The normalized solutions to the angular part of the TISE for *any* spherically symmetric potential $V(r)$ are given by complex-valued functions defined on a sphere, called the "spherical harmonics:"

$$Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\, e^{im\phi}\, P_\ell^m(\cos\theta)\ , \quad \ell = 0,1,2,...Griffiths Eq. 4.32$$

- $m = -\ell,\ -\ell+1, ..., \ell-1,\ \ell \quad \Longrightarrow \quad 2\ell+1$ values of m.
- For negative values of m, the convention used is $P_\ell^{-m}(x) = (-1)^m \frac{(\ell-m)!}{(\ell+m)!} P_\ell^m(x)$
- The special functions $P_\ell^m(x)$, $-1 \le x \le +1$, are the *associated Legendre functions*.

The explicit forms of Y_ℓ^m up through $\ell = 3$ are given in Griffiths Table 4.3. Note that the convention used in the 2nd edition of Griffiths is different from the one listed here (which is used in the 3rd edition). These definitions are equivalent and give the same spherical harmonics.

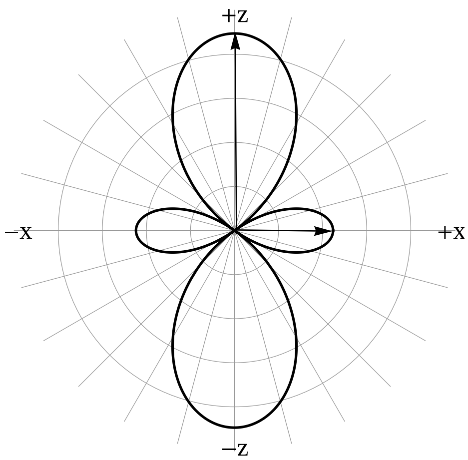
Several different methods are used in physics and chemistry to visualize the spherical harmonics. None of them depict all the information. In this activity, we will explore a method to depict the spherical harmonics.

One way to visualize the spherical harmonics is to plot the *absolute value* of Y_ℓ^m as a function of the azimuthal and polar angles, ϕ and θ. This type of visualization allows us to see where $|Y_\ell^m|$ is large and where it is not, and as a result get a picture of the probability distribution of the electron as a function of (θ,ϕ), *for fixed r*.

Questions: Is Y_ℓ^m axially symmetric about the z-axis? How about $|Y_\ell^m|$? Does your response depend on the value of ℓ or m?

[0.5cm]A function is axially symmetric about the z-axis if it has no ϕ dependence. $\Longrightarrow$
Y_ℓ^m in *not* axially symmetric about the z-axis because of the factor $e^{im\phi}$, except for the case $m = 0$.
$|Y_\ell^m|$ is axially symmetric about the z-axis since $|e^{im\phi}| = 1$.

-1-1**Visualization -1.** In the visualization, we will take a two-dimensional cut (a slice) through three-dimensional space and restrict ourselves to the (x, z) plane. As an example, consider this spherical harmonic:



$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} \left(3\cos^2\theta - 1\right).$$

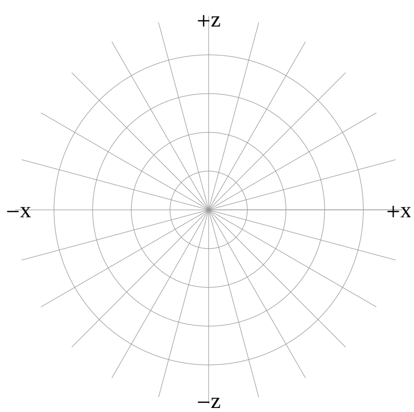
Calculate the ratio of magnitudes at two polar angles:

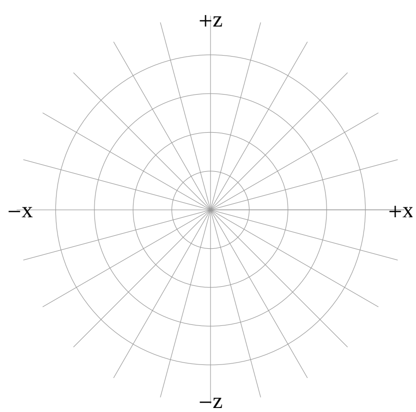
$$\frac{|Y_2^0(\theta = 0)|}{|Y_2^0(\theta = \pi/2)|} = \frac{|3-1|}{|0-1|} = 2\,.$$

