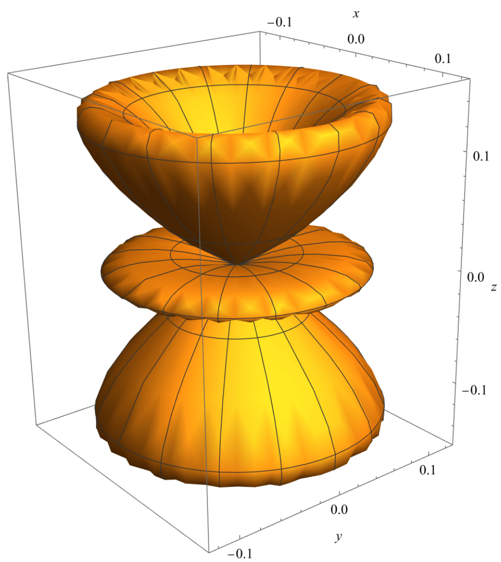




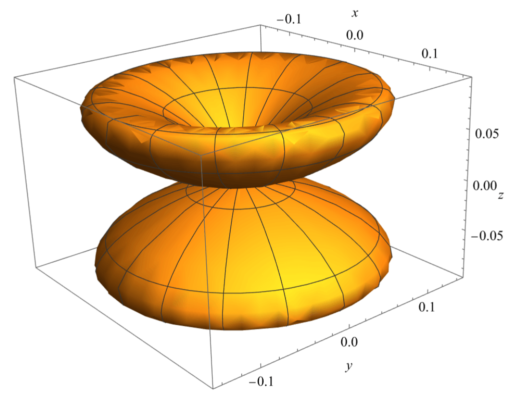


$$Y_4^2(\theta,\phi) = \frac{3}{8}\sqrt{\frac{5}{2\pi}}\, e^{2i\phi}(7\cos^2\theta - 1)\sin^2\theta \qquad Y_4^3(\theta,\phi) = -\frac{3}{8}\sqrt{\frac{35}{\pi}}\, e^{3i\phi}\cos\theta\sin^3\theta \qquad Y_4^4(\theta,\phi) = \frac{3}{16}\sqrt{\frac{35}{2\pi}}\, e^{4i\phi}\sin^4\theta$$

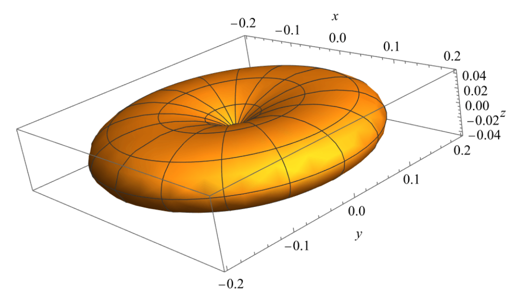
$$\left|Y_4^2(\theta,\phi)\right|^2$$



$$\left|Y_4^3(\theta,\phi)\right|^2$$

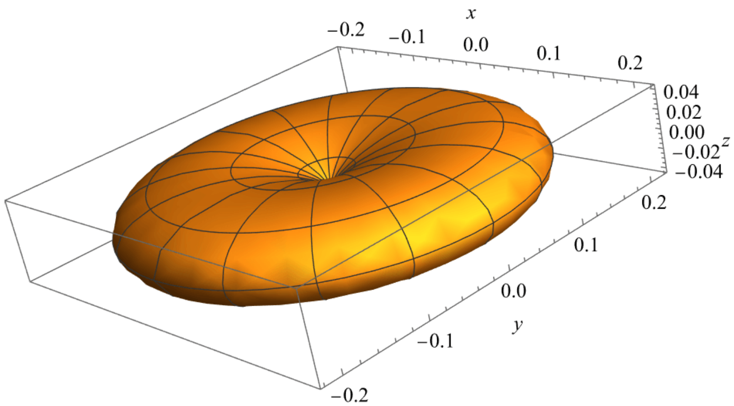


$$\left|Y_4^4(\theta,\phi)\right|^2$$



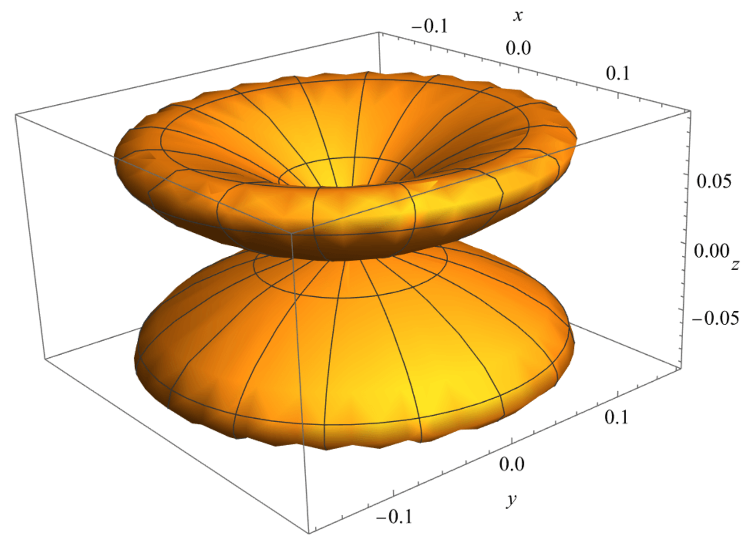
$$Y_5^{-5}(\theta,\phi) = \frac{3}{32}\sqrt{\frac{77}{\pi}}\, e^{-5i\phi} \sin^5\theta$$

