PHYS 250

Lecture 6.2

Schrodinger in 3D #2

Today

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Review
- xyz Schrodinger
- Rectangular Box Potential
- Spherical Derivatives
- Separating Spherical Schrodinger
- Spherical Harmonics solutions for θ, ϕ dependence

Radial Schrodinger Equation

Spherical Square Well

Spherical Shell Potential

Schrodinger Hydrogen Atom

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- Students will be using the online system, Blue by Explorance, specifically designed to deliver and complete course surveys. The system is housed on a secure server located in Canada.
- You can log into Blue via Canvas during the survey period to check your response rates.

Suggestions for increasing response rate:

- Consider letting students know how the survey responses are used at UBC so they are aware that their input can make a difference, such as by providing feedback that you can use to make improvements in the future.
- Assure students that the surveys are confidential. You will receive a summary report only after all grades are submitted and finalized. There is no risk of repercussions to students for giving honest, constructive feedback.
- Where feasible, provide 10-15 minutes in class for students to complete the survey using their devices to log into Canvas.

Schrodinger in *xyz*

$$\psi(x,t) \rightarrow \psi(x,y,z,t) = \psi(\vec{x},t) \qquad V(x) \rightarrow V(x,y,z) = V(\vec{x},t)$$

$\frac{\partial^2 \psi}{\partial x^2} \rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \nabla^2 \psi$ where $\nabla^2 \psi$ is called the Laplacian operator.

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

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

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

Particle in Rectangular Box

$V(\vec{x}) = 0$ if $0 < x < w_x$, and $0 < y < w_y$, and $0 < z < w_z$, otherwise $V(\vec{x}) = +\infty$

Boundary conditions: $\psi(\vec{x}) = 0$ at all 6 faces

Solutions: $\psi_{nx,\,ny,\,nz}(\vec{x}) = \sin\left(\frac{n_x \pi}{w_x} x\right) \cdot \sin\left(\frac{n_y \pi}{w_y} y\right) \cdot \sin\left(\frac{n_z \pi}{w_z} z\right)$ with $n_x, n_y, n_z > 0$

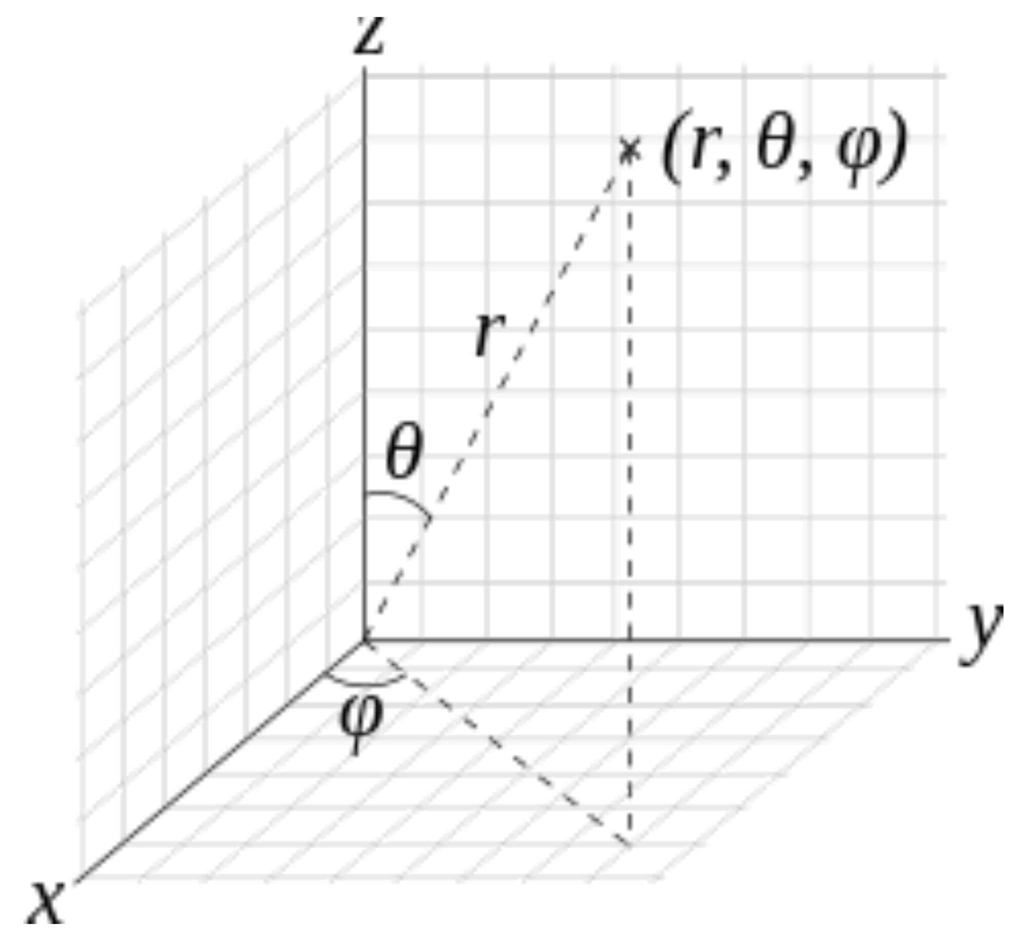
Energies: $E_{nx,\,ny,\,nz} = \left[\frac{n_x^2}{w_x^2} + \frac{n_y^2}{w_y^2} + \frac{n_z^2}{w_z^2}\right] \cdot \frac{\hbar^2 \pi^2}{2m}$

Note that there are 3 different n values in 3D (there was only 1 in 1D)

There could be more than one wavefunction with the same energy.
These are called degenerate states.

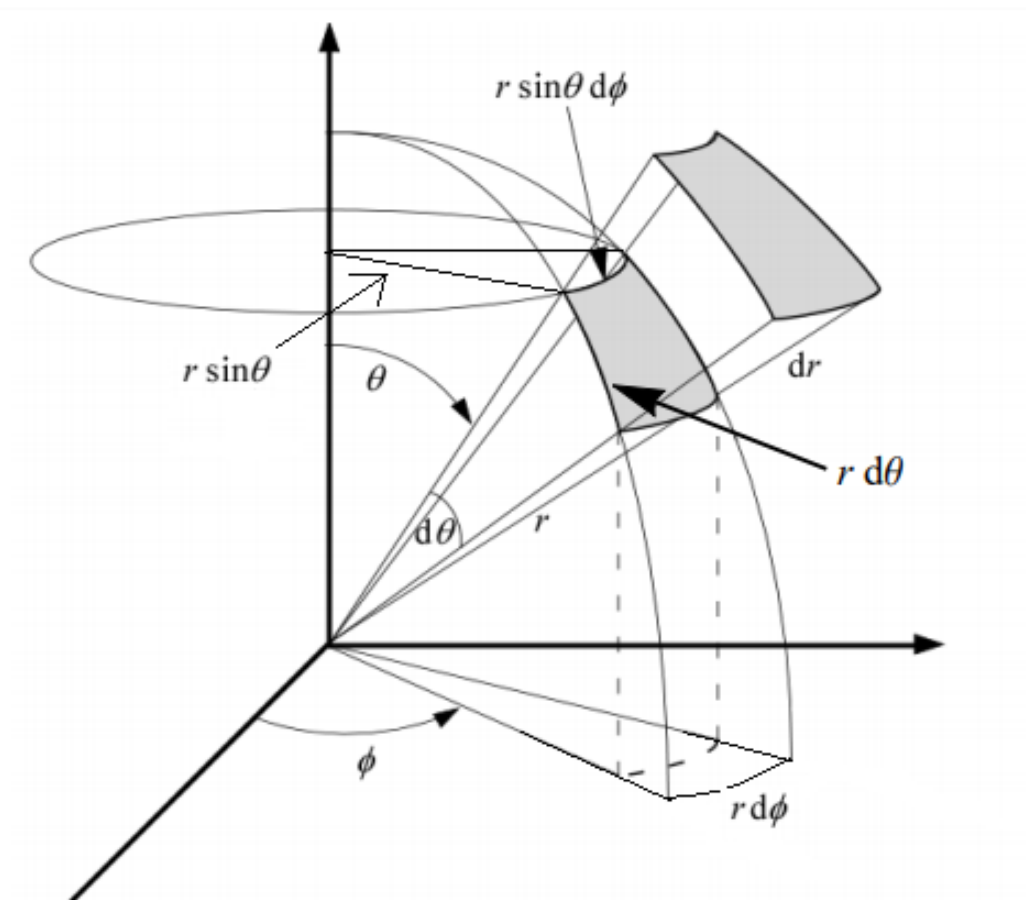
Spherical Coordinates

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



The coordinate "steps" are
$\Delta_r = \Delta r,\ \Delta_\theta = r\Delta\theta,$ and $\Delta_\phi = r\sin\theta\,\Delta\phi$

The volume element looks like this:



Spherical Derivatives

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

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

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

Spherical Schrodinger

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

Separable into $\psi(r,\theta,\phi)=F(r)\cdot G(\theta)\cdot H(\phi)$

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

Separate θ and ϕ: $\lambda\sin^2\theta+\sin\theta\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial G}{\partial\theta}\right]\frac{1}{G}=\mu=-\left[\frac{\partial^2 H}{\partial\phi^2}\right]\frac{1}{H}$

Solve ϕ: $H(\phi)=\exp\left[im\phi\right]$ with $\mu=m^2$ with $m=0,\pm1,\pm2,$ etc.

Associated Legendre Functions

Solutions for θ are the Legendre Functions $P_\ell^m(\theta)$ with $\lambda = \ell(\ell+1)$

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

These are normalized so

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

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 (spherical) potential.

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

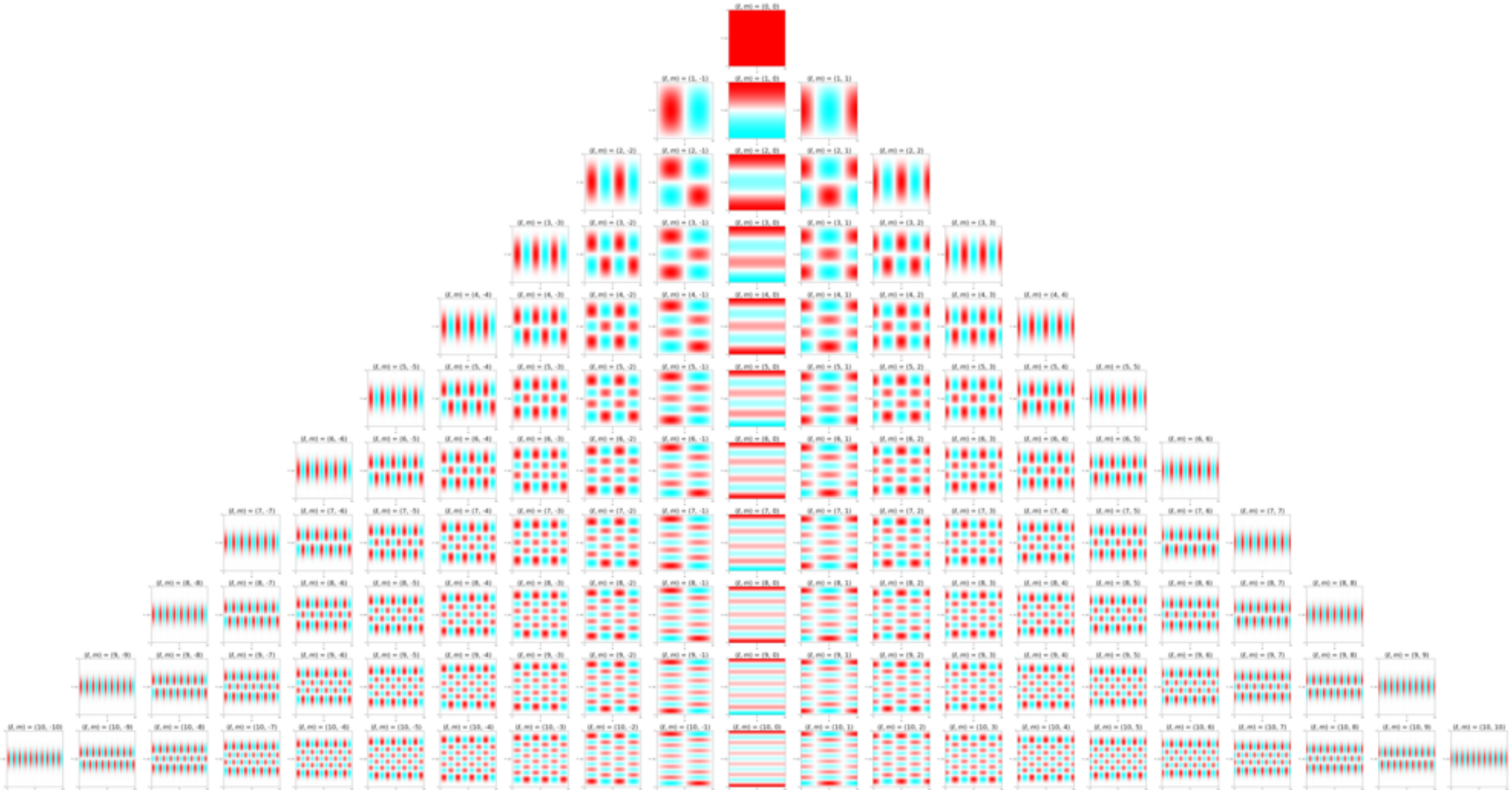
The power of $\sin\theta$ is $|m|$.

