The hydrogen atom (and other one-electron atoms)

Now let's look at the hydrogen atom, in which an electron "orbits" a proton. This is the problem that Schroedinger used to show that his equation worked.

The electron has -*q*, the proton +*q*, so the two are attracted through the electrostatic potential.

$$U(x, y, z) = -\frac{q^2}{4\pi\epsilon_o \sqrt{x^2 + y^2 + z^2}}$$

This has some intuitive appeal as a classical problem, since it looks like a bit like a planet revolving a sun. The electrostatic potential has the same basic form as the gravitational potential. However, as we've already seen, it cannot be handled classically.

The electron orbits in a circular path, much like the earth around the sun.

The orbits are quantized such that the angular momentum is quantized.
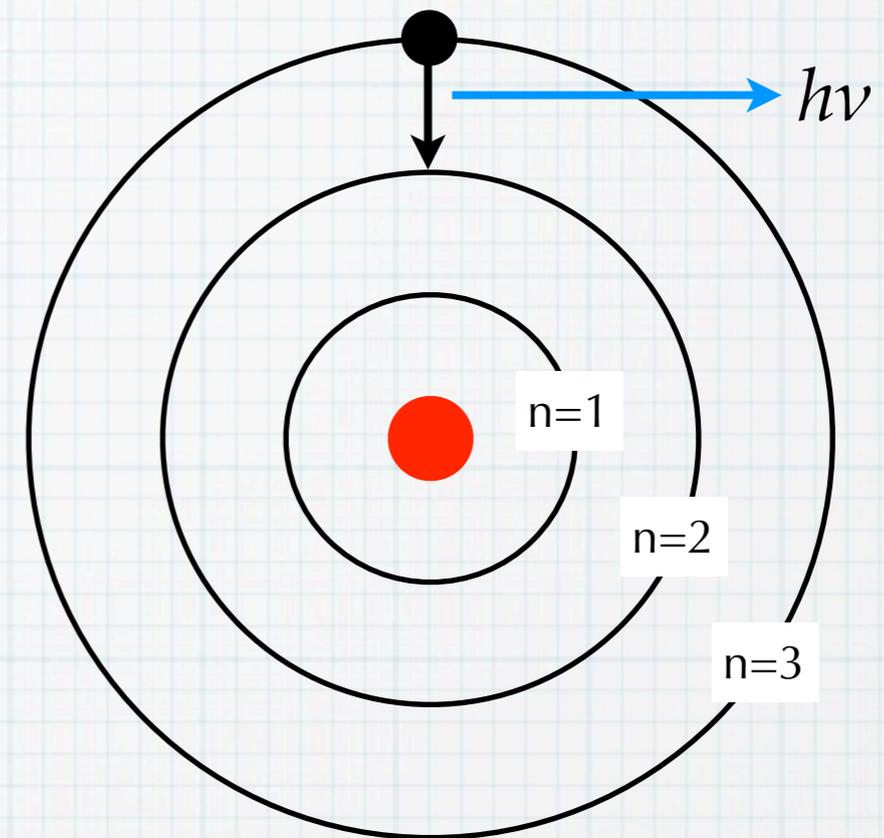
$$|\vec{L}| = |\vec{r} \times \vec{p}| = n\hbar$$

where n is an integer.

hv

n=1

n=2

n=3

The energy of the electron in the nth orbital is

$$E_n = -\left[\frac{mq^4}{2\left(4\pi\epsilon\right)^2 \hbar^2}\right]\frac{1}{n^2} = -\frac{13.6\text{ eV}}{n^2}$$

The radius of the nth orbital is

$$a_n = \frac{4\pi\epsilon_o \hbar^2}{q^2 m}n^2 = \left(0.0531\text{ nm}\right)n^2$$

Excited atoms (electrons in orbits with $n > 1$) can relax to lower orbits by emitting a photon with $hv = E_{n+1} - E_n$.

The emitted photon energies match exactly with experimental observations.

Schroedinger equation in rectangular coordinates:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right] + \frac{q^2}{4\pi\epsilon_o \sqrt{x^2 + y^2 + z^2}}\psi = E\psi$$

The potential is not separable. We need an alternative description. Use spherical coordinates.
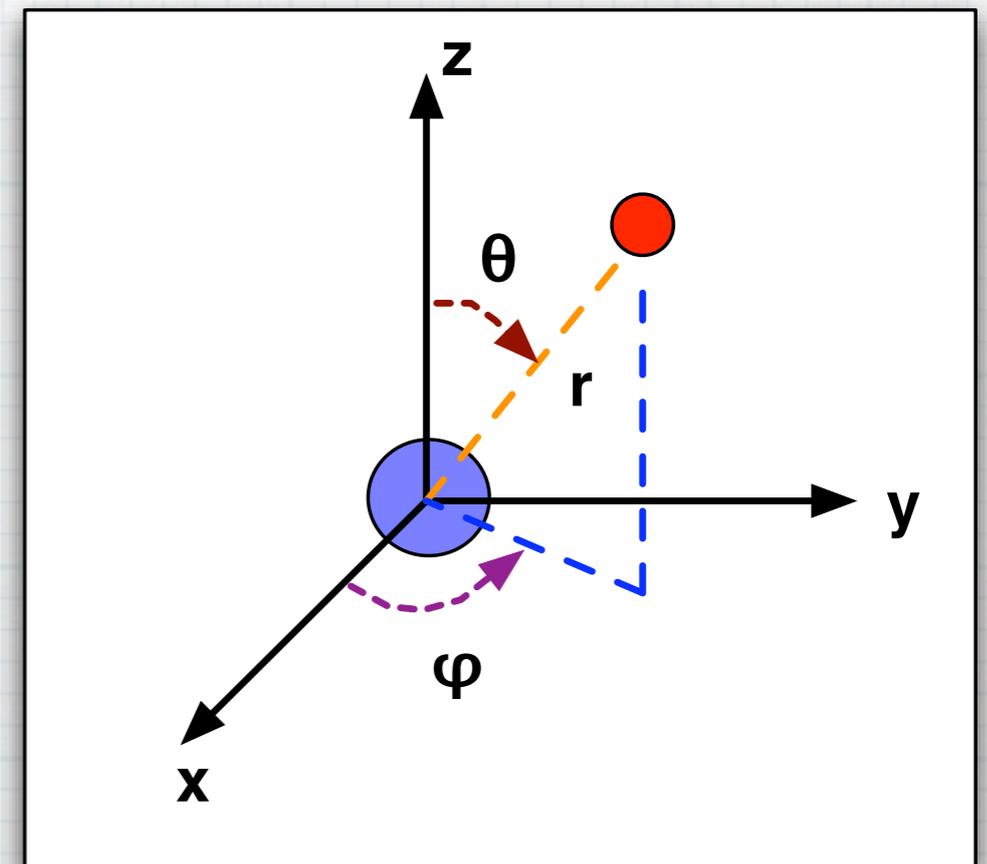
$r \rightarrow$ radius (0 to ∞)

$\theta \rightarrow$ polar angle (0 to π)

$\phi \rightarrow$ azimuthal angle (0 to 2π)