$$\left|Y_5^{-5}(\theta,\phi)\right|^2$$



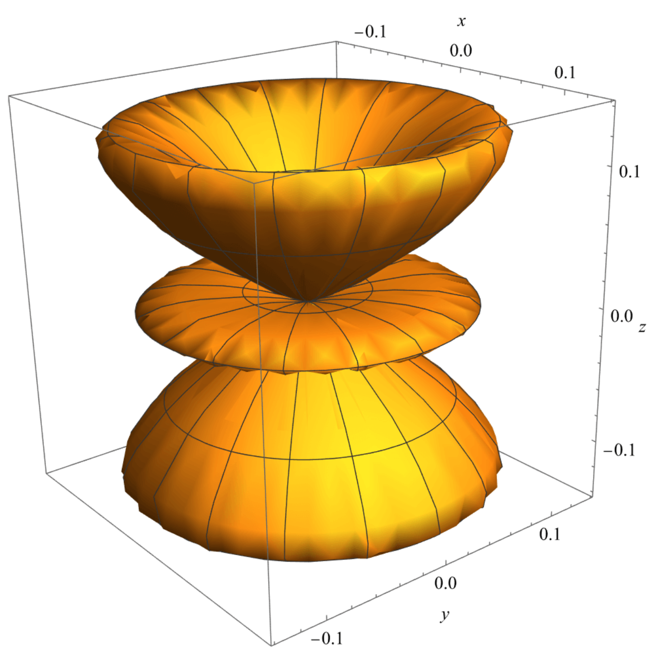
$$Y_5^{-4}(\theta,\phi) = \frac{3}{16}\sqrt{\frac{385}{2\pi}}\, e^{-4i\phi} \cos\theta \sin^4\theta$$

$$\left|Y_5^{-4}(\theta,\phi)\right|^2$$



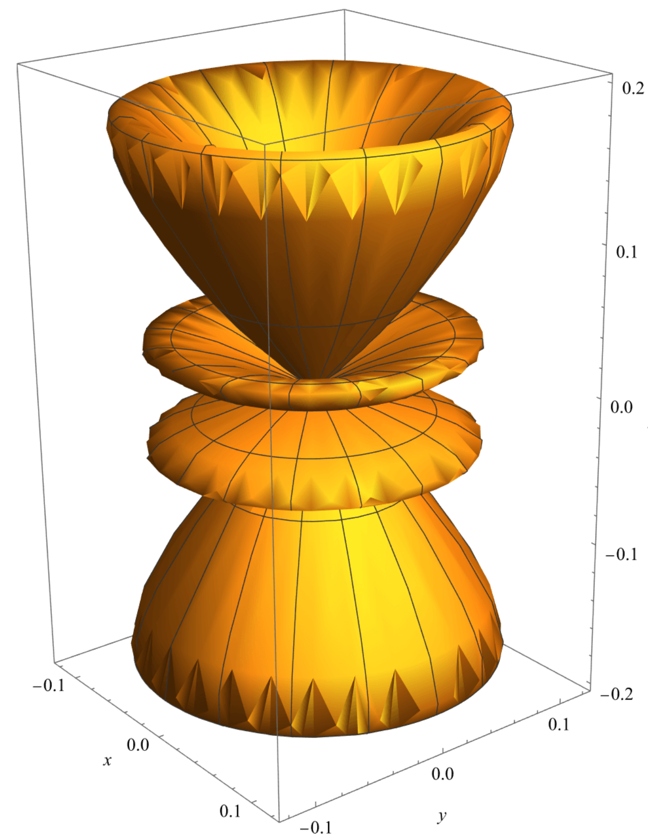
$$Y_5^{-3}(\theta,\phi) = \frac{1}{32}\sqrt{\frac{385}{\pi}}\, e^{-3i\phi}(9\cos^2\theta - 1)\sin^3\theta$$

$$\left|Y_5^{-3}(\theta,\phi)\right|^2$$



$$Y_5^{-2}(\theta,\phi) = \frac{1}{8}\sqrt{\frac{1155}{2\pi}}\, e^{-2i\phi}\cos\theta(3\cos^2\theta - 1)\sin^2\theta$$