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 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.



Radial Schrodinger Equation

The radial Schrodinger Equation is

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

Capital M to avoid confusion with little m from the Spherical Harmonics.

Multiply both sides by $\frac{\hbar^2}{2Mr^2}F(r)$ and re-arrange to get

$$-\frac{\hbar^2}{2Mr^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial F}{\partial r}\right] + \left[V(r) + \frac{\hbar^2 \lambda}{2Mr^2}\right]F(r) = EF(r)$$

This looks a little like the 1D Schrodinger equation, except for the red stuff.

Radial Schrodinger Equation 2

One new term comes in like a correction to the potential:

$$V(r) \rightarrow V(r) + \frac{\hbar^2 \lambda}{2Mr^2} = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2}$$

The term $\frac{\hbar^2 \ell(\ell+1)}{2Mr^2}$ is the kinetic energy due to angular momentum,

which classically is $\frac{p_{orbital}^2}{2M} = \frac{(r \cdot p_{orbital})^2}{2Mr^2} = \frac{L^2}{2Mr^2}$ with $L^2 = \hbar^2 \ell(\ell+1)$

So angular momentum is $L = \hbar\ell$ (almost).

There is also a transformation that gets rid of the extra factors of r^2.

Radial Schrodinger Equation 3

Substitute $F(r)=\dfrac{U(r)}{r}$ and $\dfrac{\partial F}{\partial r}=\dfrac{r\dfrac{\partial U}{\partial r}-U}{r^2}$

into

$$-\frac{\hbar^2}{2Mr^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial F}{\partial r}\right]+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]F(r)=EF(r)$$

and we get

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r\frac{\partial U}{\partial r}-U\right)+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]\frac{U}{r}=E\frac{U}{r}$$

Now do the derivative to get

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\left(\frac{\partial U}{\partial r}+r\frac{\partial^2 U}{\partial r^2}-\frac{\partial U}{\partial r}\right)+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]\frac{U}{r}=E\frac{U}{r}$$

Do the cancellation

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\left(r\frac{\partial^2 U}{\partial r^2}\right)+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]\frac{U}{r}=E\frac{U}{r}$$

Radial Schrodinger Equation 4

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\left(r\frac{\partial^2 U}{\partial r^2}\right)+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]\frac{U}{r}=E\frac{U}{r}$$

Multiply both sides by r to get

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial r^2}U(r)+\left[V(r)+\frac{\hbar^2\lambda}{2Mr^2}\right]U(r)=EU(r)$$

This is exactly the same form as the 1D Schrodinger Equation, except for the extra term due to angular kinetic energy.

But $F(r)=\frac{U(r)}{r}$, so if $U(r)$ is finite at $r=0$, we get infinite $F(0)$.

So unlike 1D Schrodinger, we have the condition that $U(r)=0$ at $r=0$.

In order for the wavefunction to be normalizable, we must have $F(r)\rightarrow 0$ as $r\rightarrow\infty$ faster than $1/r^2$. That implies $U(r)\rightarrow 0$ faster than $1/r$.

The Form of Spherical Solutions

The full wavefunction is $\psi_{k\ell m}(r,\theta,\phi) = \dfrac{U_{k\ell}(r)}{r} \cdot Y_\ell^m(\theta,\phi)$

The same ℓ appears in both $U_{k\ell}(r)$ and $Y_\ell^m(\theta,\phi)$

The U-function satisfies the radial Schrodinger equation:

$$-\frac{\hbar^2}{2M}\frac{\partial^2 U_{k\ell}}{\partial r^2} + \left[V(r) + \frac{\hbar^2 \ell \cdot (\ell+1)}{2Mr^2}\right] U_{k\ell} = EU_{k\ell} \quad \text{with} \quad U_{k\ell}(0) = 0$$

This must be solved for $\ell = 0$, then $\ell = 1$, then $\ell = 2$, etc.

Each $\psi_{k\ell m}(r,\theta,\phi)$ has an energy $E_{k\ell}$. Since m doesn't appear in the radial equation, the different m states for given k and ℓ have the same energy.

Quantum Indices

Solutions to 1D Schrodinger have 1 quantum index, usually called n.

Solutions to *xyz* Schrodinger have 3 quantum indices n_x, n_y, n_z.

The spherical wavefunction $\psi_{k\ell m}(r,\theta,\phi)=\dfrac{U_{k\ell}(r)}{r}\cdot Y_\ell^m(\theta,\phi)$ has 3 indices

The $H_m(\phi)=e^{im\phi}$ function has 1 quantum index m.

The $P_\ell^m(\theta)$ function has 2 quantum indices ℓ and the same m.

The Spherical Harmonics $Y_\ell^m(\theta,\phi)$ have 2 quantum indices: ℓ and m.

The $U_{k\ell}(r)$ radial function has 2 quantum indices: k, and the same ℓ as $Y_\ell^m(\theta,\phi)$

Energy vs k and ℓ

The lowest k value is set by convenience: 0 some potentials, 1 for others.

The lowest value for ℓ is always zero, which gives the lowest potential correction

$$\frac{\hbar^2 \ell(\ell+1)}{2Mr^2} = 0$$

The lowest energy will be for $\ell = 0$ and whatever the smallest k value is.

Increasing k for a given ℓ will increase the energy.

Increasing ℓ for a given k will increase the energy.

It turns out for a $1/r$ potential (and <u>only</u> $1/r$), increasing k by 1 at fixed ℓ gives <u>exactly</u> the same energy as <u>increasing</u> ℓ by 1 at fixed k.

So we talk about $n = k + \ell$. But <u>only</u> for $1/r$ potentials! In general, it's k and ℓ.

Infinite Spherical Square Well

The potential is zero inside a sphere with radius R, and infinite outside.

The reduced radial equation inside is $-\frac{\hbar^2}{2M}\frac{\partial^2 U}{\partial r^2}+\frac{\hbar^2 \ell(\ell+1)}{2Mr^2}U = EU$

The U function must be zero at $r = 0$ (so U/r is not infinite), and zero at radius R.

If $\ell = 0$, it's just $-\frac{\hbar^2}{2M}\frac{\partial^2 U}{\partial r^2}+0 = EU$

The equation and boundary conditions are exactly the same as for the infinite square well in 1D. So the solutions are the same:

$$U_{k0}(r) = \sin\frac{k\pi r}{R} \text{ with } k = 1, 2, 3, \dots$$

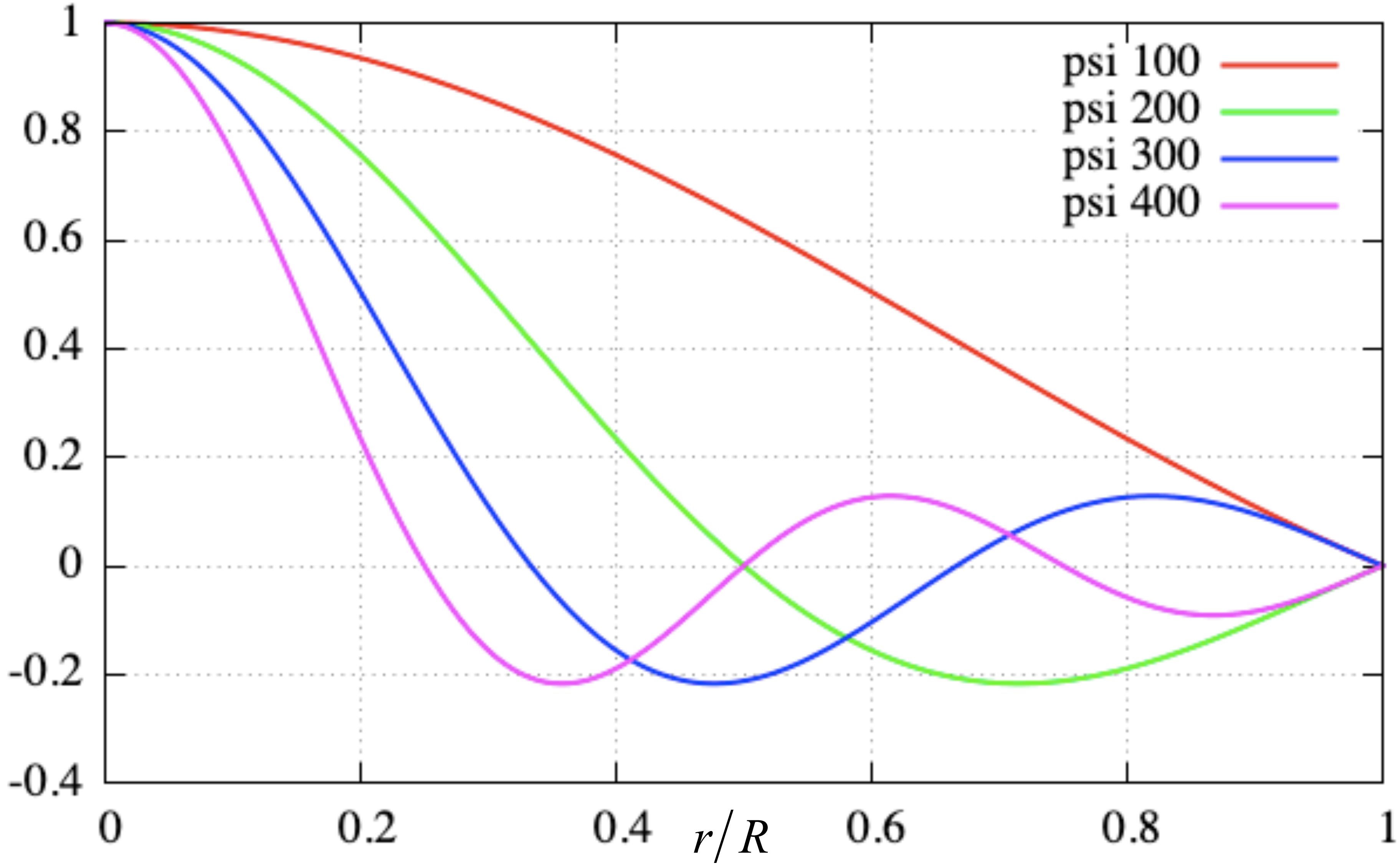
and energies

$$E_{k0} = k^2 \frac{\hbar^2\pi^2}{2MR^2}$$

Infinite Spherical Square Well 2

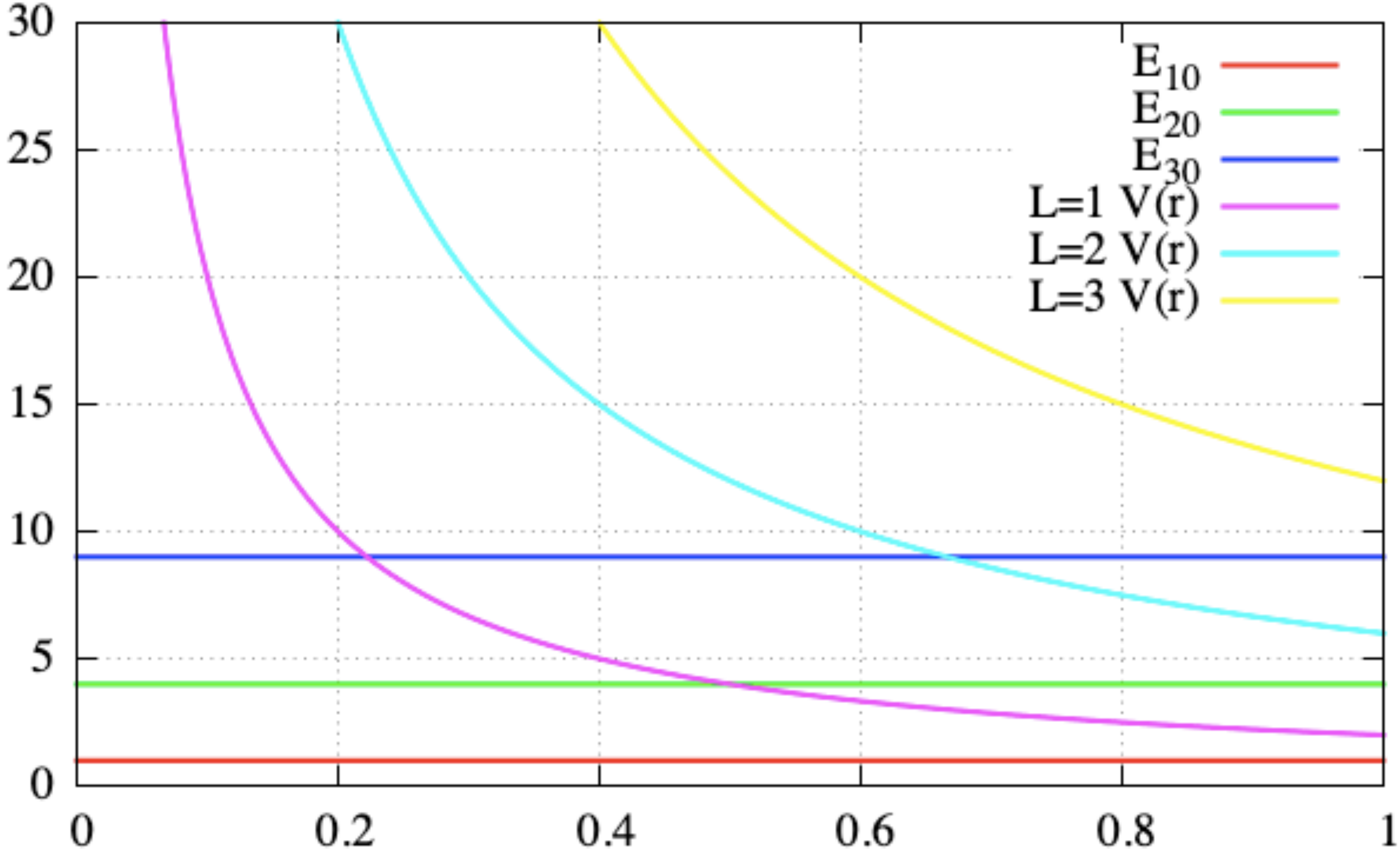
For ψ, we divide by r, and multiply by the Spherical Harmonic.
Since $\ell = 0$, only $m = 0$ is possible. That Spherical Harmonic is constant.
So the complete wavefunctions (not normalized) for $\ell = 0$ are

$$\psi_{k00} = \frac{1}{r}\sin\frac{k\pi r}{R} \cdot Y_0^0(\theta,\phi) = \frac{1}{r}\sin\frac{k\pi r}{R}$$