$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$
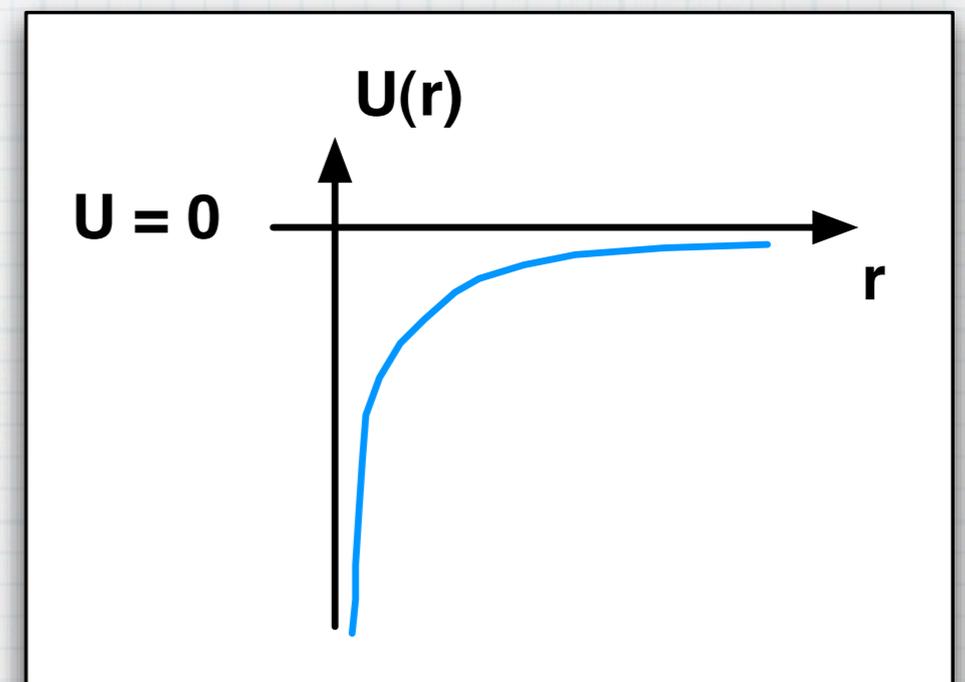

$$r^2 = x^2 + y^2 + z^2$$

In spherical coordinates, the potential is

$$U(r, \theta, \phi) = -\frac{q^2}{4\pi\epsilon_o r}$$

Depends only on r! In spherical coordinates, we might be able to separate variables.

The hydrogen atom potential is a form of quantum well.

Quantum mechanically, we expect to have bound states and quantized energies. We'll be looking for bound-state solutions such that as $r \rightarrow \infty$, $\psi \rightarrow 0$. Also, we'll require that ψ be single-valued as well as continuous and finite at all points (as always).

$$-\frac{\hbar^2}{2m} \nabla^2 \psi\left(r, \theta, \phi\right) = U\left(r\right) \psi\left(r, \theta, \phi\right) = E\psi\left(r, \theta, \phi\right)$$

$$\hat{H}\psi\left(r, \theta, \phi\right) = E\psi\left(r, \theta, \phi\right)$$

This doesn't seem bad at all. However, this is where it hits the fan. When expressed in terms of polar coordinates, the Laplacian (∇^2 operator) becomes very unfriendly.

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}$$

Yikes! But before we panic, let's poke around at this for a bit. If we proceed carefully, we can work out the separation of variables without too much mental anguish.

Trudge ahead. In spherical form, the wavefunction can be separated into independent factors of r, θ, and ϕ.

Start by writing $\quad \psi\left(r, \theta, \phi\right) = R\left(r\right) T\left(\theta\right) F\left(\phi\right)$

Insert into the Schroedinger equation

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\left(RTF\right)}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\left(RTF\right)}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\left(RTF\right)}{\partial\phi^2}\right\}$$

$$-\frac{q^2}{4\pi\epsilon_o r}\left(RTF\right) = E\left(RTF\right)$$

Carry out the partial differentiation

$$-\frac{\hbar^2}{2m}\left\{\frac{TF}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right] + \frac{RF}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right] + \frac{RT}{r^2\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\}$$

$$-\frac{q^2}{4\pi\epsilon_o r}\left(RTF\right) = E\left(RTF\right)$$

Divide every term by RTF

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right]+\frac{1}{T}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]+\frac{1}{F}\frac{1}{r^2\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\}-\frac{q^2}{4\pi\epsilon_o r}=E$$

Multiply by r^2 and multiply by $-\dfrac{2m}{\hbar^2}$

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right]+\frac{1}{T}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]+\frac{1}{F}\frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}+\frac{mq^2 r}{2\pi\epsilon_o\hbar^2}=\frac{2mEr^2}{\hbar^2}$$

Re-arrange the terms

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right]+\frac{mq^2 r}{2\pi\epsilon_o\hbar^2}+\frac{2mEr^2}{\hbar^2}=-\left\{\frac{1}{T}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]+\frac{1}{F}\frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\}$$

Examine it. We've accomplished the first separation. Everything on the left is depends *only* on r. The right side depends on θ and ϕ.

As is usual in separation problems, we equate both sides to a constant. The value we choose is an odd one, but we do it to stick with custom.

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right] + \frac{mq^2 r}{2\pi\epsilon_o \hbar^2} + \frac{2mEr^2}{\hbar^2} = l(l+1)$$

$$-\left\{\frac{1}{T}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right] + \frac{1}{F}\frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\} = l(l+1)$$

We have taken the first step of separation. Everything in the first equation depends only on distance of the electron to the proton. Everything in the second equations depends on angular position.

A point for future reference: The second equation, involving the angular components, can be re-written in operator form, where the angular functions TF are eigenfunctions of the of the operator with eigenvalues $l(l+1)$.

$$\hat{L}(TF) = -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial(TF)}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2(TF)}{\partial\phi^2}\right\} = l(l+1)(TF)$$

This operator is the angular momentum operator, and we will examine in more detail later

Finally, separate the two angular functions

$$-\left\{\frac{1}{T}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]+\frac{1}{F}\frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\}=l\left(l+1\right)$$

Multiply by $\sin^2\theta$, and re-arrange the terms

$$-\frac{\sin\theta}{T}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]-l\left(l+1\right)\sin^2\theta=\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2}$$

Once again, we have separated the variables into polar (left-side) and azimuthal components (right-side) .As before, we will set each side equal to a constant. In this case, we call the constant $-m_l^2$.

$$\frac{\sin\theta}{T}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right]-l\left(l+1\right)\sin^2\theta=m_l^2$$

$$\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2}=-m_l^2$$

Three separated equations

radial
$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) + \left[\frac{mq^2 r}{2\pi\epsilon_o \hbar^2} + \frac{2mEr^2}{\hbar^2} - l\left(l+1\right)\right] R = 0$$

polar
$$\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial T}{\partial\theta}\right] - \left[l\left(l+1\right)\sin^2\theta - m_l^2\right] T = 0$$

azimuthal
$$\frac{\partial^2 F}{\partial\phi^2} + m_l^2 F = 0$$

In the separation process, we have introduced two constants, l and m_l Presumably, we will need to impose some conditions on those and they will become two of the quantum numbers needed for bound state solutions. We expect a third quantum number to appear as we work through the solutions in detail.

