Lecture #1
PHYS 598 AQG
Fall 2017

Hydrogen & (single-electron) Hydrogen-like atoms

He^+ (He II)
Li^{2+} (Li III)
etc.

We'll start simple:
- non-relativistic
- ignore spin

for

- Charge of nucleus $q_N = +Ze$
- atomic # Z
- net mass of nucleus m_N
- electron mass m_e

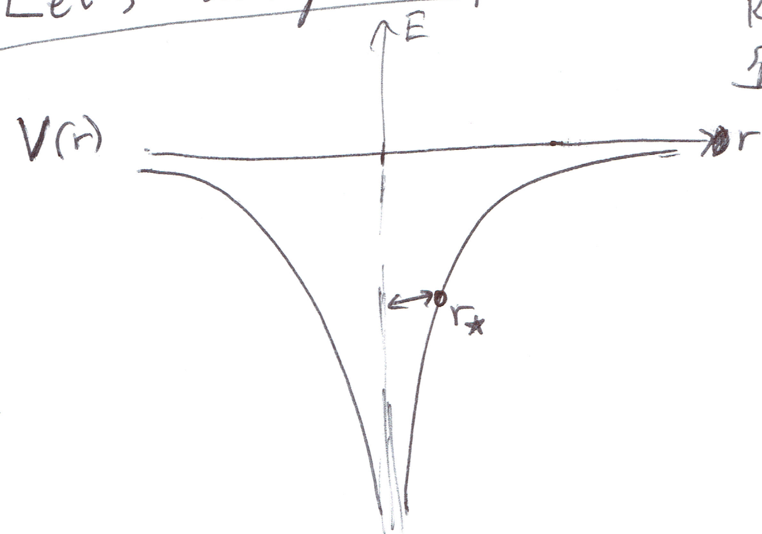
$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

where

$\mu = \frac{m_e m_N}{m_e + m_N} \approx m_e$ is the reduced mass

and r is the distance of the electron from the nucleus

Let's survey the problem and make some estimates



Roughly Speaking
- should have bound states for $E<0$
- unbound, scattering states for $E>0$
- 3D problem, so we'll have 3 spatial quantum #'s

Let's estimate the minimum allowed energy, based on Heisenberg uncertainty

$\Delta p \Delta r \sim \hbar$

If we confine the electron to a region such that $\Delta r \simeq r_\star^{=\langle r\rangle}$, this will necessarily be accompanied by a momentum uncertainty $\Delta p \sim \frac{\hbar}{r_\star}$

②

For our lowest energy bound state, having $\langle p \rangle = 0$, we can say $\Delta p^2 \simeq \langle p^2 \rangle$ and recast our "ground state" energy as

$$E = \langle \psi_{gs} | \hat{H} | \psi_{gs} \rangle \approx \underbrace{\frac{\hbar^2}{2\mu r_\star^2}}_{\text{repulsive "potential" due to wave function confinement.}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0 r_\star}}_{\text{attractive Coulomb potential}}$$

have student do

Let's minimize E w.r.t. $r_\star$: take $\frac{\partial E}{\partial r_\star} = 0$ to find extremum

$$\frac{\partial E}{\partial r_\star} = \frac{\hbar^2}{2\mu}\left(-2 r_\star^{-3}\right) - \frac{Ze^2}{4\pi\varepsilon_0}\left(-r^{-2}\right) = 0$$

$$\Rightarrow r_{\star,min} = \frac{\hbar^2}{\mu e^2}\left(\frac{4\pi\varepsilon_0}{Z}\right) \equiv \frac{a_\mu}{Z}$$

where $a_\mu = a_0 \frac{m_e}{\mu}$

and $a_0 = \frac{\hbar^2}{m_e c^2} 4\pi\varepsilon_0$

average distance $\langle r \rangle \sim \Delta r = r_\star$ should get smaller like $1/Z$ for increasing atomic #.

Energy estimate, let's plug back into $E(r_\star)$

$$E(r_\star) = \frac{\hbar^2}{2\mu r_\star^2} - \frac{Ze^2}{4\pi\varepsilon_0 r_\star} = -\frac{Ze^2}{8\pi\varepsilon_0}\frac{1}{r_\star} = -\frac{Z^2 \mu e^4}{2(4\pi\varepsilon_0)^2\hbar^2} \approx -Z^2 \underbrace{hcR_\infty}_{\text{the Rydberg unit of energy}}$$

$= -13.6\,\text{eV}$

→ these "estimates" are spot on, but let's do things more formally

③ With a bit more rigor

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\frac{p^2}{2\mu} \to -\frac{\hbar^2}{2\mu}\vec{\nabla}^2 \to \text{see Foot}$$

ansatz try separating into radial and angular coordinates

$$\psi_{n\ell m} = R_{n\ell}(r)\,Y_{\ell m}(\theta,\varphi)$$

→ plug into Schrödinger Eqn. (expressed in spherical coordinates)

and find it to be separable with separate expressions for radial + angular parts.

from Foot 2.1.2

Let $P(r) = r\,R(r)$

and let $b = \ell(\ell+1)$ be related to an integer ℓ satisfying the eigenvalue problem.