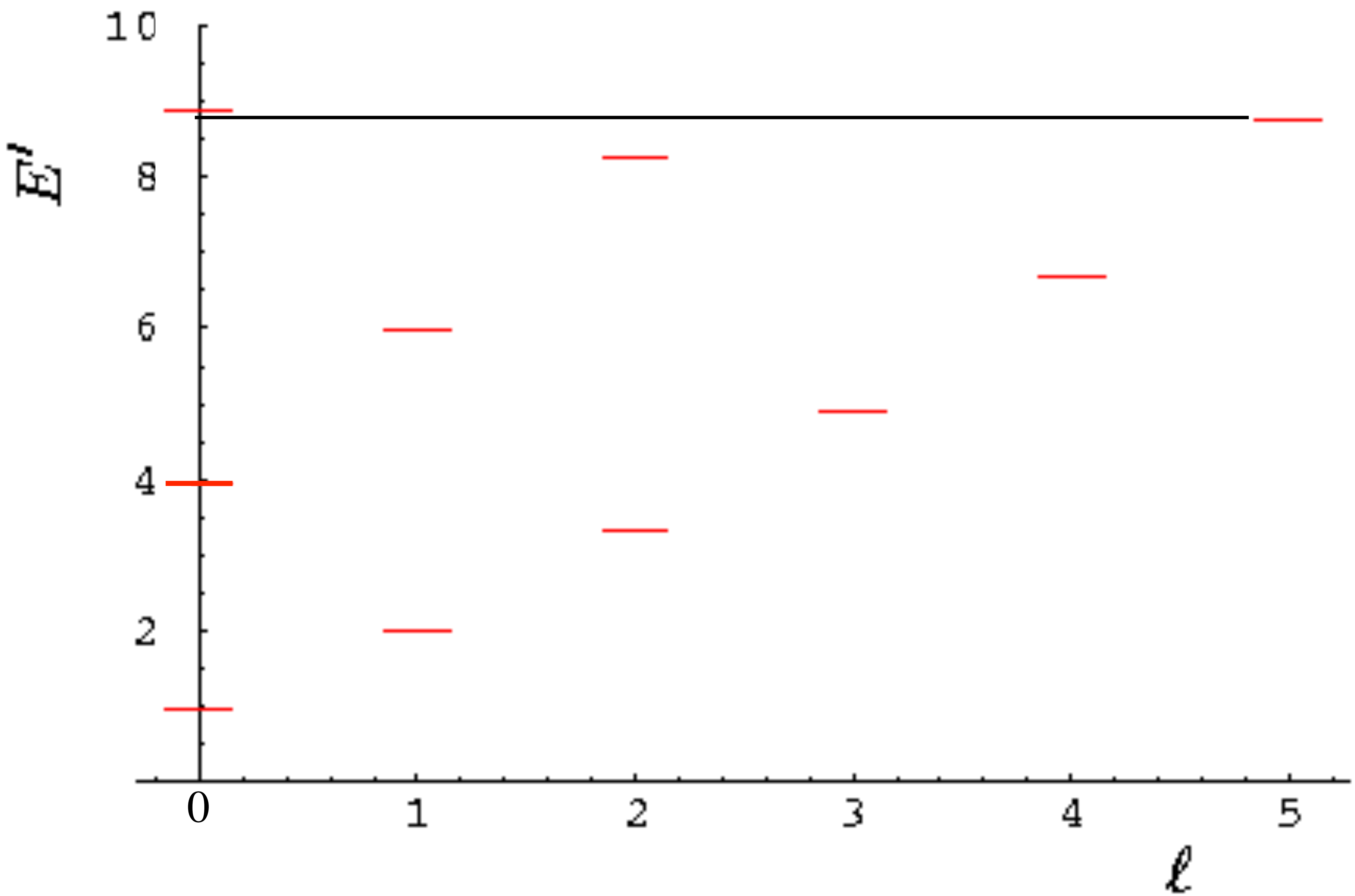
Infinite Spherical Square Well 3

When $\ell > 0$, the effective potential looks like $1/r^2$.



The solutions are Bessel functions, and we won't do them here.

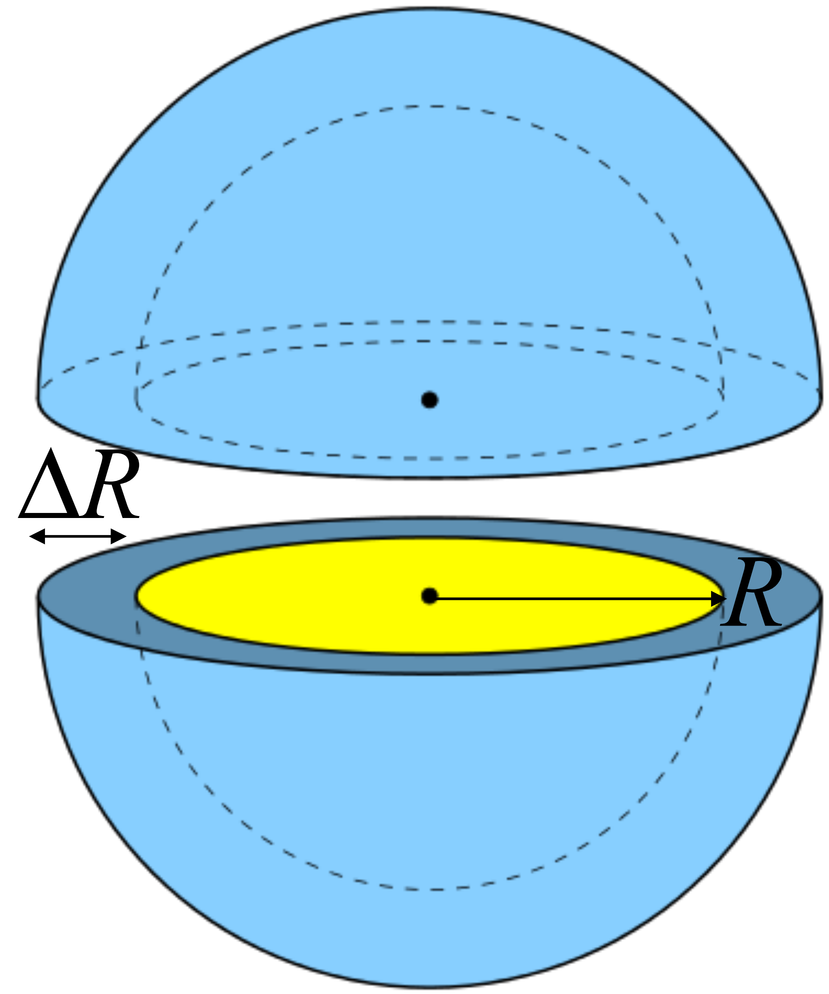
Infinite Spherical Square Well 4



Increasing k (going up at fixed ℓ) increases the energy.
Increasing ℓ at fixed k (diagonal) increases the energy. But nothing lines up.

Spherical Shell Potential

$V = 0$ for $R < r < R + \Delta R$, $V = \infty$ elsewhere



The reduced radial equation inside is

same as before: $-\dfrac{\hbar^2}{2M}\dfrac{\partial^2 U}{\partial r^2} + \dfrac{\hbar^2 \ell(\ell+1)}{2Mr^2}U = EU$

The U function must go to zero at R and $R + \Delta R$.

For $\ell = 0$, $-\dfrac{\hbar^2}{2M}\dfrac{\partial^2 U}{\partial r^2} + 0 = EU$

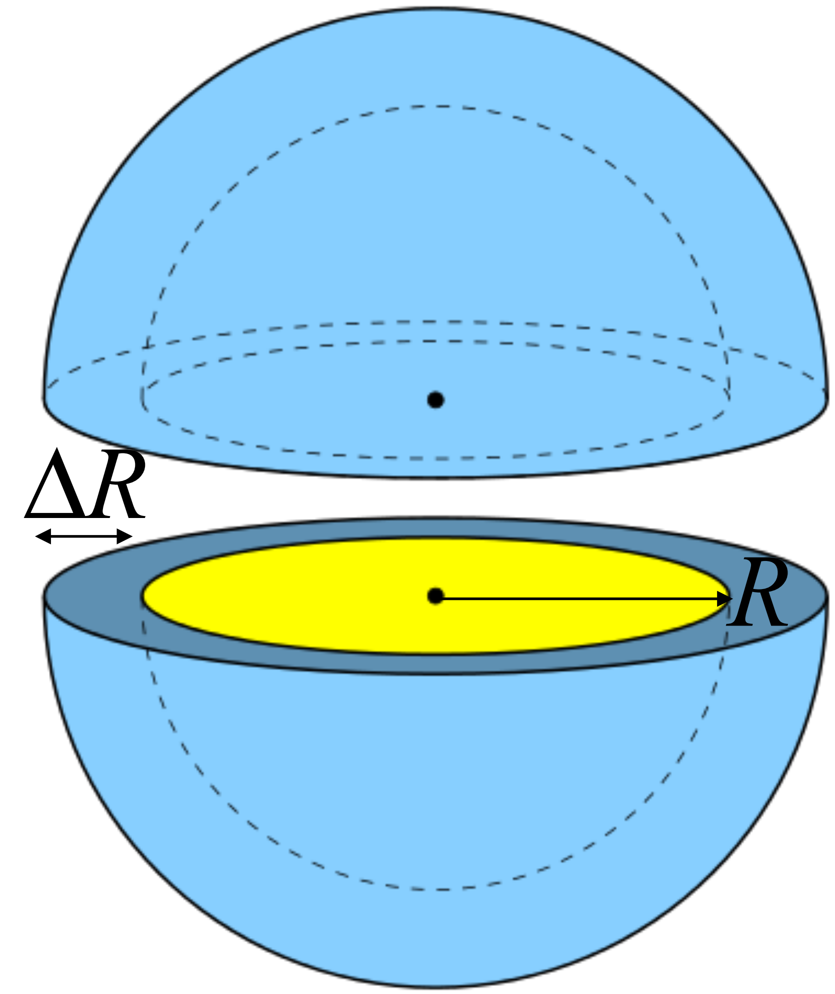
So the solutions are

$$U_{k0}(r) = \sin\frac{k\pi \cdot (r - R)}{\Delta R} \text{ with } k = 1, 2, 3, \ldots$$

and energies
$$E_{k0} = k^2 \frac{\hbar^2 \pi^2}{2M \cdot (\Delta R)^2}$$

Spherical Shell Potential 2

$$-\frac{\hbar^2}{2M}\frac{\partial^2 U}{\partial r^2}+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}U=EU$$



If $\Delta R \ll R$, the extra term is essentially constant.

$$\frac{\hbar^2\ell(\ell+1)}{2Mr^2}\to\frac{\hbar^2\ell(\ell+1)}{2M\cdot\left(R+\Delta R/2\right)^2}\to\frac{\hbar^2\ell(\ell+1)}{2MR^2}$$