Aziumuthal function

This is one is easy – we've seen this form before. The solutions are complex exponentials (or sinusoids, if you prefer).

$$F(\phi) = \exp(im_l\phi)$$

Now to impose a condition on m_l. The wave function must be single-valued, so when when revolving around the z-axis by 2π, it must come back to the same value.

$$F(\phi + 2\pi) = F(\phi)$$

$$\exp[im_l(\phi + 2\pi)] = \exp[im_l\phi]$$

$$\exp[im_l(2\pi)] = 1$$

meaning that m_l must be an integer. We'll need further restrictions later.

Polar function

$$\sin\theta \frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right] - \left[l(l+1)\sin^2\theta - m_l^2\right]T = 0$$

This is known as Legendre's equation. The general form of this type of equation was solving in the late 1700's (by Legendre, obviously). So this was not a new piece of math for Schroedinger.

The details of the solution are a bit involved, and we'll regulate that to an appendix, for those who like to work the details. The basic approach is similar to what we did with the harmonic oscillator — assume a polynomial solution. The polynomial, with unknown coefficients is inserted into the equation and then, with some effort, the coefficients can be determined.

What is interesting in this case, is that the polynomials are in powers of $\cos\theta$. The general solution takes the from of ($\sin^{|m_l|}\theta$) x (polynomial in $\cos\theta$).

$$P(\cos\theta) = a_1\cos\theta + a_2\cos^2\theta + a_3\cos^3\theta + ...$$

$$T(\theta) = \left[\sin^{|m_l|}\theta\right]P(\cos\theta)$$

$$P(\cos\theta) = \sum_{0}^{l}a_l\cos^l\theta$$

$$T\left(\theta\right) = \left[\sin^{|m_l|}\theta\right] \sum_0^l a_l \cos^l\theta$$

where l is an integer ≥ 0. The polynomials are known as Legendre polynomials.

In order to keep the polar function <u>finite</u> we must choose $|m_l| \leq l$. So our quantum numbers at this point are:

l an integer ≥ 0 and m_l an integer such that $|m_l| \leq l$.

The product of the polar and azimuthal functions form a set of functions known as <u>spherical harmonics</u>, and are denoted $Y_l^{m_l}$.

$$Y_l^m\left(\theta, \phi\right) = T_{lm}\left(\theta\right) F_m\left(\phi\right)$$

Generally, we normalize these functions to 1.

Some of the lower order spherical harmonics are listed below. These have been normalized to 1.

$l = 0$

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$l = 1$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \cos\theta \exp(\pm i\phi)$$

$l = 2$

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

$$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \exp(\pm i\phi)$$

$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \exp(\pm i2\phi)$$

Radial function

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{mq^2 r}{2\pi\epsilon_o\hbar^2} + \frac{2mEr^2}{\hbar^2} - l\left(l+1\right)\right]R = 0$$

Re-writing it a bit:

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[\frac{mq^2}{2\pi\epsilon_o\hbar^2}\frac{1}{r} + \frac{2mE}{\hbar^2} - \frac{l\left(l+1\right)}{r^2}\right]R = 0$$

This is known as Laguerre's equation, and was solved in the early 1800s. So again, there is nothing new here, math-wise.

$$\frac{mq^2}{2\pi\epsilon_o\hbar^2} = \frac{2}{a_o} \qquad \text{where } a_o \text{ is the Bohr radius.}$$

$$\frac{2m}{\hbar^2} = \frac{1}{E_1 a_o^2} \qquad \text{where } E_1 \text{ is the Bohr ground energy.}$$

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[\frac{E}{E_1 a_o^2} + \frac{2}{a_o r} - \frac{l\left(l+1\right)}{r^2}\right]R = 0$$

Again, we will leave the details of the actual solution to an appendix. However, the basic approach is similar to that of the polar function (or the harmonic oscillator seen earlier.) Since we need bound states there will be an asymptotic limit imposed by a factor that goes as exp($-r/a_o$) that dominates for large values of r. This is exponential limiting factor is multiplied by a polynomial in r.

$$R_{nl}\left(r\right) = \exp\left(-\frac{r}{na_o}\right) \sum_{j=l+1}^{1} c_j \left(\frac{r}{a_o}\right)^j$$

In order to keep the total function finite, we have to limit the number of terms in the polynomial, by forcing it to truncate at some point, which is done by limiting l to being no bigger than n-1. (n being an integer giving the highest power of r in the particular polynomial, n = 1, 2, 3, ...)

The third quantum number, n, has appeared in the building the solutions to the radial function.

A final detail of the limitation of the polynomial is the most important result of all:

$$E_n = -\frac{E_1}{n^2}$$

The quantized energy is exactly the result required to match with the observed emission spectra the hydrogen atom. (As well as with Bohr's result from his earlier model of the atom.)

$$\boldsymbol{R_{10}(r)} = \left(\frac{1}{a_o}\right)^{3/2} 2\exp\left(-\frac{r}{a_o}\right)$$

$$\boldsymbol{R_{20}(r)} = \left(\frac{1}{2a_o}\right)^{3/2} 2\left(1-\frac{r}{2a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$$

$$\boldsymbol{R_{21}(r)} = \left(\frac{1}{2a_o}\right)^{3/2} \frac{1}{\sqrt{3}}\left(\frac{r}{a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$$

The polynomials are known as Laguerre polynomials.

The complete wave functions have the general form:

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) \, T_{ll=m_l}(\theta) \, F_{m_l}(\phi)$$

The quantum number set (n,l,m_l) specifies the particular solutions.

n	E_n	$l \leq n\text{-}1$	$|m_l| \leq l$	
1	-13.6 eV	0	0	1
2	-3.4 eV	0	0	4
		1	-1, 0, 1	
3	-1.51 eV	0	0	9
		1	-1, 0, 1	
		2	-2, -1, 0, 1, 2	
4	-0.85 eV	0	0	16
		1	-1, 0, 1	
		2	-2, -1, 0, 1, 2	
		3	-3, -2, -1, 0, 1, 2, 3	

$$\psi_{100} = R_{10}(r)\Theta_{00}(\theta)\Phi_0(\phi)$$

$$= \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\exp\left(-\frac{r}{2a_o}\right)$$

$$P(r) = r^2 R_{10}^* R_{10} = \frac{r^2}{\pi a_o^3}\exp\left(-\frac{r}{a_o}\right) \qquad P(\theta) = F_{00}^* F_{00} = constant$$

Radial plot

polar plot

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(2 - \frac{r}{a_o}\right) \exp\left(-\frac{r}{2a_o}\right)$$

$$P(r) = r^2 R_{20}^* R_{20} = \frac{r^2}{32\pi a_o^3} \left(2 - \frac{r}{a_o}\right) \exp\left(-\frac{r}{a_o}\right)$$