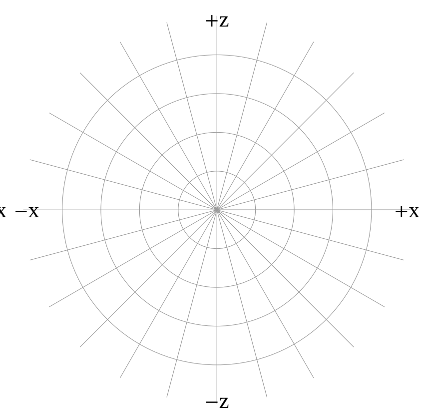
These two points are indicated by the two arrows on the plot to the left. If we do this sort of calculation and plot the corresponding arrows for all angles, and draw a curve through the tips of all the arrows, we get the solid black line in the plot. *Be sure everyone in your group understands all the features of this plot before moving on.* For example, where are the nodes?

Now, consider Y_0^0, Y_1^{+1} and Y_2^{+1}. What is their functional dependence on θ and ϕ? We will sketch the θ dependence (on a 1D plot of $|Y_\ell^m|$ versus θ) for each. Then we will plot $|Y_\ell^m|$ on the figures below, as we did for Y_2^0 above.

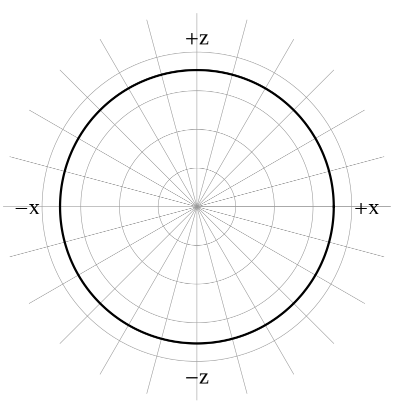
$Y_0^0 =$ $\qquad$ $Y_1^{+1} =$ $\qquad$ $Y_2^{+1} =$

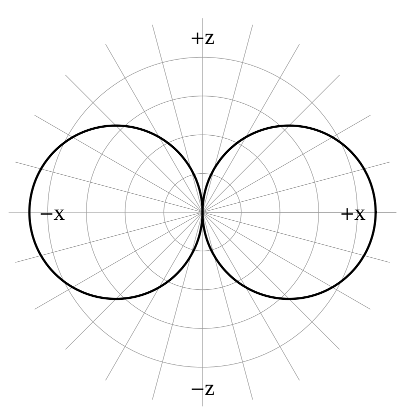


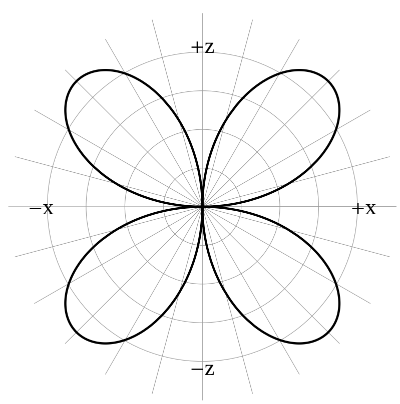




$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_1^{+1} = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{+i\phi} \qquad Y_2^{+1} = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{+i\phi}$$