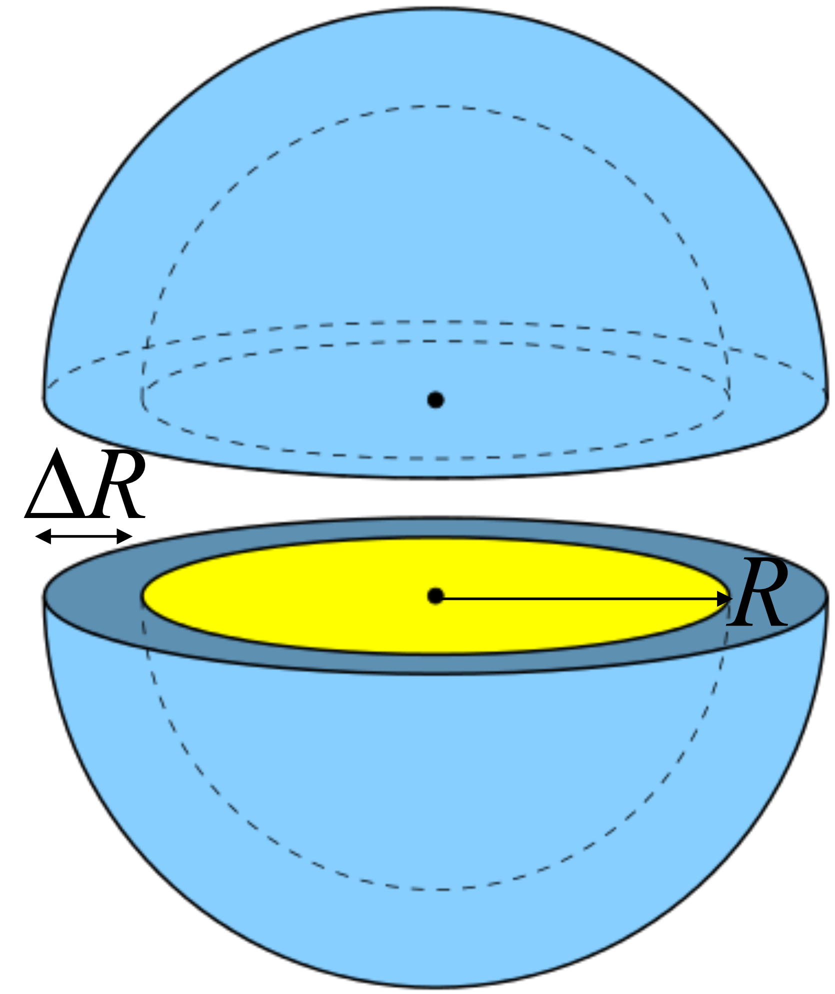
So the energy goes up by $\Delta E_\ell \approx \frac{\hbar^2\ell(\ell+1)}{2MR^2}$ for $\ell > 0$

Since we assumed $\Delta R \ll R$, this is much less than $E_{k0} = k^2\frac{\hbar^2\pi^2}{2M\cdot(\Delta R)^2}$

We can combine these into $E_{k\ell} \approx \frac{\hbar^2\pi^2}{2M\cdot(\Delta R)^2}\cdot\left[k^2+\frac{\ell\cdot(\ell+1)}{\pi^2}\cdot\frac{\Delta R^2}{R^2}\right]$

Spherical Shell Potential 3

$$E_{k\ell} \approx \frac{\hbar^2 \pi^2}{2M \cdot (\Delta R)^2} \cdot \left[k^2 + \frac{\ell \cdot (\ell+1)}{\pi^2} \cdot \frac{\Delta R^2}{R^2} \right]$$



For $\ell = 0$, the bracket factor is 1 for $k = 1$ and 4 for $k = 2$, an increase of 3.

What ℓ value makes $E_{1\ell}$ be as large as E_{20}?

$$\frac{\ell \cdot (\ell+1)}{\pi^2} \cdot \frac{\Delta R^2}{R^2} = 3 \rightarrow \ell \cdot (\ell+1) = 3 \cdot \left(\frac{\pi R}{\Delta R} \right)^2$$

If $R = 10 \cdot \Delta R$, the right side is 2961 so $\ell \approx 54$.

There are $2\ell + 1$ allowed m-values for each ℓ value,
so there are about $55^2 = 3025$ different $k = 1$ states below the first $k = 2$ state.

Rotating Molecules

We could change the radial potential from a square well to something more realistic, like an offset harmonic oscillator: $V(r) = \frac{1}{2}k \cdot (r - R)^2$.

That would be a decent model of the potential for small vibrations of a molecule made of 2 atoms with average separation R.

That molecule could also rotate.

There could easily be hundreds or thousands or rotational states between successive radial states.

This is the origin of "molecular absorption bands."

Radial Equation for Coulomb Potential

We plug in the Coulomb potential $V(r) = -\frac{q^2}{4\pi\varepsilon_0 r}$ to get

$$-\frac{\hbar^2}{2M}\frac{\partial^2 U}{\partial r^2} + \left[-\frac{q^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2}\right]U = EU(r)$$

Put the derivative on one side, and everything else on the other side

$$-\frac{\hbar^2}{2M}\frac{\partial^2 U}{\partial r^2} = \left[E + \frac{q^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2 \ell(\ell+1)}{2Mr^2}\right]U(r)$$

Multiply by $-\frac{2M}{\hbar^2}$

$$\frac{\partial^2 U}{\partial r^2} = \left[-\frac{2M}{\hbar^2}E - \frac{2Mq^2}{4\pi\hbar^2\varepsilon_0}\frac{1}{r} + \ell(\ell+1)\frac{1}{r^2}\right]U(r)$$

Radial Equation for Coulomb Potential 2

$$\frac{\partial^2 U}{\partial r^2} = \left[-\frac{2M}{\hbar^2} E - \frac{2Mq^2}{4\pi\hbar^2\varepsilon_0} \frac{1}{r} + \ell(\ell+1)\frac{1}{r^2} \right] U(r)$$

Define $X = \frac{2M}{\hbar^2}$ and $Y = \frac{Mq^2}{2\pi\hbar^2\varepsilon_0}$ to save some writing

$$\frac{\partial^2 U}{\partial r^2} = \left[-XE - Y\frac{1}{r} + \ell(\ell+1)\frac{1}{r^2} \right] U(r)$$

At large radius, this is approximately $\frac{\partial^2 U}{\partial r^2} = -X \cdot E \cdot U(r)$.

X is positive, but we expect the bound state energies to be negative.

So the second derivative is proportional to the function, with a plus sign.
So the solutions should be exponential at large radius.

First Guess

A decaying exponential satisfies the boundary condition as $r \to \infty$, but violates the condition that $U(r=0)=0$. Let's try

$$U(r) = r^n \cdot \exp\left(-\frac{r}{b}\right)$$

$$\frac{\partial U}{\partial r} = nr^{n-1} \cdot \exp\left(-\frac{r}{b}\right) - \frac{r^n}{b} \cdot \exp\left(-\frac{r}{b}\right)$$

$$\frac{\partial^2 U}{\partial r^2} = n(n-1)r^{n-2} \cdot \exp\left(-\frac{r}{b}\right) - \frac{nr^{n-1}}{b} \cdot \exp\left(-\frac{r}{b}\right) - \frac{nr^{n-1}}{b} \cdot \exp\left(-\frac{r}{b}\right) + \frac{r^n}{b^2} \cdot \exp\left(-\frac{r}{b}\right)$$

$$= \left[n(n-1)\frac{1}{r^2} - \frac{2n}{b}\frac{1}{r} + \frac{1}{b^2} \right] r^n \exp\left(-\frac{r}{b}\right)$$

Plug into $\frac{\partial^2 U}{\partial r^2} = \left[-XE - Y\frac{1}{r} + \ell(\ell+1)\frac{1}{r^2} \right] U(r)$ which gives

$$\left[n(n-1)\frac{1}{r^2} - \frac{2n}{b}\frac{1}{r} + \frac{1}{b^2} \right] r^n \exp\left(-\frac{r}{b}\right) = \left[-XE - Y\frac{1}{r} + \ell(\ell+1)\frac{1}{r^2} \right] r^n \exp\left(-\frac{r}{b}\right)$$

First Guess 2

$$\left[n(n-1)\frac{1}{r^2}-\frac{2n}{b}\frac{1}{r}+\frac{1}{b^2}\right]r^n\exp\left(-\frac{r}{b}\right)=\left[-XE-Y\frac{1}{r}+\ell(\ell+1)\frac{1}{r^2}\right]r^n\exp\left(-\frac{r}{b}\right)$$

Divide out $r^n\exp(-br)$ and rearrange the terms

$$\left[n(n-1)\frac{1}{r^2}-\frac{2n}{b}\frac{1}{r}+\frac{1}{b^2}\right]=\left[\ell(\ell+1)\frac{1}{r^2}-Y\frac{1}{r}-XE\right]$$

For this to be true at all r, we need

$$\frac{2n}{b}=Y\rightarrow b=\frac{2n}{Y}=2n\cdot\frac{2\pi\hbar^2\varepsilon_0}{Mq^2}=n\cdot\frac{4\pi\hbar^2\varepsilon_0}{Mq^2}$$

The Bohr Model radius is $a_0=\dfrac{4\pi\hbar^2\varepsilon_0}{q^2M}$ so $b=na_0$.

First Guess 3

We also need

$$\frac{1}{b^2} = -X \cdot E \rightarrow E = -\frac{1}{b^2}\frac{1}{X} = \left(\frac{1}{n}\frac{Mq^2}{4\pi\hbar^2\varepsilon_0}\right)^2 \cdot \frac{\hbar^2}{2M} = -\frac{1}{n^2}\frac{M}{2}\left(\frac{q^2}{4\pi\hbar^2\varepsilon_0}\right)^2$$

Those are exactly the Bohr Model energies!

We also need $n(n-1) = \ell(\ell+1)$. This requires $n = \ell + 1$.

The lowest $\ell = 0$, so the lowest power n in $r^n \cdot \exp\left(-\frac{r}{b}\right)$ is $n = 1$.

First Few $U(r)$ Solutions

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$
$n = 4$				$r^4 \exp\left(-\frac{r}{4a_0}\right)$
$n = 3$			$r^3 \exp\left(-\frac{r}{3a_0}\right)$	
$n = 2$		$r^2 \exp\left(-\frac{r}{2a_0}\right)$		
$n = 1$	$r \exp\left(-\frac{r}{a_0}\right)$			

Observations

In the Bohr Model, the lowest state has angular momentum = $\hbar$.

In Schrodinger, the lowest state has $\ell = 0$, which means zero angular momentum.

In the Bohr Model, an atom is planar, no matter what the angular momentum.

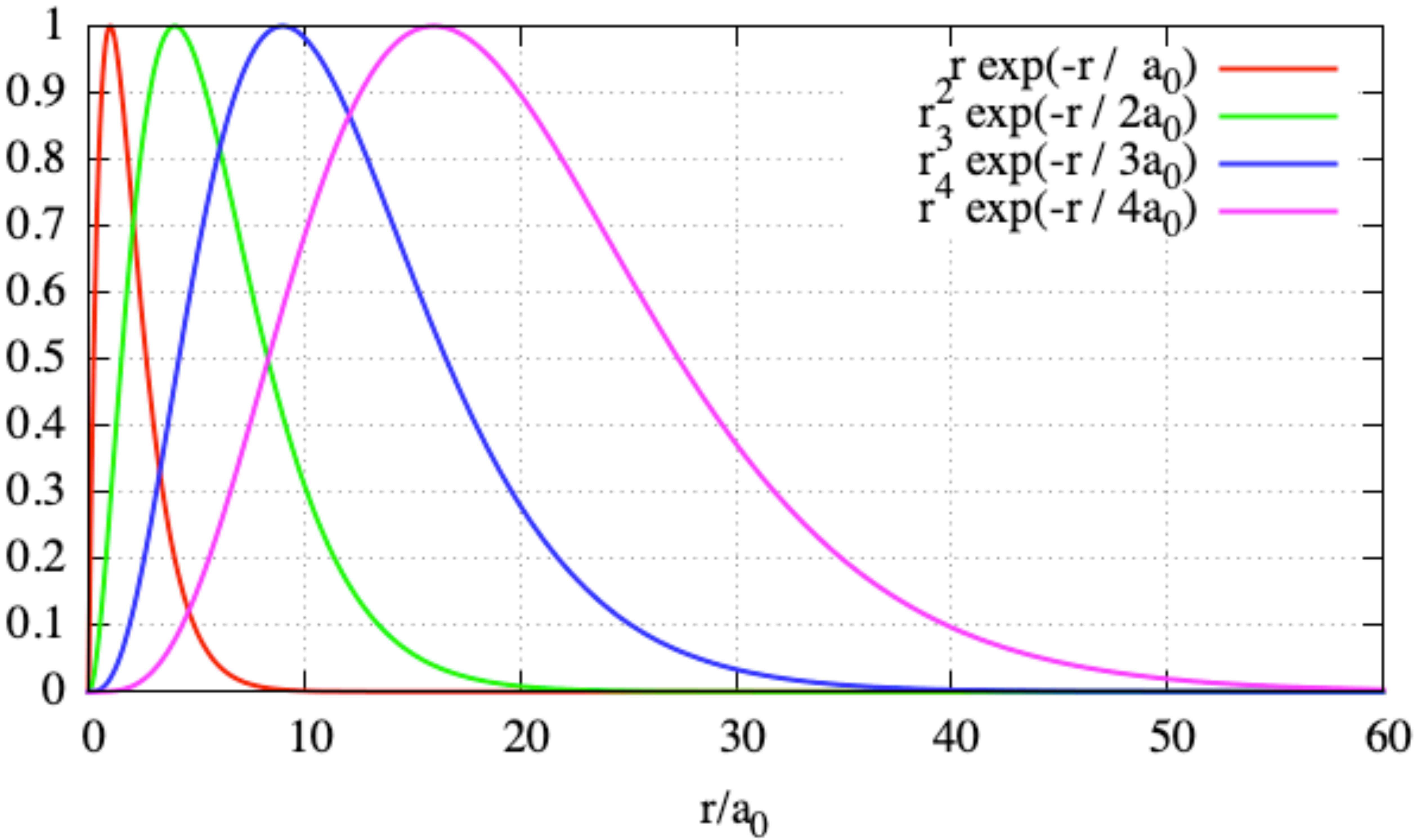
In Schrodinger, atoms are not flat.

The $\ell = 0$ states are spherical, because that Spherical Harmonic is uniform.