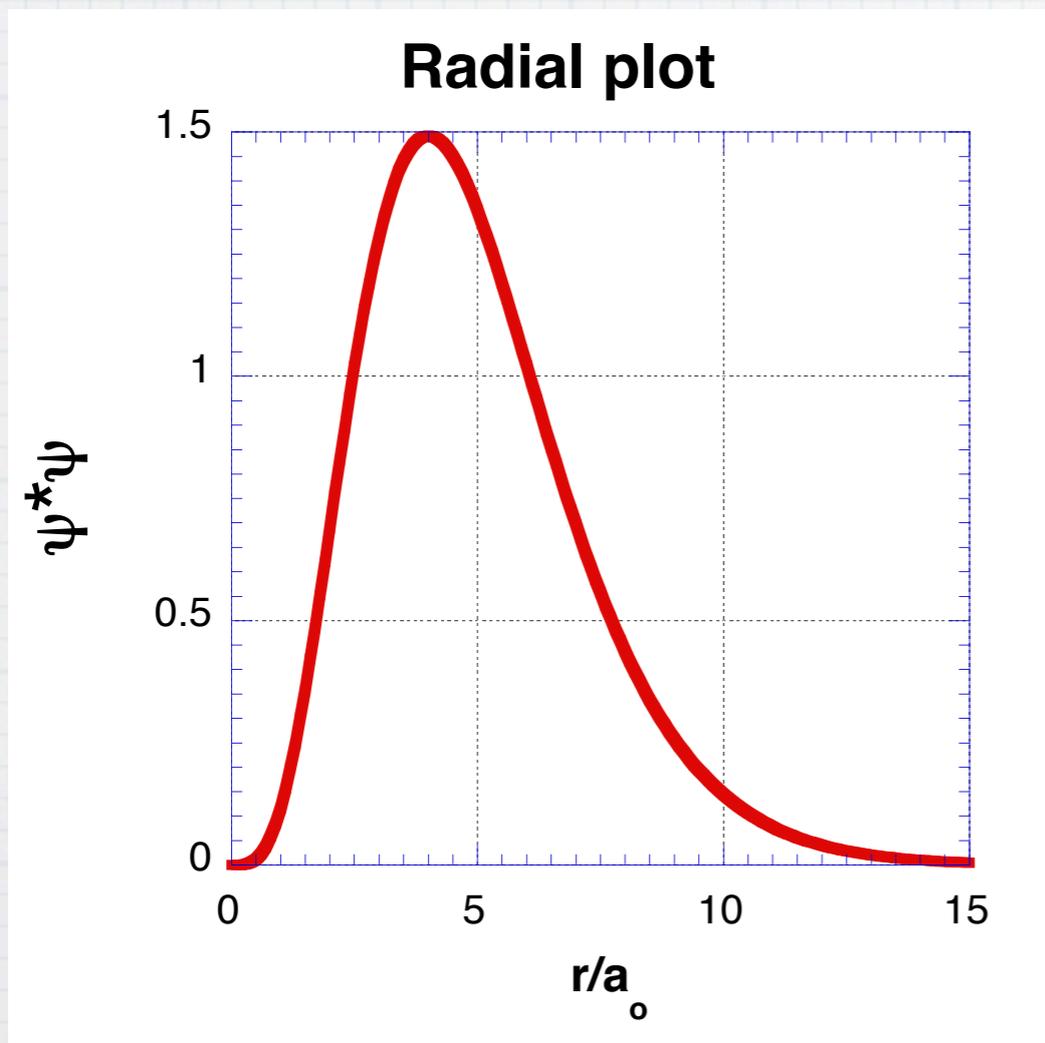$$P(\theta) = F_{00}^* F_{00} = constant$$

Radial plot

polar plot

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(\frac{r}{a_o}\right) \exp\left(-\frac{r}{2a_o}\right) \cos\theta$$

$$P(r) = r^2 R_{21}^* R_{21} = \frac{r^2}{32\pi a_o^3} \left(\frac{r}{a_o}\right)^2 \exp\left(-\frac{r}{a_o}\right)$$
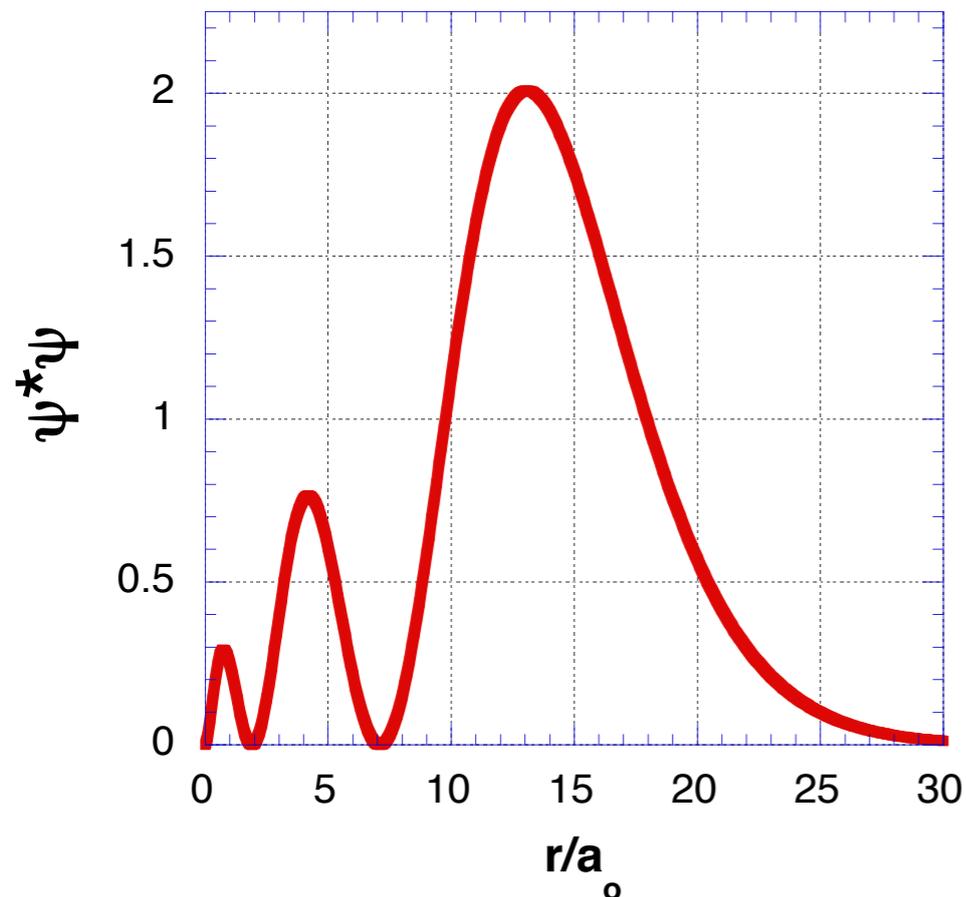
$$P(\theta) = F_{10}^* F_{10} = \cos^2\theta$$