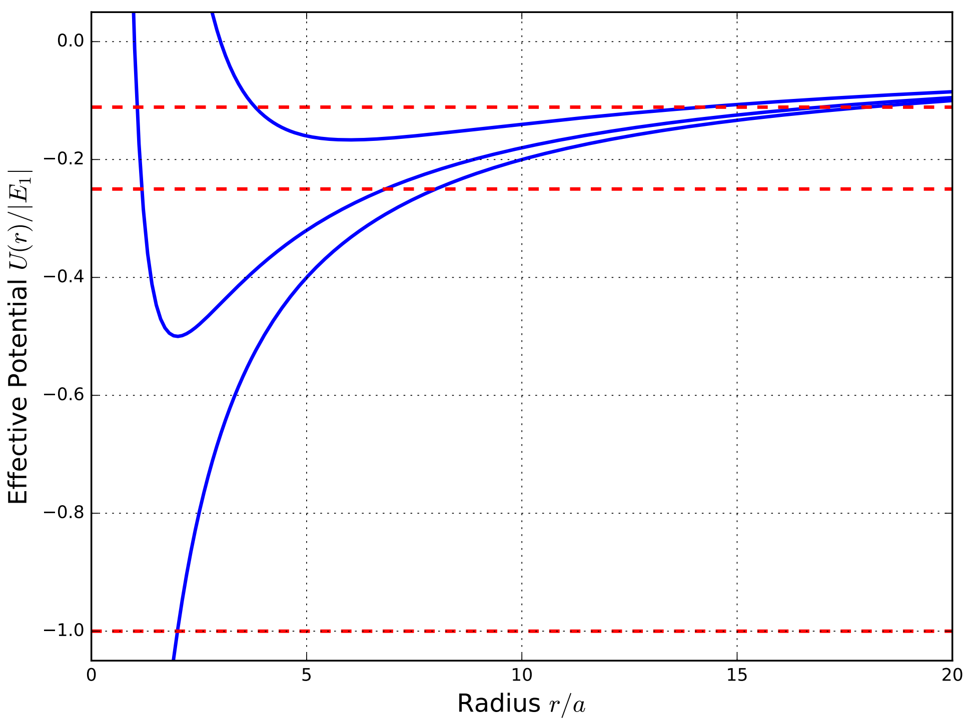
The plot below shows the effective potential for the hydrogen atom ($E_1 < 0$) for three values of ℓ:

$$U(r) = -E_1\left[-\frac{2}{(r/a)} + \frac{\ell(\ell+1)}{(r/a)^2}\right], \quad \ell = 0, 1, 2.$$

The lowest three total energy eigenvalues are also superimposed as horizontal dashed lines:

$$E_n = \frac{E_1}{n^2}, \quad n = 1, 2, 3.$$

Note that the potential and total energies are divided by $|E_1|$ (vertical axis) and the radius is divided by the Bohr radius a (horizontal axis) to make each scale dimensionless.



-1-1**Q -1.** Label each potential-energy curve to identify the corresponding value of $\ell = 0, 1, 2$.

Starting with the lowest curve and moving upwards, the potential energies show $\ell = 0, 1, 2$. The curves are strictly increasing with ℓ at all values of r/a because of the centrifugal term in the effective potential.

-1-1**Q -1.** Label the horizontal energy lines with the corresponding value of $n = 1, 2, 3$. Draw circles on each energy line to indicate where a wave function inflection point occurs.

Starting with the lowest energy line and moving upwards, the lines show $n = 1, 2, 3$, according to $E_n = E_1/n^2$.

-1-1**Q -1.** List any combinations of $n = 1, 2, 3$ and $\ell = 0, 1, 2$ that are not possible for a stationary (bound) state. Generalize to a condition on n and ℓ.

When $\ell \geq n$, the energy E_n is everywhere below $U(r)$, so there is no possible bound state. All other combinations (i.e., those with $\ell < n$) are possible.

-1-1**Q -1.** On the accompanying grid of graphs, the top row shows the effective potentials

$U(r)$ for $\ell = 0, 1, 2$ with vertical dotted lines indicating inflection points for each n. Sketch *entirely plausible* 1D equivalent wave functions $u_{n\ell}(r) = rR_{n\ell}(r)$ in the graphs corresponding to each valid combination of energy quantum number $n = 1, 2, 3$ and $\ell = 0, 1, 2$. Think carefully about how you expect the "local" wave number and amplitude to vary with r (or, more significantly, with $E_n - U(r)$.

See the graphs on the last page, which show the exact solutions described in Griffiths based on the Laguerre polynomials.

-1-1**Q -1.** Indicate the approximate expectation value of the electron radius on each of your

sketches:

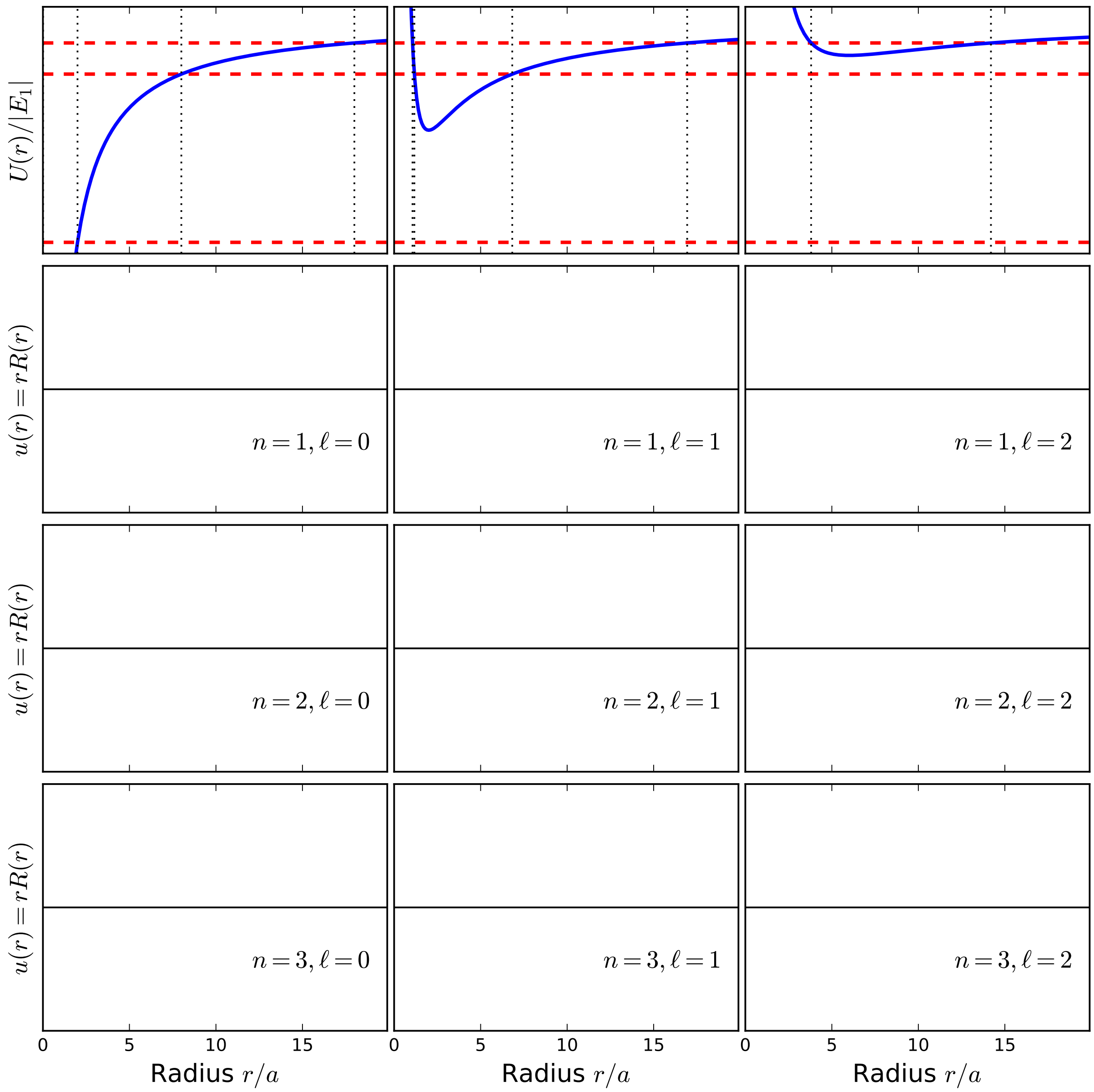
$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \left|\psi_{n\ell m}(r,\theta,\phi)\right|^2 r^2 \, dr \sin\theta \, d\theta \, d\phi = \int_0^\infty r \left|u_{n\ell}(r)\right|^2 dr \ .$$

Describe how $\langle r \rangle$ varies with n (for fixed ℓ) and with ℓ (for fixed n). What is the general pattern with n and ℓ both varying?