The states with $\ell > 0$ are neither spherical nor flat. They are the product of a radial wavefunction and a non-uniform Spherical Harmonic.

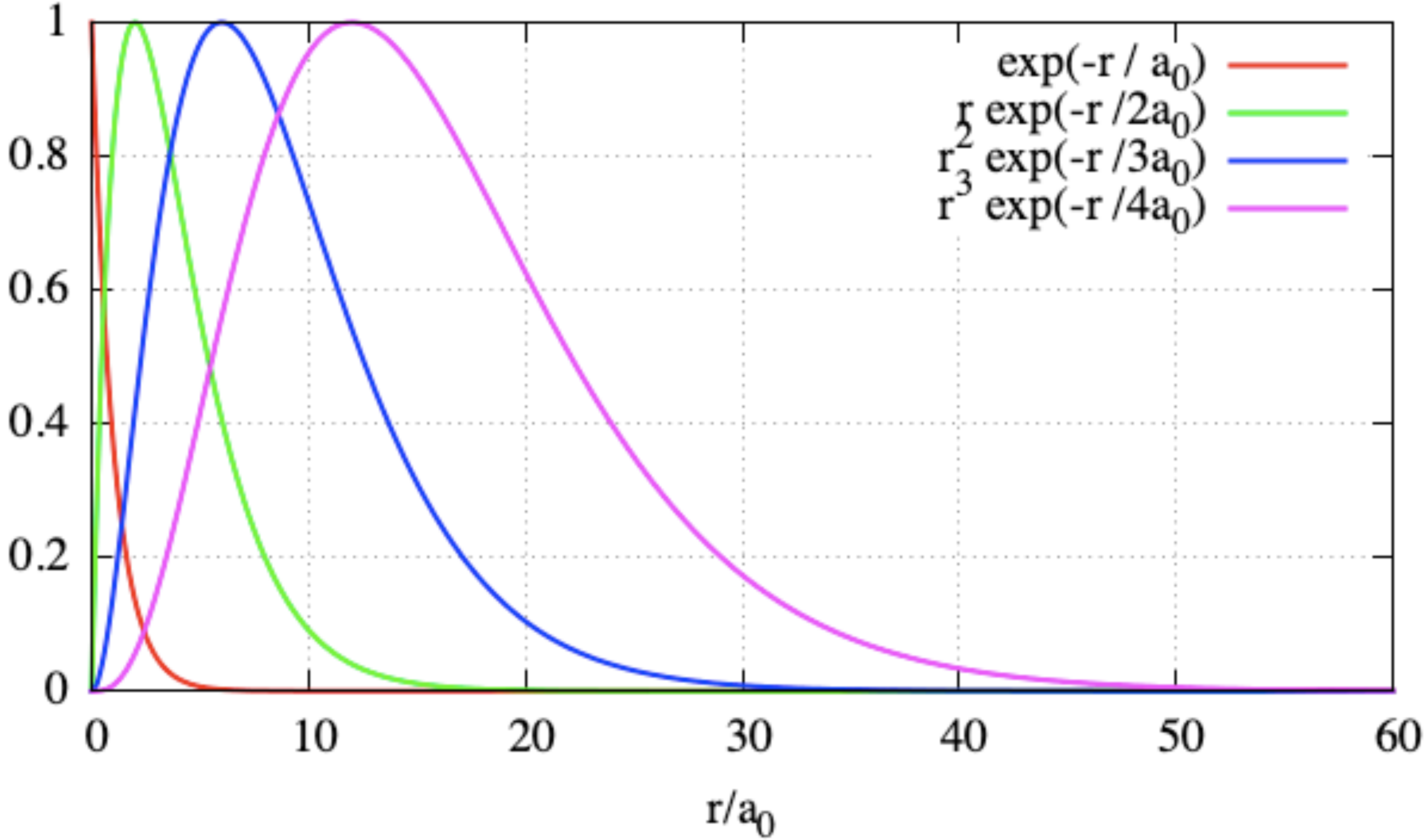
We will see soon that the r-dependence of the wavefunction can get complicated.

First Few $U(r)$ Solutions



The peaks are at $1, 4, 9$, and 16, which is how the Bohr orbit radius depends on n.

First Few $F(r)$ Solutions



Another Guess

Let's guess that the solutions are polynomials in r times exponentials.
The simplest is a 2-term polynomial.

$$U(r) = \left[r^n + Ar^{n-1}\right]\cdot \exp\left(-\frac{r}{b}\right)$$

$$\frac{\partial U}{\partial r} = \left[nr^{n-1} + A(n-1)r^{n-2}\right]\cdot \exp\left(-\frac{r}{b}\right) - \frac{r^n + Ar^{n-1}}{b}\cdot \exp\left(-\frac{r}{b}\right)$$

$$\frac{\partial^2 U}{\partial r^2} = \left[n(n-1)r^{n-2} + A(n-1)(n-2)r^{n-3}\right]\cdot \exp\left(-\frac{r}{b}\right) - \frac{nr^{n-1} + A(n-1)r^{n-2}}{b}\cdot \exp\left(-\frac{r}{b}\right)$$

$$-\frac{nr^{n-1} + A(n-1)r^{n-2}}{b}\cdot \exp\left(-\frac{r}{b}\right) + \frac{r^n + Ar^{n-1}}{b^2}\cdot \exp\left(-\frac{r}{b}\right)$$

$$= \left\{A(n-1)(n-2)r^{n-3} + \frac{bn(n-1) - 2A(n-1)}{b}r^{n-2} + \frac{-2bn + A}{b^2}r^{n-1} + \frac{1}{b^2}r^n\right\}\exp\left(-\frac{r}{b}\right)$$

Another Guess 2

Expand the right-hand side of the reduced radial Schrodinger Equation:

$$\left[-XE - Y\frac{1}{r} + \ell(\ell+1)\frac{1}{r^2}\right]\left[r^n + Ar^{n-1}\right]\exp\left(-\frac{r}{b}\right)$$

$$= \left[-XEr^n - Yr^{n-1} + \ell(\ell+1)r^{n-2} - AXEr^{n-1} - AYr^{n-2} + A\ell(\ell+1)r^{n-3}\right]\exp\left(-\frac{r}{b}\right)$$

So the total equation is

$$\left\{A(n-1)(n-2)r^{n-3} + \frac{bn(n-1) - 2A(n-1)}{b}r^{n-2} + \frac{-2bn + A}{b^2}r^{n-1} + \frac{1}{b^2}r^n\right\}\exp\left(-\frac{r}{b}\right)$$

$$= \left\{-XEr^n - Yr^{n-1} + \ell(\ell+1)r^{n-2} - AXEr^{n-1} - AYr^{n-2} + A\ell(\ell+1)r^{n-3}\right\}\exp\left(-\frac{r}{b}\right)$$

Match coefficients of r^{n-3}: $A(n-1)(n-2) = A\ell(\ell+1)$. This requires $n = \ell + 2$.

Match coefficients of r^n: $-XE = \frac{1}{b^2}$. The same result as the first guess.

Another Guess 3

$$\left\{A(n-1)(n-2)r^{n-3}+\frac{bn(n-1)-2A(n-1)}{b}r^{n-2}+\frac{-2bn+A}{b^2}r^{n-1}+\frac{1}{b^2}r^n\right\}\exp\left(-\frac{r}{b}\right)$$

$$=\left\{-XEr^n-Yr^{n-1}+\ell(\ell+1)r^{n-2}-AXEr^{n-1}-AYr^{n-2}+A\ell(\ell+1)r^{n-3}\right\}\exp\left(-\frac{r}{b}\right)$$

Match coefficients of r^{n-1}: $\frac{-2bn+A}{b^2}=-Y-AXE$.

Plug $-XE=\frac{1}{b^2}$ into the above: $\frac{-2bn+A}{b^2}=-Y+\frac{A}{b^2}$.

Do some cancellations and $\frac{-2n}{b}=-Y\rightarrow b=\frac{2n}{Y}=na_0$, same as the first guess.

Another Guess 4

$$\left\{A(n-1)(n-2)r^{n-3}+\frac{bn(n-1)-2A(n-1)}{b}r^{n-2}+\frac{-2bn+A}{b^2}r^{n-1}+\frac{1}{b^2}r^n\right\}\exp\left(-\frac{r}{b}\right)$$

$$=\left\{-XEr^n-Yr^{n-1}+\ell(\ell+1)r^{n-2}-AXEr^{n-1}-AYr^{n-2}+A\ell(\ell+1)r^{n-3}\right\}\exp\left(-\frac{r}{b}\right)$$

Match coefficients of r^{n-2}:

$$\frac{bn\cdot(n-1)-2A\cdot(n-1)}{b}=\ell\cdot(\ell+1)-AY$$

$$n\cdot(n-1)-\frac{2A\cdot(n-1)}{b}=\ell\cdot(\ell+1)-AY$$

Plug $n=\ell+2\rightarrow\ell=n-2$ and $Y=\frac{2n}{b}$ into right, and expand:

$$n^2-n-\frac{2nA}{b}+\frac{2A}{b}=(n-2)\cdot(n-1)-\frac{2nA}{b}=n^2-3n+2-\frac{2nA}{b}$$

Do some cancellations : $\frac{2}{b}A=2-2n\rightarrow A=\frac{2-2n}{2}b=\frac{1-n}{b}$

Another Guess 5

$$A = \frac{1-n}{b}$$

Plug in $b = na_0$ to get $A = n \cdot (1-n) a_0$

A <u>should</u> have dimensions of length for $U_{n\ell}(r) = \left[r^n + Ar^{n-1} \right] \exp\left(-\frac{r}{b} \right)$.

Another Guess 6

$U_{n\ell}(r) = \left[r^n + Ar^{n-1}\right]\exp\left(-\frac{r}{b}\right)$ with $n = \ell + 2$, meaning the minimum $n = 2$.

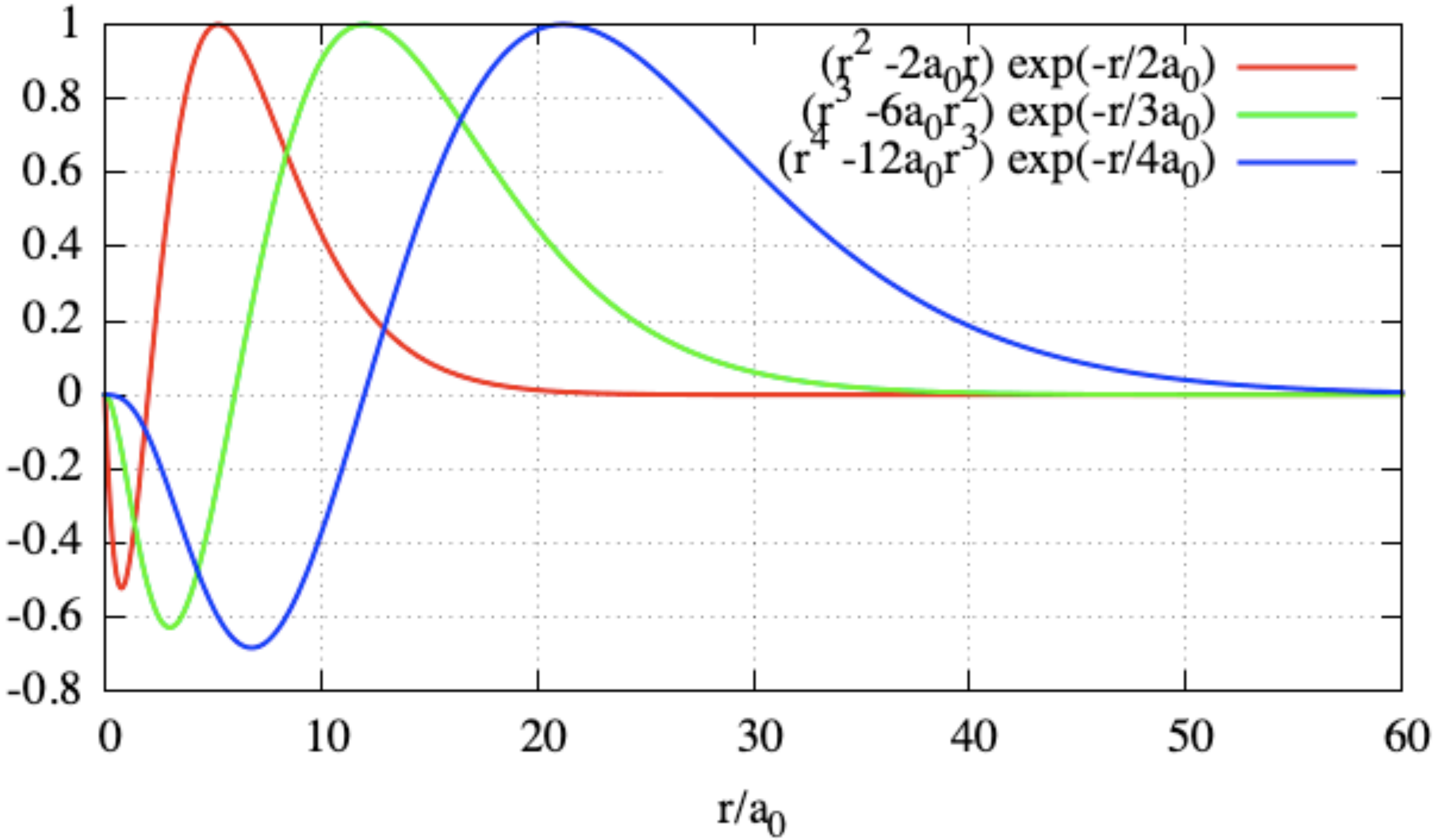
The values of $b = \frac{2n}{Y} = n \cdot \frac{4\pi\hbar^2\varepsilon_0}{Mq^2} = na_0$, the same as the first guess.