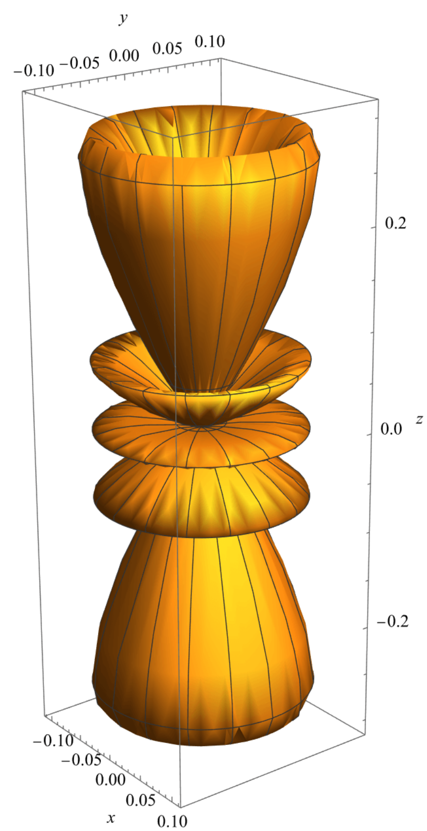
$$\left|Y_5^{-2}(\theta,\phi)\right|^2$$



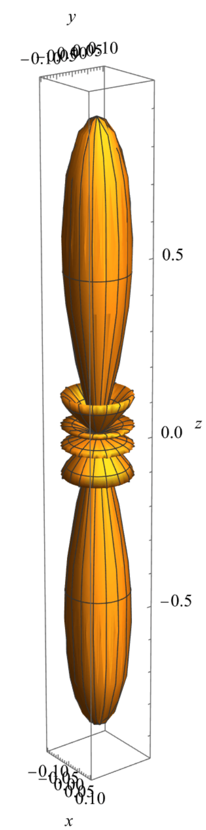
$$Y_5^{-1}(\theta,\phi) = \frac{1}{16}\sqrt{\frac{165}{2\pi}}\,e^{-i\phi}(21\cos^4\theta - 14\cos^2\theta + 1)\sin\theta$$

$$Y_5^{0}(\theta,\phi) = \frac{1}{16}\sqrt{\frac{11}{\pi}}\,\cos\theta(63\cos^4\theta - 70\cos^2\theta + 15)$$