Radial plot

polar plot

$$\psi_{211} = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(\frac{r}{a_o}\right) \exp\left(-\frac{r}{2a_o}\right) \sin\theta \exp(j\phi)$$

$$P(r) = r^2 R_{21}^* R_{21} = \frac{r^2}{64\pi a_o^3} \left(\frac{r}{a_o}\right)^2 \exp\left(-\frac{r}{a_o}\right)$$

$$P(\theta) = F_{11}^* F_{11} = \sin^2\theta$$

Radial plot

polar plot

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(27 - 18 \left[\frac{r}{a_o}\right] + 2 \left[\frac{r}{a_o}\right]^2\right) \exp\left(-\frac{r}{3a_o}\right)$$

$$P(r) = r^2 R_{21}^* R_{21} \propto \left(\frac{r}{a_o}\right)^2 \left(27 - 18 \left[\frac{r}{a_o}\right] + 2 \left[\frac{r}{a_o}\right]^2\right)^2 \exp\left(-\frac{2r}{3a_o}\right)$$
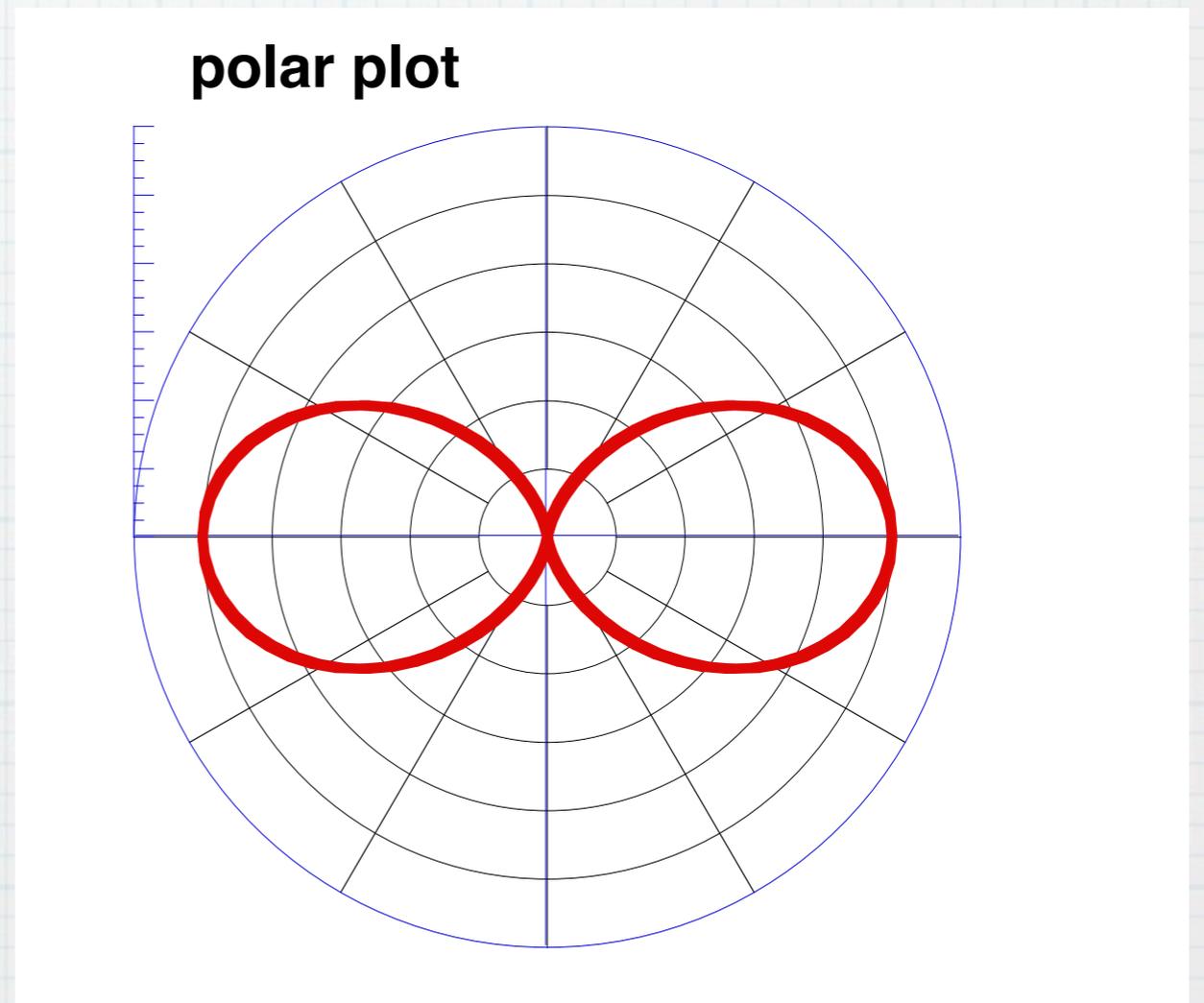
$$P(\theta) = F_{00}^* F_{00} = constant$$
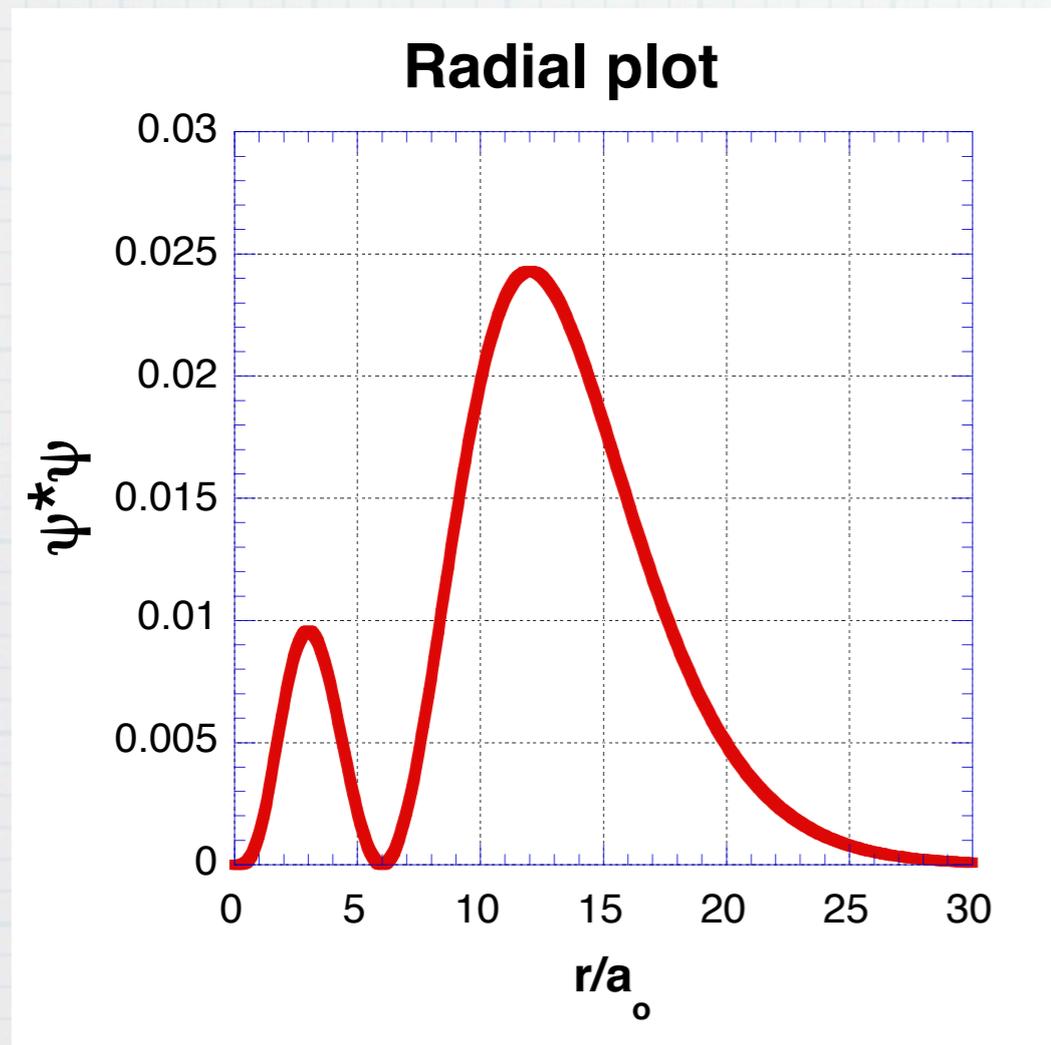
Radial plot