The values of $E_n = -\frac{1}{b^2}\frac{1}{X} = -\frac{1}{n^2}\frac{M}{2}\left(\frac{q^2}{4\pi\hbar^2\varepsilon_0}\right)^2$, the same as the first guess.

The value of $A = n \cdot (1-n)a_0$.

So we can write $U_{n\ell}(r) = \left[r^n + n(1-n)a_0 r^{n-1}\right]\exp\left(-\frac{r}{na_0}\right)$

Next Few $U(r)$ Solutions



Both Sets of U-Functions

	$\ell = 0$		$\ell = 1$		$\ell = 2$		$\ell = 3$
$n = 4$					$\left(r^4 - 12a_0r^3\right)e^{\frac{-r}{4a_0}}$	$r^4e^{\frac{-r}{4a_0}}$	
$n = 3$			$\left(r^3 - 6a_0r^2\right)e^{\frac{-r}{3a_0}}$	$r^3e^{\frac{-r}{3a_0}}$			
$n = 2$	$\left(r^2 - 2a_0r\right)e^{\frac{-r}{2a_0}}$	$r^2e^{\frac{-r}{2a_0}}$					
$n = 1$	$re^{\frac{-r}{a_0}}$						

The n value is in the denominator of the exponential, and the highest power of r.

But remember the actual wavefunction has a factor of $\frac{1}{r}$

Observations

We have found 2 solutions (so far) with the same n and different ℓ, for any $n > 0$.

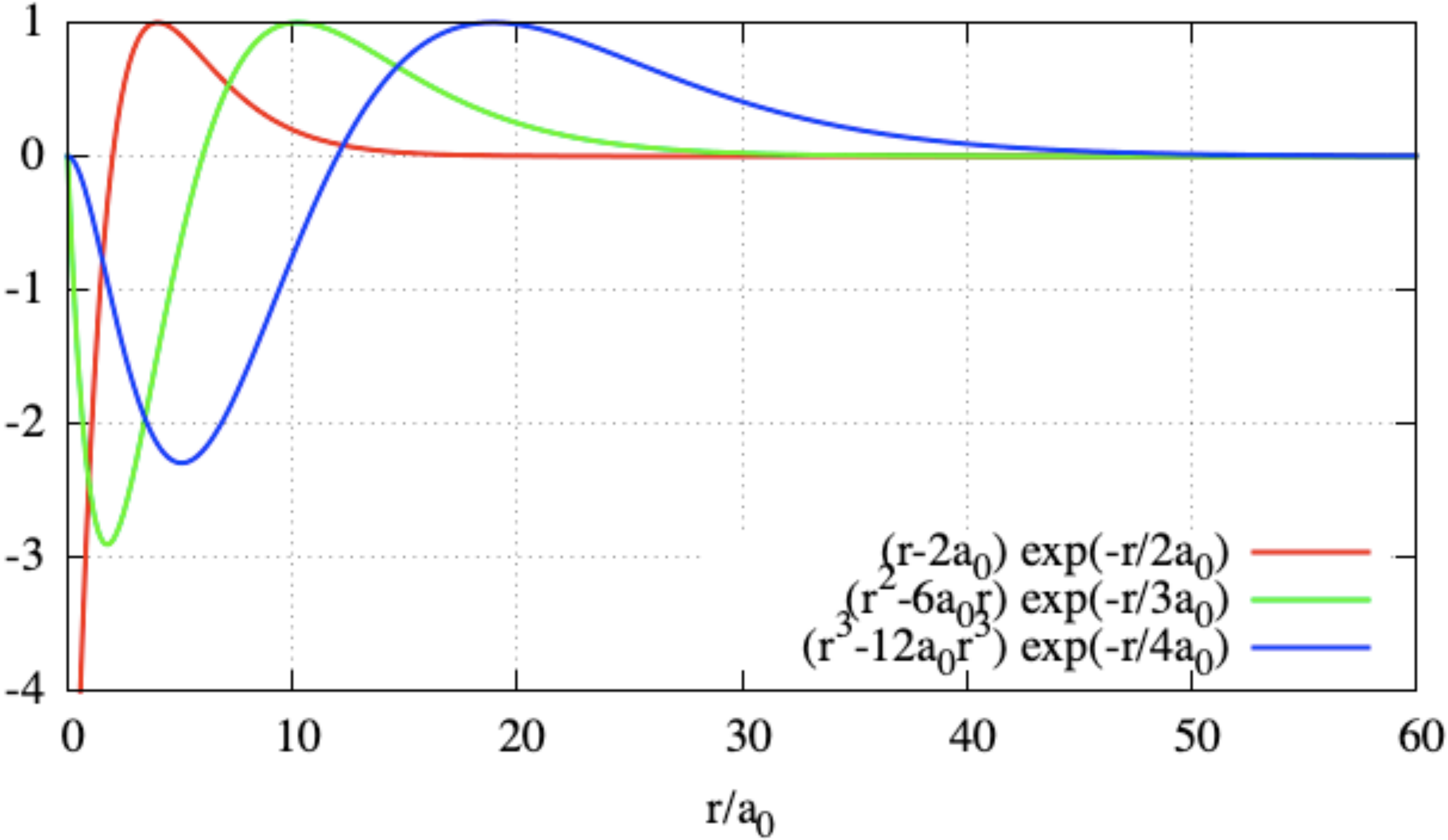
For both our first guesses and second guesses, the energy depended only on n, and not also on ℓ.

That turns out to be true for all solutions (but ONLY for the Coulomb potential).

I've done the solution in terms of n, because that's cleaner.

But the n value does NOT tell you whether you are in a state with high k and low ℓ, or a state with low k and high ℓ.

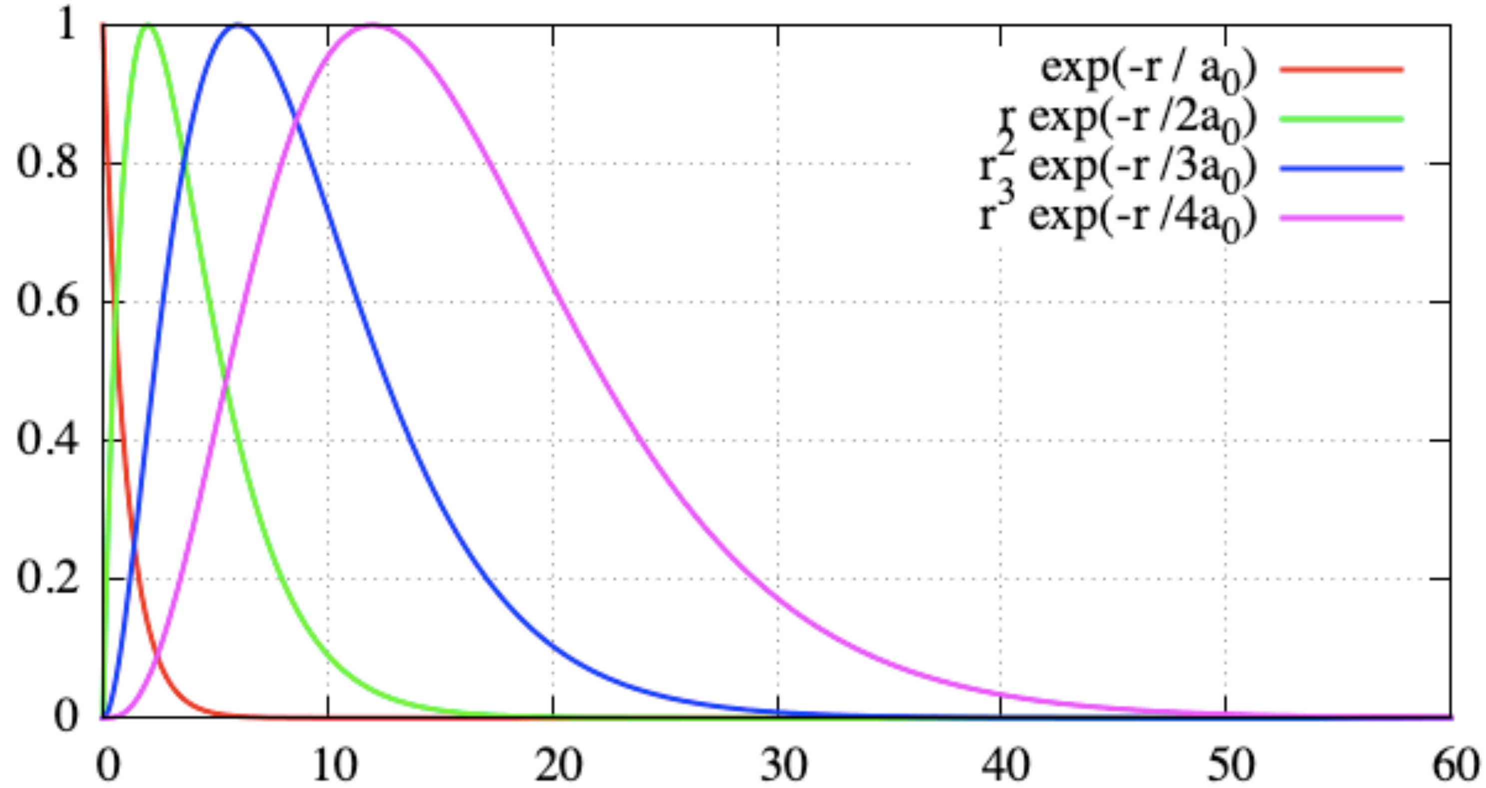
Next Few $F(r)$ Solutions



Observations

Our first $F(r)$ functions looked like this.

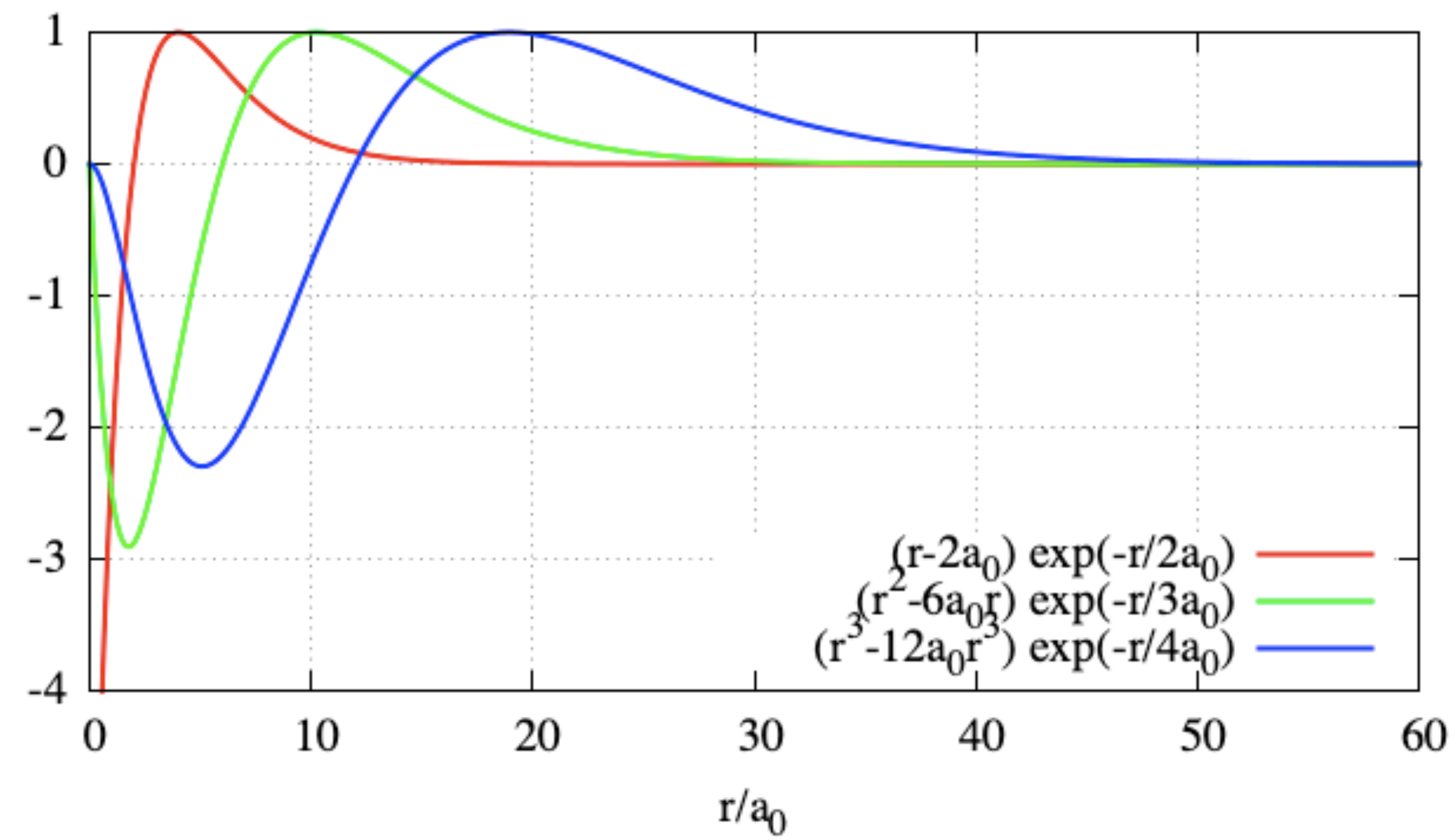
They have a single peak that moves out in radius.