$$\left|Y_5^{-1}(\theta,\phi)\right|^2$$



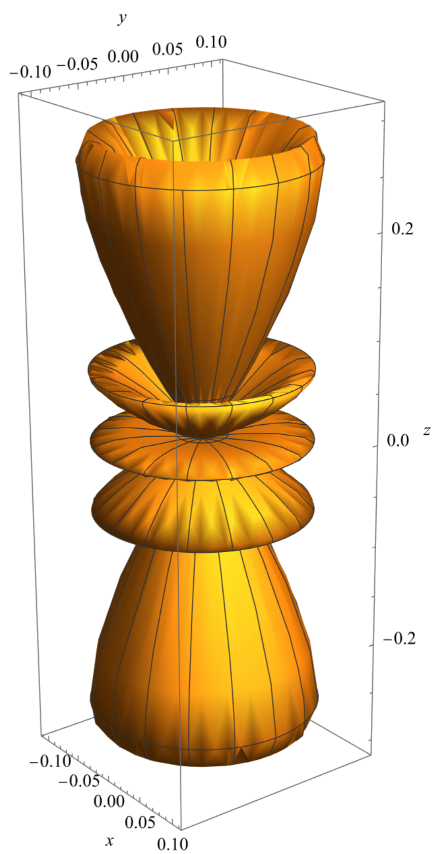
$$\left|Y_5^{0}(\theta,\phi)\right|^2$$



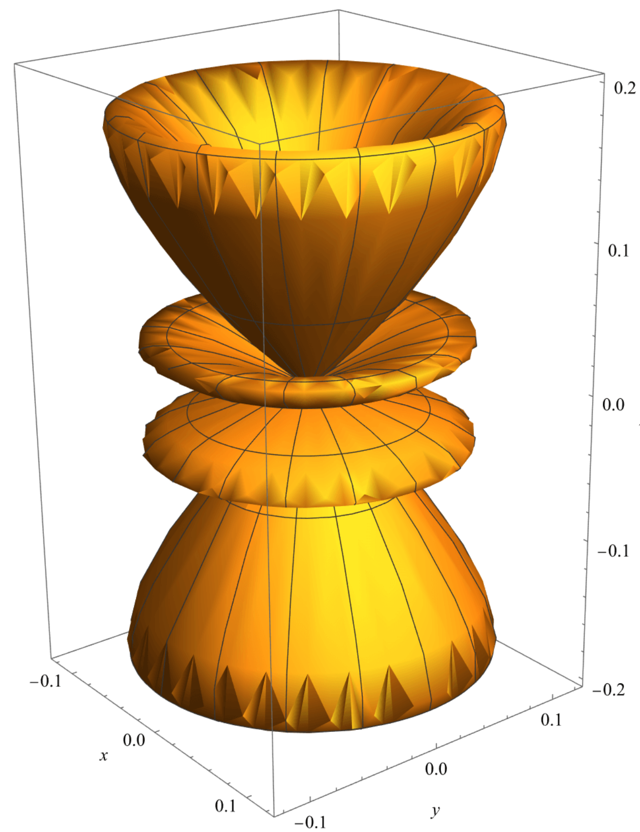
$$Y_5^1(\theta,\phi) = -\frac{1}{16}\sqrt{\frac{165}{2\pi}}\, e^{i\phi}(21\cos^4\theta - 14\cos^2\theta + 1)\sin\theta$$

$$Y_5^2(\theta,\phi) = \frac{1}{8}\sqrt{\frac{1155}{2\pi}}\, e^{2i\phi}\cos\theta(3\cos^2\theta - 1)\sin^2\theta$$

$$\left|Y_5^1(\theta,\phi)\right|^2$$

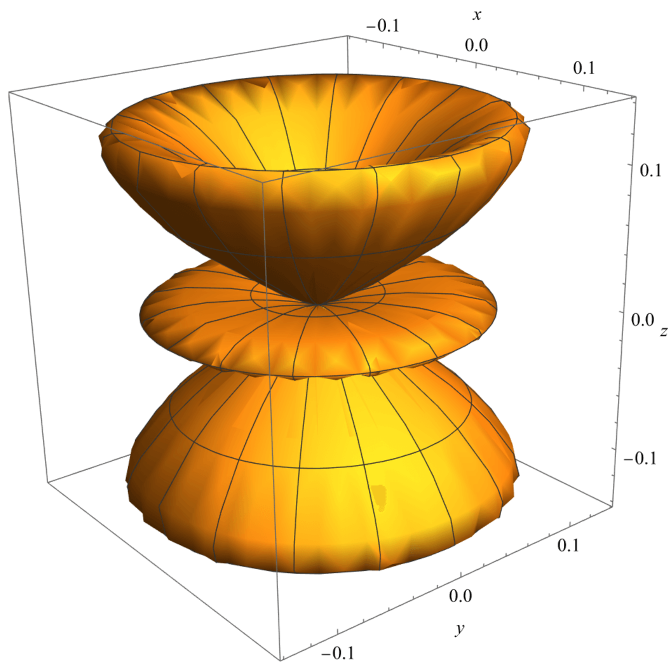


$$\left|Y_5^2(\theta,\phi)\right|^2$$



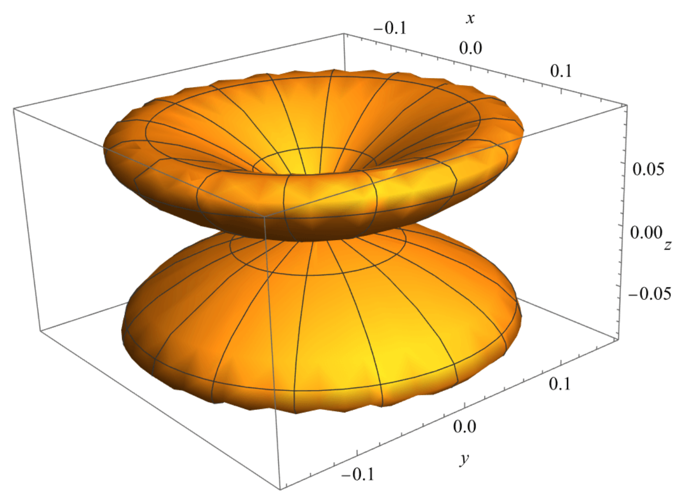
$$Y_5^3(\theta,\phi) = -\frac{1}{32}\sqrt{\frac{385}{\pi}}\, e^{3i\phi}(9\cos^2\theta - 1)\sin^3\theta$$

$$\left|Y_5^3(\theta,\phi)\right|^2$$



$$Y_5^4(\theta,\phi) = \frac{3}{16}\sqrt{\frac{385}{2\pi}}\, e^{4i\phi}\cos\theta\sin^4\theta$$

$$\left|Y_5^4(\theta,\phi)\right|^2$$



$$Y_5^5(\theta,\phi) = -\frac{3}{32}\sqrt{\frac{77}{\pi}}\, e^{5i\phi}\sin^5\theta$$

$$\left|Y_5^5(\theta,\phi)\right|^2$$