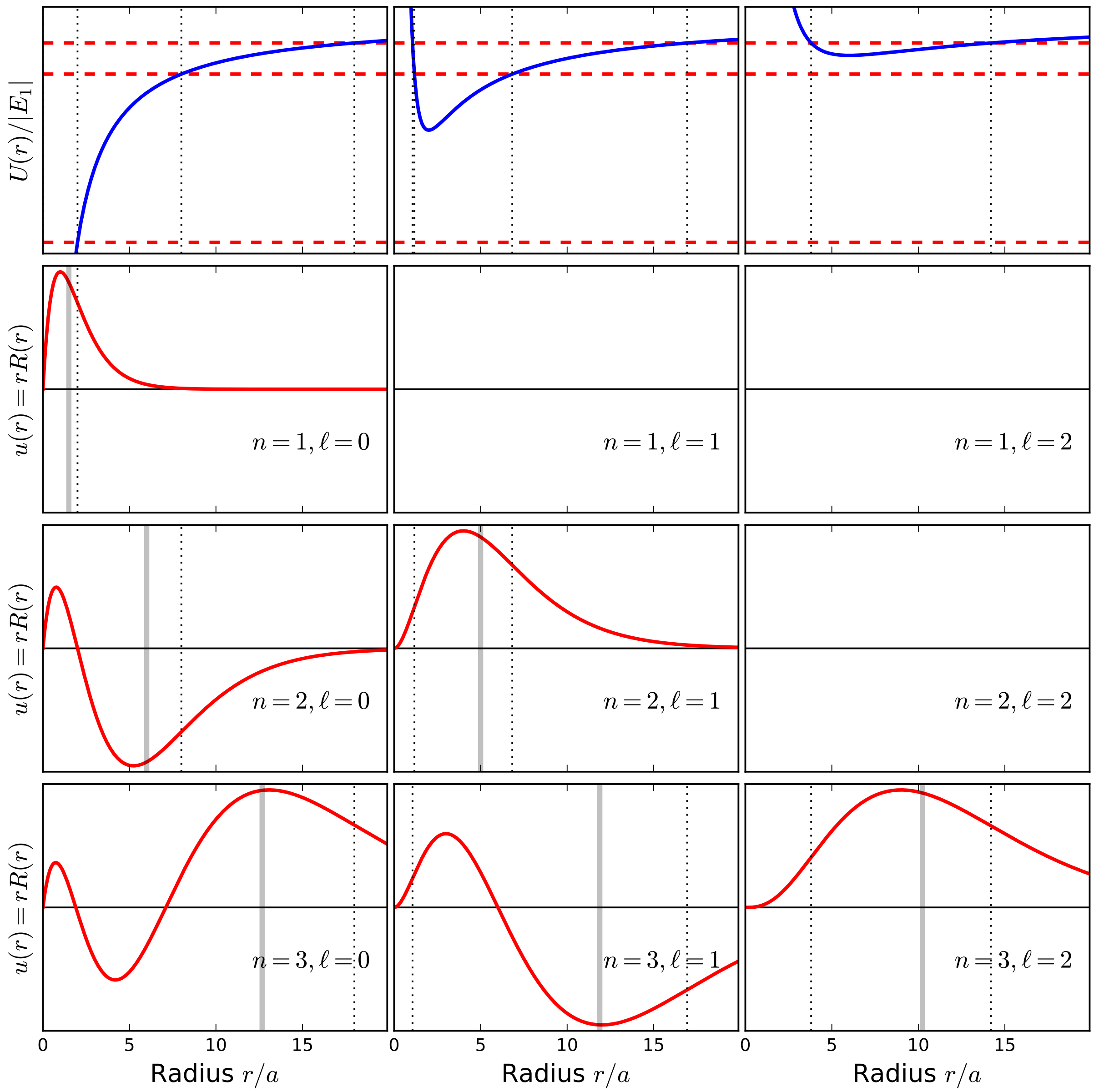
The values of $\langle r \rangle / a$ are tabulated below and represented by vertical gray bars in the plots:

	$\ell = 0$	$\ell = 1$	$\ell = 2$
$n = 1$	1.50		
$n = 2$	6.00	5.00	
$n = 3$	12.67	11.89	10.24

For a fixed ℓ, they increase with n. For a fixed n, they decrease with ℓ. The general pattern is that $\langle r \rangle$ increases with both n and $n - \ell$.



$U(r)/|E_1|$
$u(r) = rR(r)$
$n=1, \ell=0$
$n=1, \ell=1$
$n=1, \ell=2$
$u(r) = rR(r)$
$n=2, \ell=0$
$n=2, \ell=1$
$n=2, \ell=2$
$u(r) = rR(r)$
$n=3, \ell=0$
$n=3, \ell=1$
$n=3, \ell=2$
0
5
10
15
Radius r/a
Radius r/a
Radius r/a



When completely finished, compare the number and location of nodes in your sketches of $u(r)$ to those of $R(r) = u(r)/r$ in Figure 4.7 on p. 152 in Griffiths.