The new $F(r)$ functions look like this.

They have a positive peak and a negative peak.

Probability vs r has 2 peaks, and a zero between them.



More Guesses

We continue adding a coefficient times a lower power of r:

$$U(r) = \left\{ r^n + Ar^{n-1} + Br^{n-2} \right\} \exp\left(-\frac{r}{b} \right)$$

This time, as well as solving for b, n vs ℓ, E, and A, we have to solve for B.

This time we get $n = \ell + 3$.

We continue to get $E = -\frac{M}{2}\left(\frac{q^2}{4\pi\hbar\varepsilon_0} \right)^2 \frac{1}{n^2}$, and $b = na_0$.

This can be continued indefinitely.

Fill In a Blank

It's pretty hard to find tables of Hydrogen $U(r)$ functions past $n = 3$, although it's all been tabulated. So I'll just fill in the $n = 3$, $\ell = 0$ space, with the normalization convention I've been using.

	$\ell = 0$	$\ell = 1$	$\ell = 2$
$n = 3$	$\left(r^3 - 9a_0 r^2 + \frac{27}{2}a_0^2 r\right)e^{\frac{-r}{3a_0}}$	$\left(r^3 - 6a_0 r^2\right)e^{\frac{-r}{3a_0}}$	$r^3 e^{\frac{-r}{3a_0}}$
$n = 2$	$\left(r^2 - 2a_0 r\right)e^{\frac{-r}{2a_0}}$	$r^2 e^{\frac{-r}{2a_0}}$	
$n = 1$	$re^{\frac{-r}{a_0}}$		

Normalized Hydrogen Wavefunctions

The most common thing are wavefunctions $\psi_{n\ell m}(r,\theta,\phi) = \frac{U_{n\ell}(r)}{r} \cdot Y_\ell^m(\theta,\phi)$ that have been normalized, and the polynomial has been made dimensionless.

n	ℓ	m_ℓ		$\Psi_{n\ell m_\ell}(r,\theta,\varphi)$
1	0	0	1s	$\frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0}$
2	0	0	2s	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	2p	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	±1	2p	$\frac{1}{8\sqrt{\pi}a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta e^{\pm i\phi}$

Normalized Hydrogen Wavefunctions

n	ℓ	m_ℓ		$\Psi_{n\ell m_\ell}(r,\theta,\varphi)$
3	0	0	3s	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left[27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right]e^{-r/3a_0}$
3	1	0	3p	$\frac{\sqrt{2}}{81\sqrt{\pi}a_0^{3/2}}\left[6-\frac{r}{a_0}\right]\frac{r}{a_0}e^{-r/3a_0}\cos\theta$
3	1	±1	3p	$\frac{1}{81\sqrt{\pi}a_0^{3/2}}\left[6-\frac{r}{a_0}\right]\frac{r}{a_0}e^{-r/3a_0}\sin\theta e^{\pm i\phi}$
3	2	0	3d	$\frac{1}{81\sqrt{6\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta-1)$
3	2	±1	3d	$\frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta e^{\pm i\phi}$
3	2	±2	3d	$\frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta e^{\pm i2\phi}$

Patterns

The n value appears in the denominator of the exponential.

The n value is one more than the highest power of r in the polynomial.

$n = k + \ell$ so $k = n - \ell$

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

The m value appears in the complex exponential, and $|m|$ is the power of $\sin\theta$.

Comments

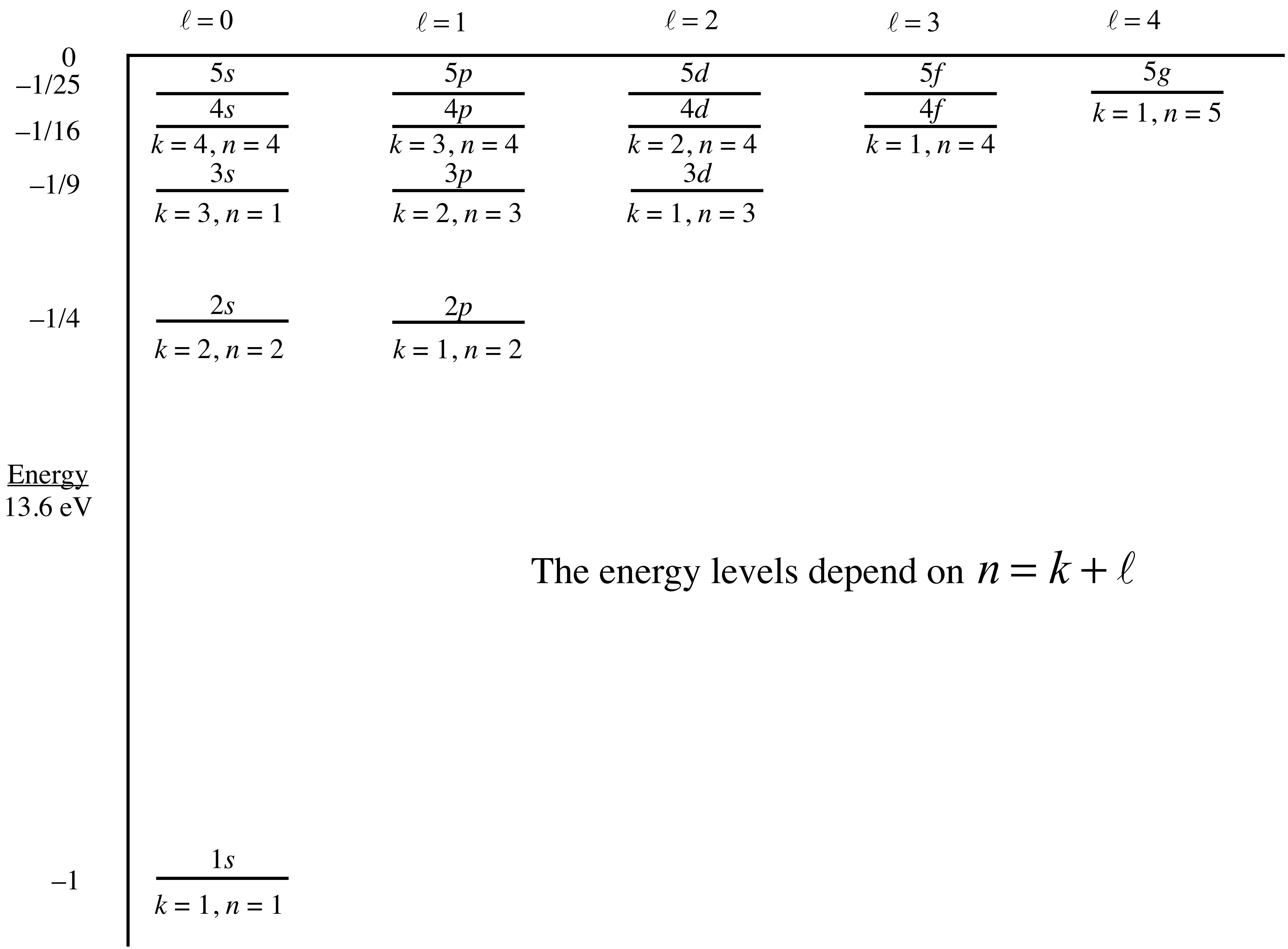
We found all the $k = 1$ states first. There were of the form $r^n \exp\left(\frac{-r}{na_0}\right)$.

Then we found the $k = 2$ states, of the form $\left(r^n + Ar^{n-1}\right)\exp\left(\frac{-r}{na_0}\right)$.

I just wrote down a $k = 3$ state, of the form $\left(r^n + Ar^{n-1} + Br^{n-2}\right)\exp\left(\frac{-r}{na_0}\right)$.

Increasing ℓ by 1 at fixed k giving the same energy change as increasing k by 1 at fixed ℓ is exact for the Coulomb potential in the non-relativistic Schrodinger Equation. But it's not true for any other potential.

Hydrogen Energy Levels

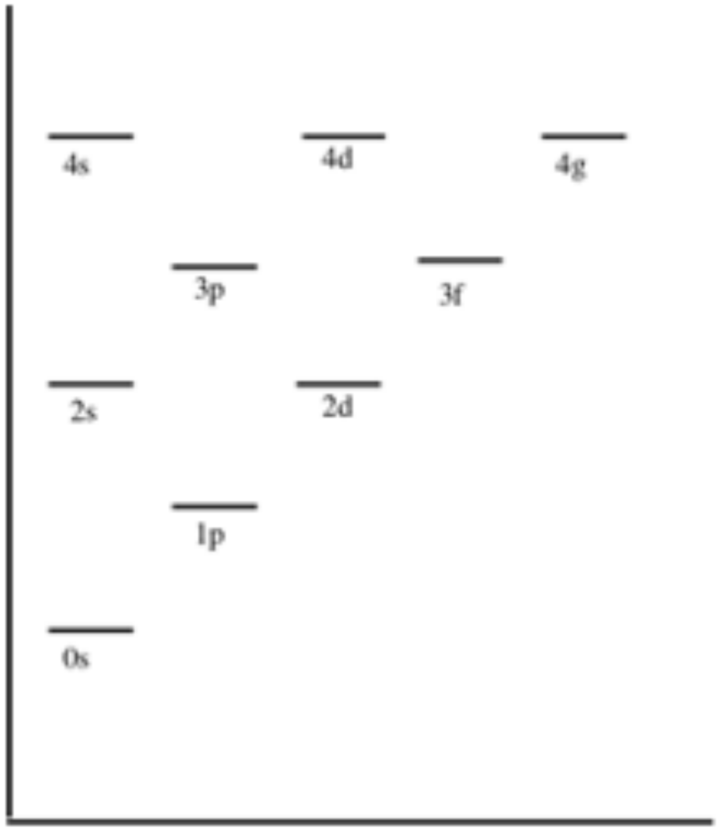


The energy levels depend on $n = k + \ell$

Not Everything Is Hydrogen!

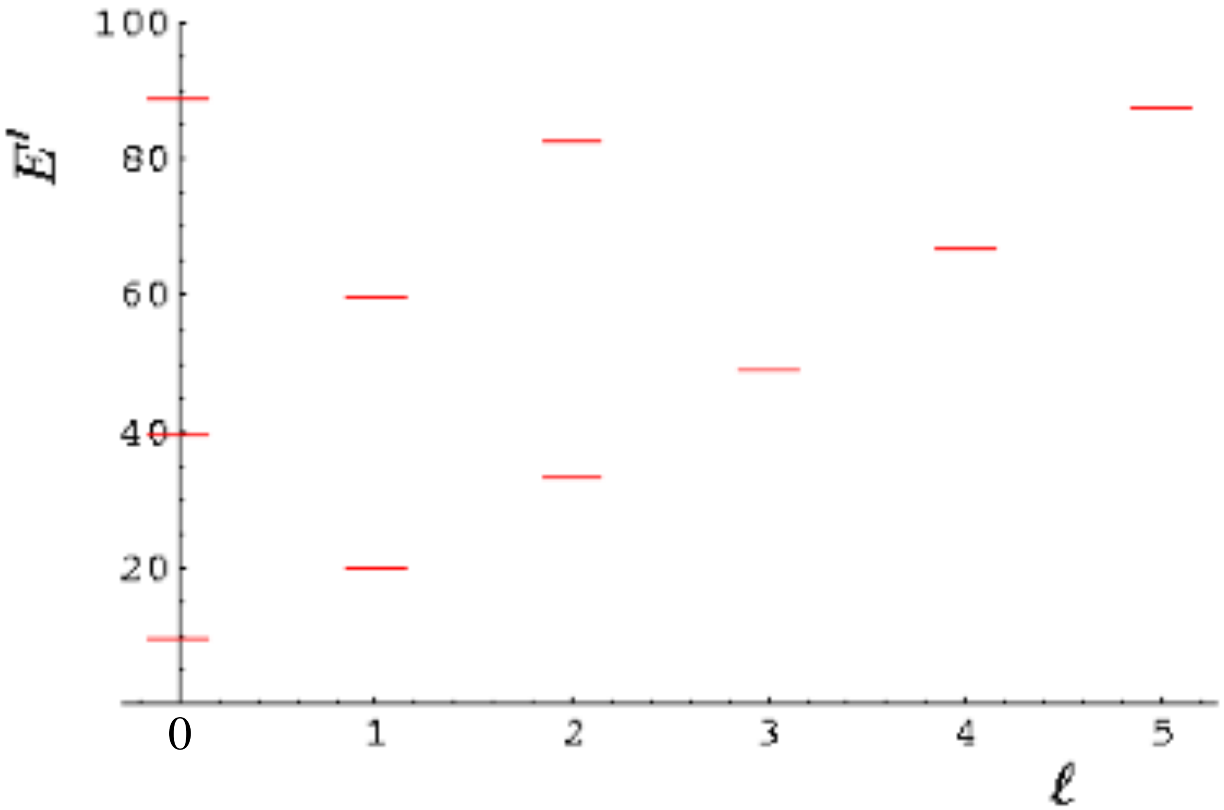
For a <u>random</u> central potential, the energy level depends on both the angular momentum quantum number ℓ, and the radial excitation quantum number k and there may be no pattern