polar plot

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left[\left(6 - \frac{r}{a_o}\right)\left(\frac{r}{a_o}\right)\right] \exp\left(-\frac{r}{3a_o}\right) \cos\theta$$

$$P(r) = r^2 R_{21}^* R_{21} \propto \left(\frac{r}{a_o}\right)^2 \left[\left(6 - \frac{r}{a_o}\right)\left(\frac{r}{a_o}\right)\right]^2 \exp\left(-\frac{2r}{3a_o}\right)$$
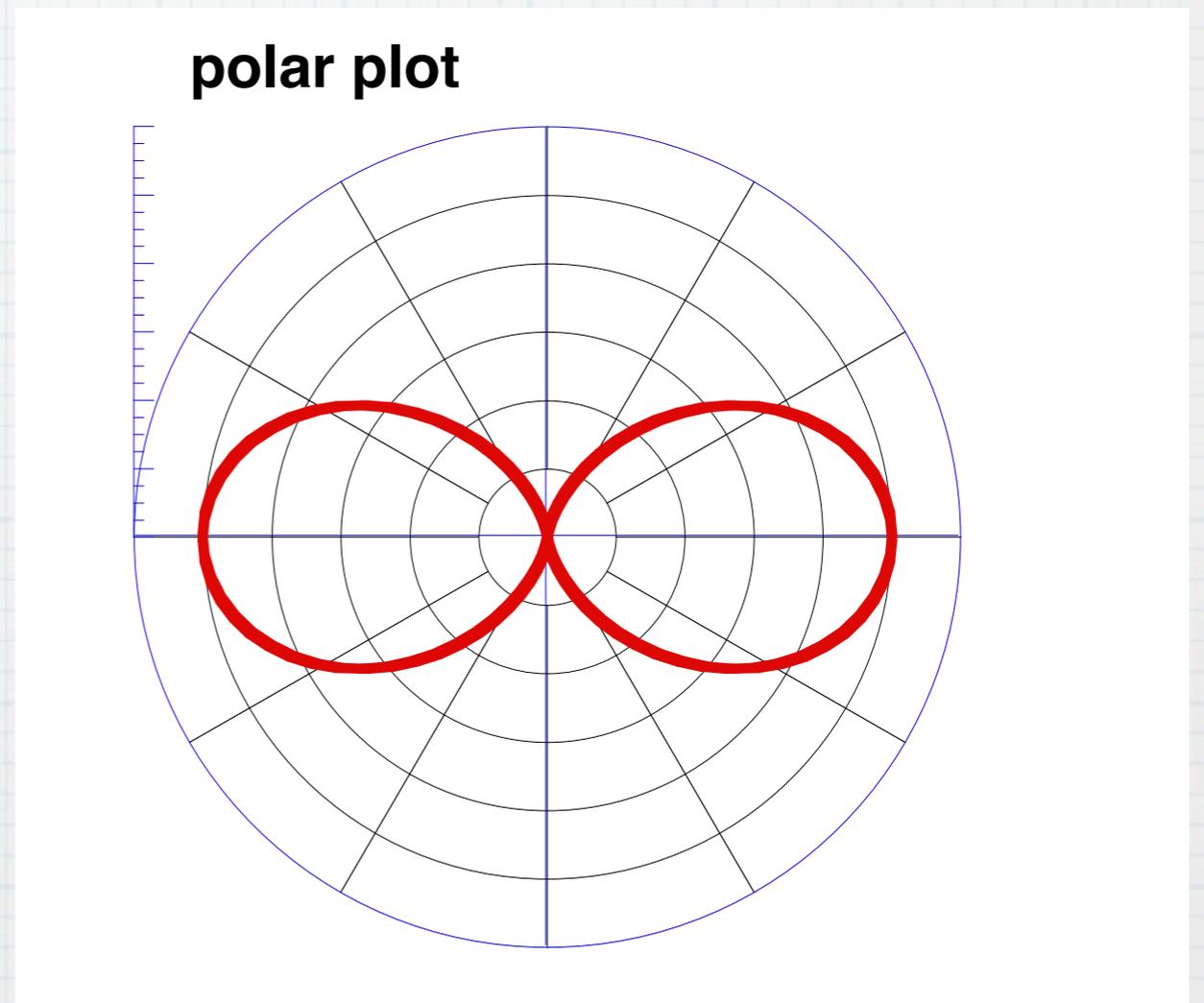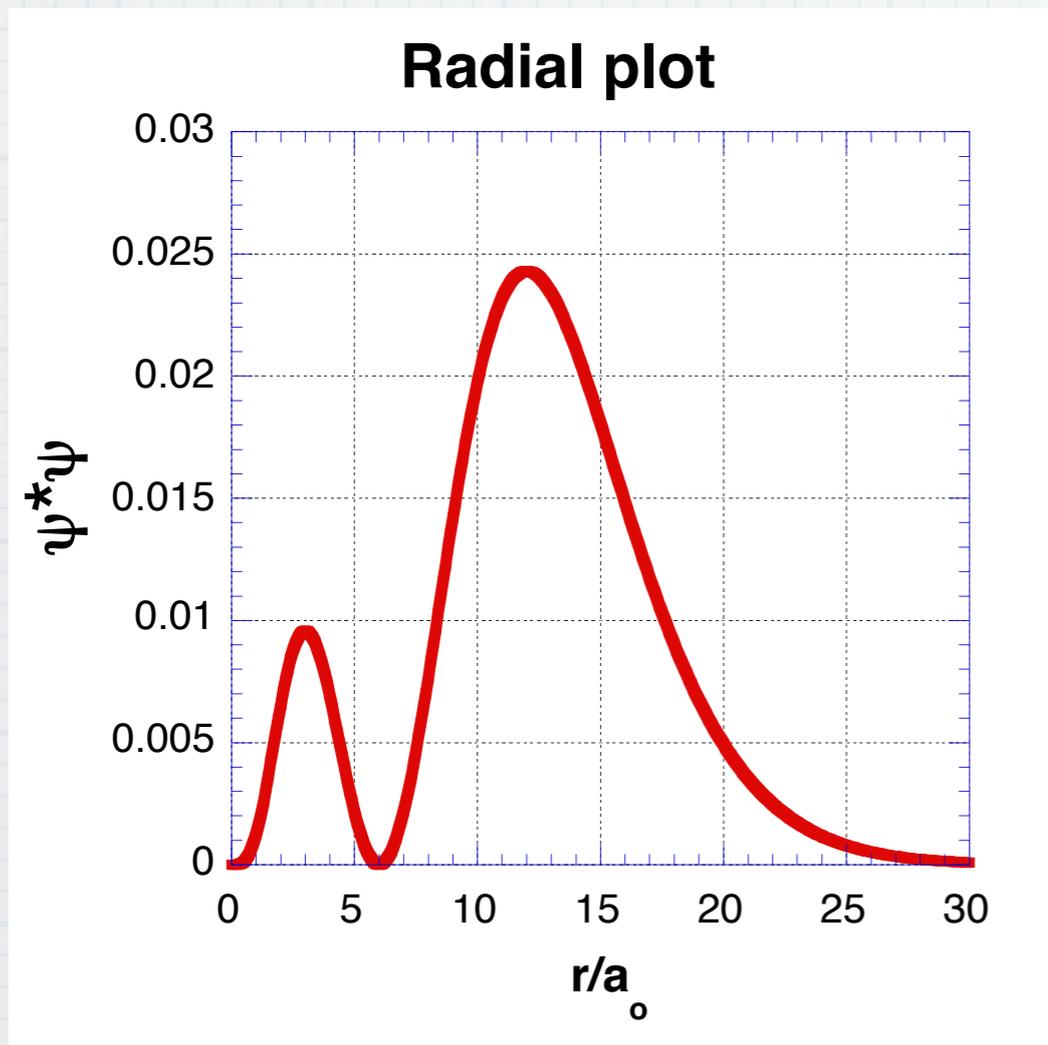
$$P(\theta) = F_{10}^* F_{10} = \cos^2\theta$$

Radial plot

polar plot

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left[\left(6 - \frac{r}{a_o}\right)\left(\frac{r}{a_o}\right)\right] \exp\left(-\frac{r}{3a_o}\right) \cos\theta$$

$$P(r) = r^2 R_{21}^* R_{21} \propto \left(\frac{r}{a_o}\right)^2 \left[\left(6 - \frac{r}{a_o}\right)\left(\frac{r}{a_o}\right)\right]^2 \exp\left(-\frac{2r}{3a_o}\right)$$
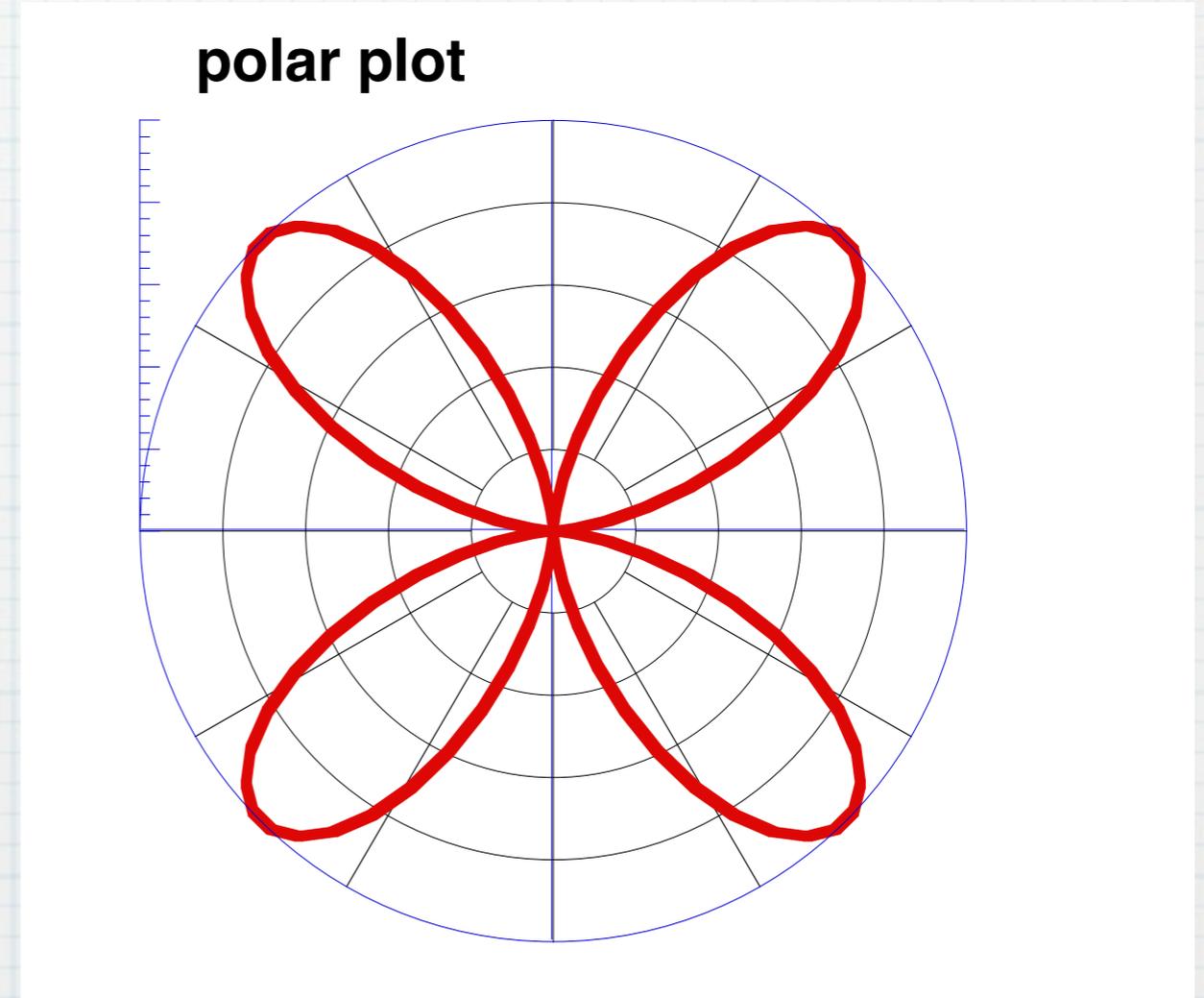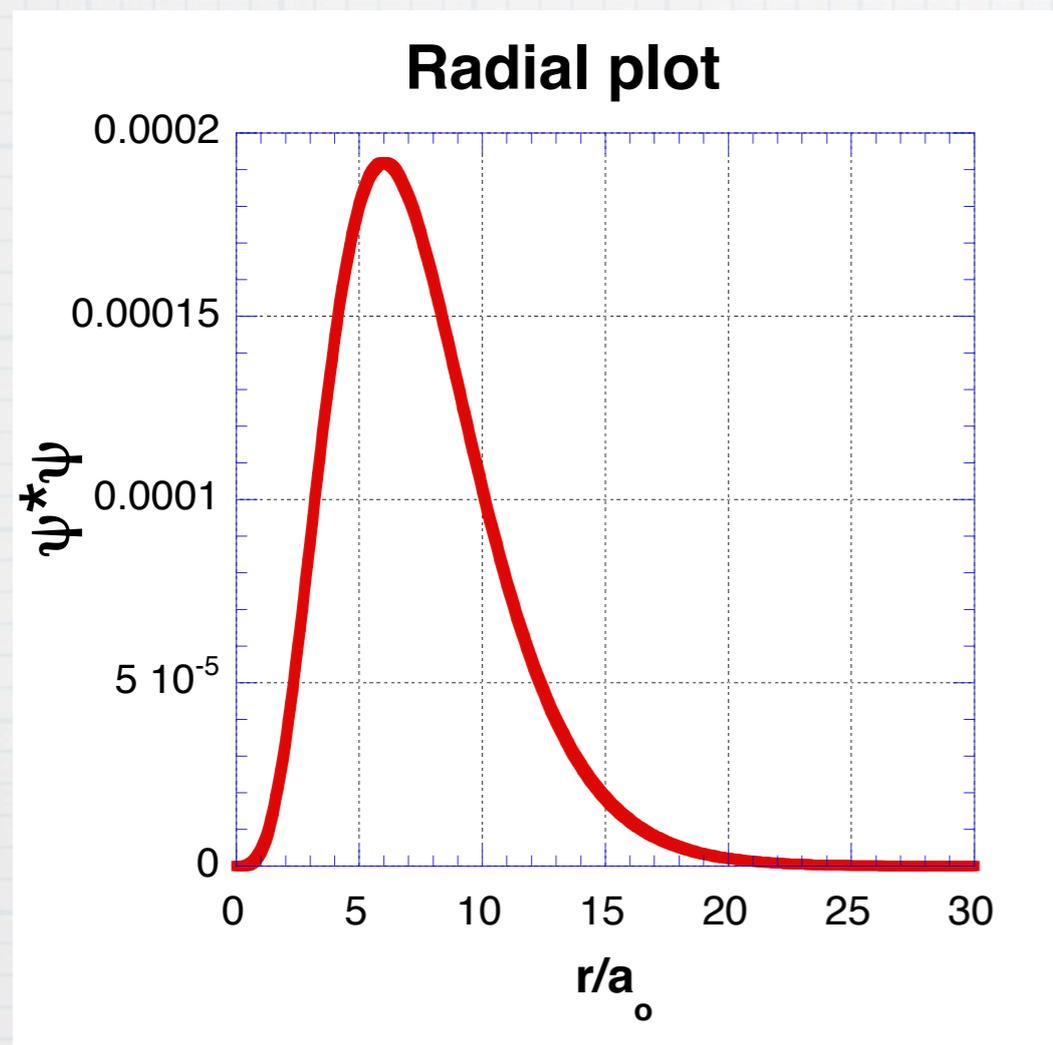
$$P(\theta) = F_{10}^* F_{10} = \cos^2\theta$$