3D Harmonic Oscillator



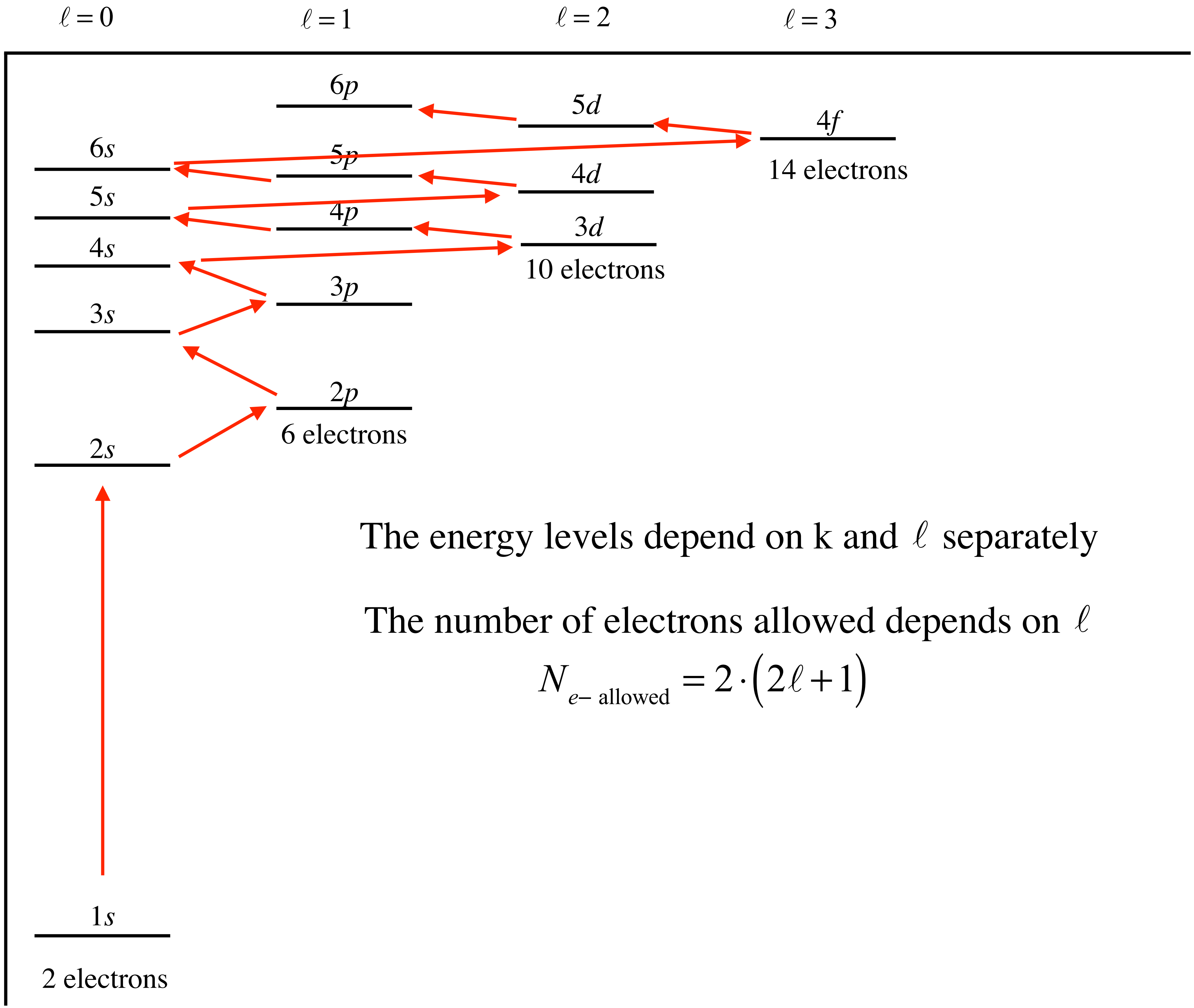
Different pattern

Spherical Square Well



No particular pattern

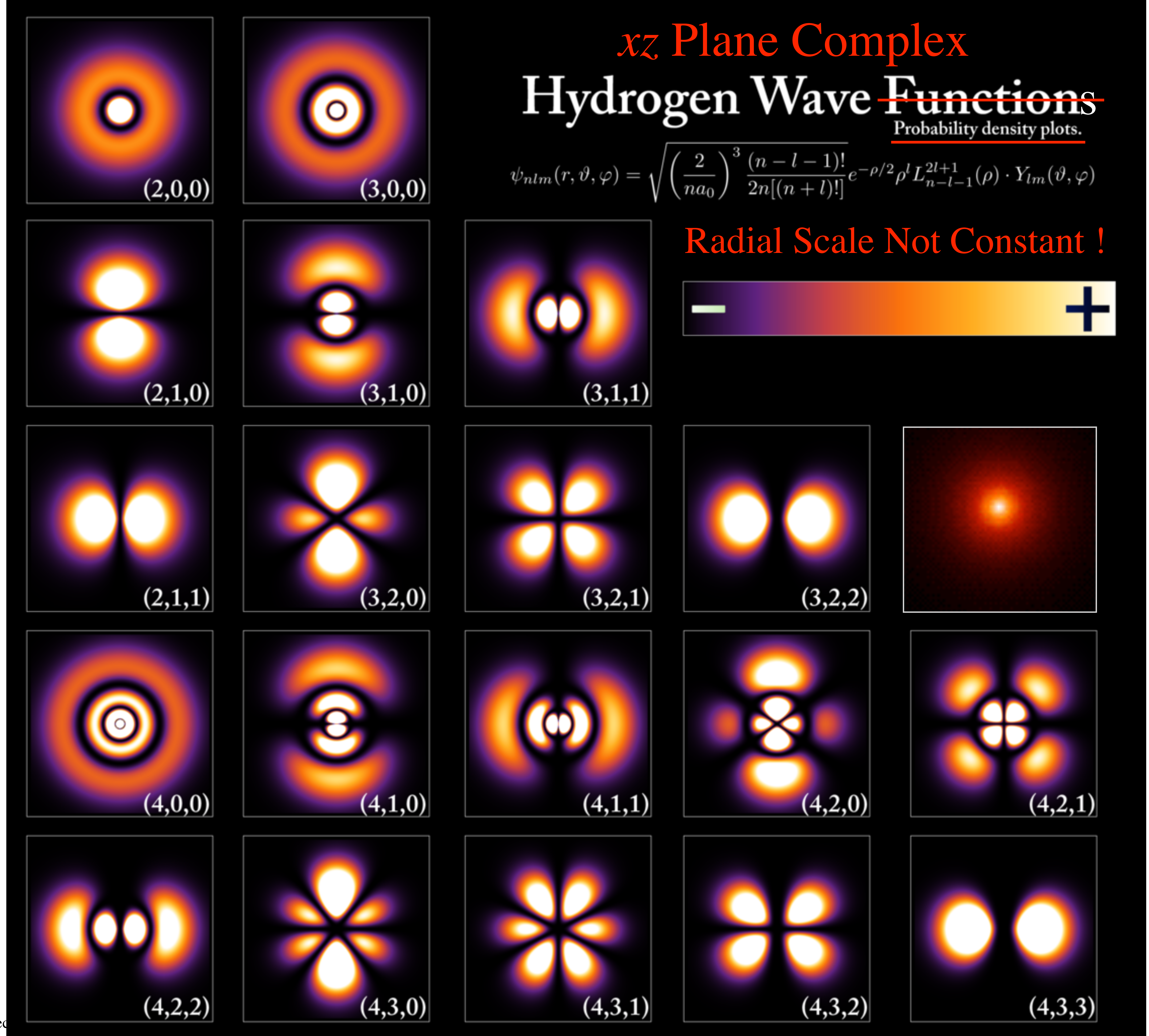
Atomic Energy Levels



The energy levels depend on k and ℓ separately

The number of electrons allowed depends on ℓ

$$N_{e-\text{ allowed}} = 2 \cdot (2\ell + 1)$$


xz Plane Complex
Hydrogen Wave ~~Functions~~s
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
Radial Scale Not Constant !
−
+
(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)
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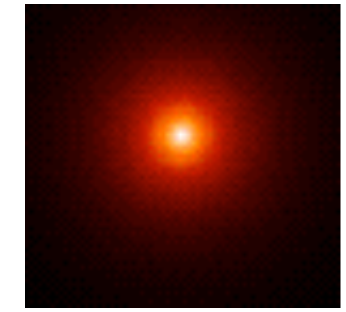
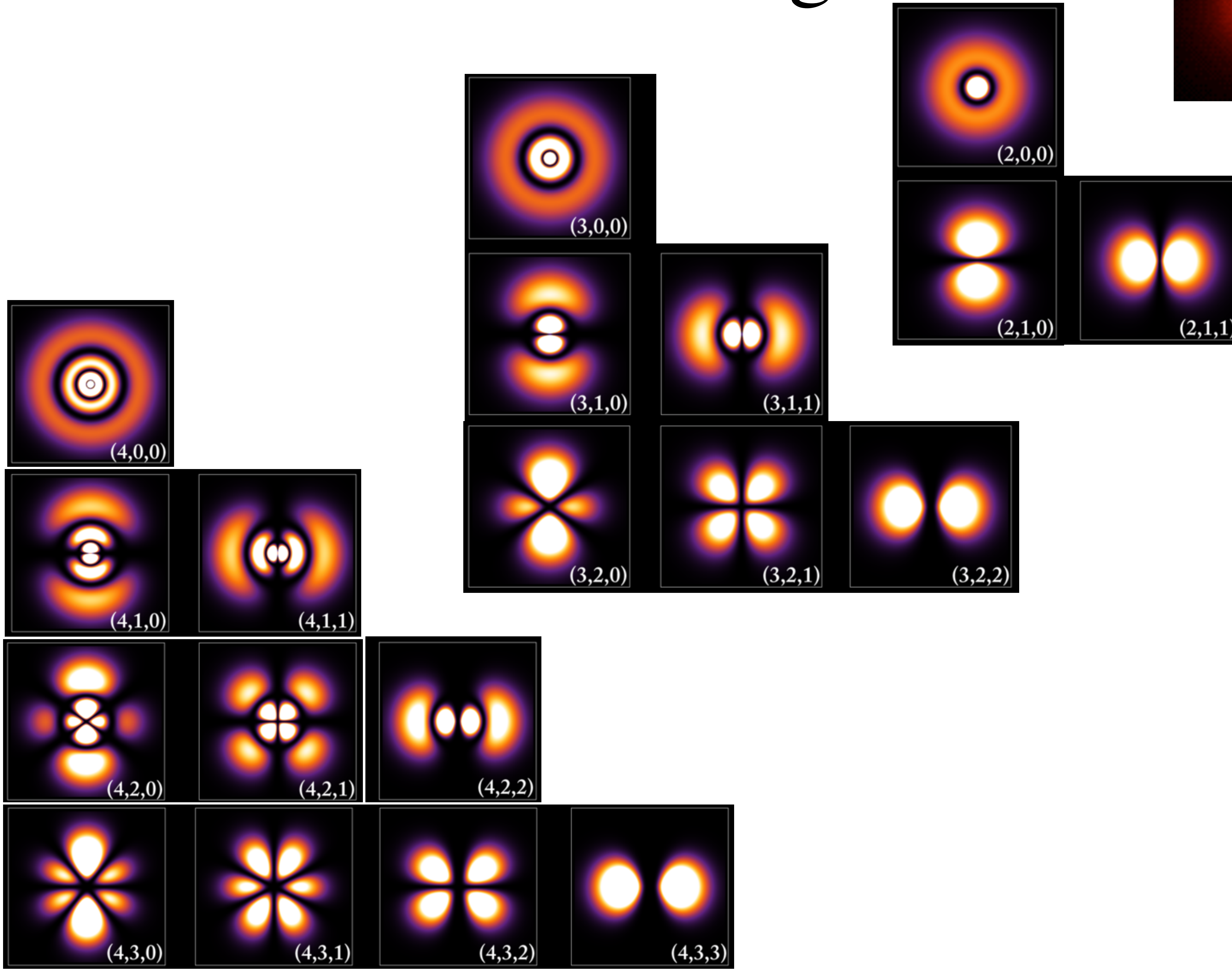
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

Better Arrangement





Visualizing the Probabilities

The probability density is independent of ϕ for the complex spherical harmonics, so the probability density in the *xz* plane tells most of the story.

1S is a small round cloud.
2S is larger with a radial zero-crossing.
3S is larger with 2 zero-crossings.

2P is about the size of 2S, and the zero-crossing is the *xy*-plane.

3P has both radial and *xy* plane zero-crossings.

3D has zero-crossings in two cones that meet at the origin.

For Next Time

Last WebWork is posted, due Sunday night.

There is a tutorial worksheet on Friday. There will still be office hours.

Final exam is 3:30-6 on Monday June 23 in BIOL 1000.

Two pages (both sides) of notes. Group notes are allowed.
Any calculator. But no tablets, laptops, phones, or wireless devices.

Some old finals are posted. Solutions will be posted Thursday morning.

Good luck!