Radial plot

polar plot

$$\psi_{321} = \frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(\frac{r}{a_o}\right)^2 \exp\left(-\frac{r}{3a_o}\right) (\cos\theta \sin\theta)$$

$$P(r) = r^2 R_{21}^* R_{21} \propto \left(\frac{r}{a_o}\right)^4 \exp\left(-\frac{2r}{3a_o}\right)$$

$$P(\theta) = F_{21}^* F_{21} = (\cos\theta \sin\theta)^2$$

Radial plot

polar plot

n determines the energy of the state.
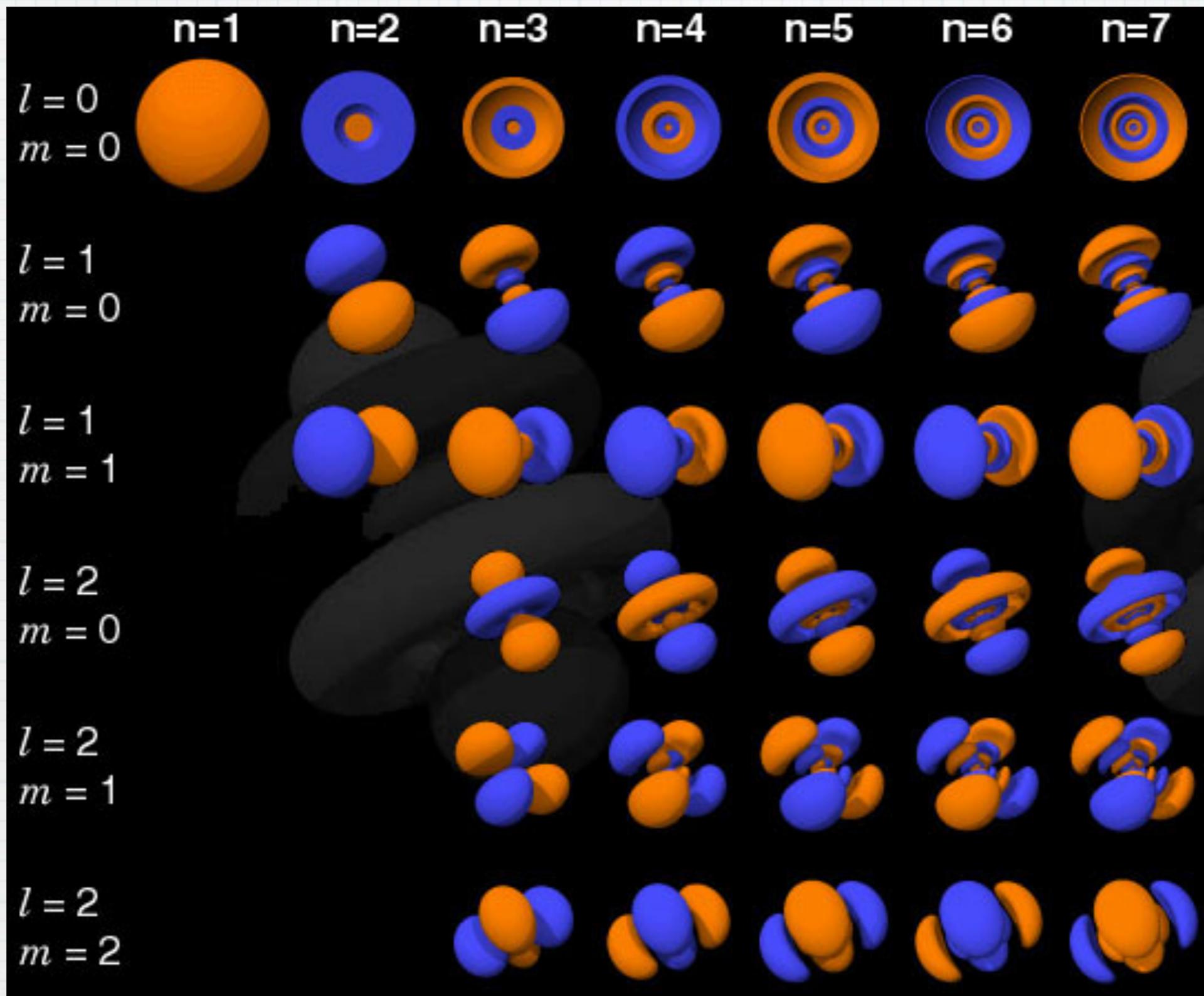(sometimes referred to as "shells")

Note that for each value of *n*, there can be several different states, all with the same energy (degenerate states).

l determines the polar shape

$l = 0$ "spherical", *s*-states

$l = 1$ "dumb-bell", 2 lobes, *p*-states

$l = 2$ "cloverleaf", 4 lobes, *d*-states

Hydrogen Wave Function
Probability density plots.

$$\psi_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$$

(2,0,0) (3,0,0)
(2,1,0) (3,1,0) (3,1,1)
(2,1,1) (3,2,0) (3,2,1) (3,2,2)
(4,0,0) (4,1,0) (4,1,1) (4,2,0) (4,2,1)
(4,2,2) (4,3,0) (4,3,1) (4,3,2) (4,3,3)