Radial part of Schröd Eqn

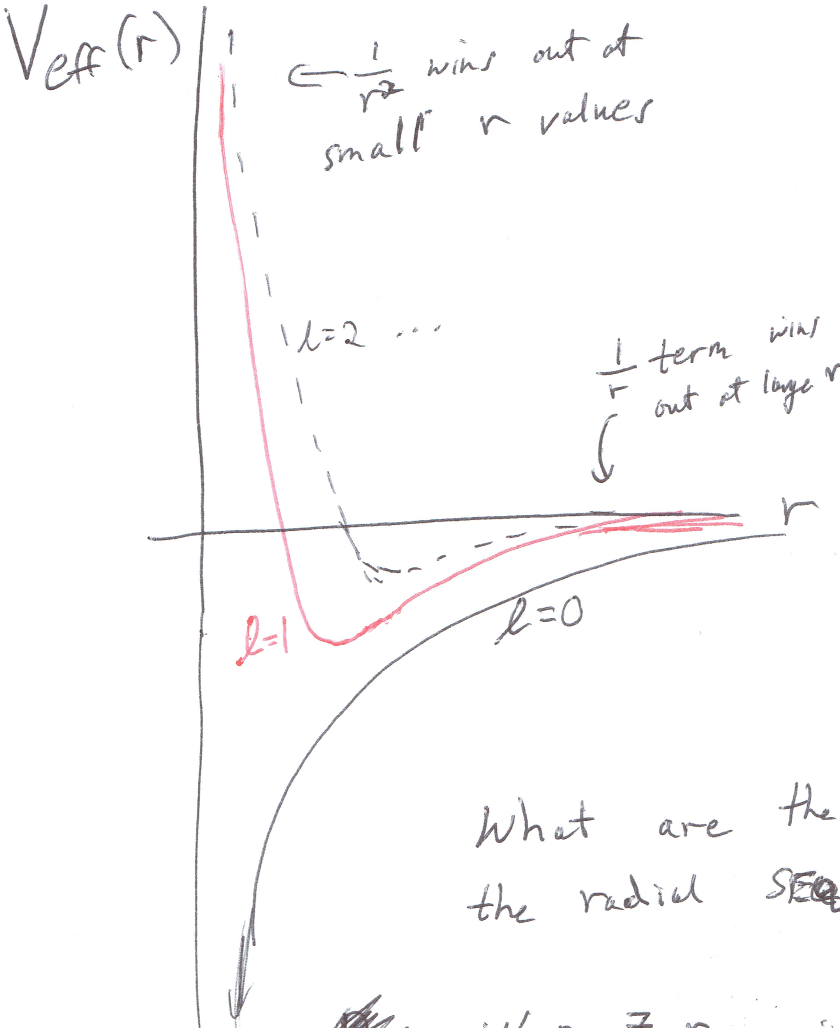
$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\frac{d^2P}{dr^2} + \frac{2\mu}{\hbar^2}\Big[\underbrace{E - V(r) - \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}}_{E - V_{eff}(r)}\Big]P = 0$$

the two r-dependent terms can be incorporated into the effective radial potential

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}}_{\text{centrifugal term}}$$

④



minimum or V_{eff} moves to larger r values as l increases, i.e. for larger centrifugal barrier term

Foot p. 27

What are the solution that satisfy the radial SEQ for integer l?

w/ $\rho = \frac{Z}{n}\frac{r}{a_\mu}$, in terms of R_{nl} (i.e., not $P(r) = rR($

$$R_{nl} = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-\rho}(2\rho)^l \underbrace{L_{n-l-1}^{2l+1}(2\rho)}_{\text{associated (generalized) Laguerre polynomials}}$$

$n = 1, 2, 3, \ldots$

a few things: no radial solutions for $l \geq n$

for $n=1$, only $l=0$ $\Rightarrow R_{1,0}(r) \propto e^{-\rho}$

for $n=2$, $l=0$ solution $\Rightarrow R_{2,0}(r) \propto (1-\rho)e^{-\rho}$

$l=1$ solution $\Rightarrow R_{2,1}(r) \propto \rho e^{-\rho}$

see table in Foot (Table 2.2) for more

Some Key properties

at small r (small ρ)

$$\boxed{R_{nl} \propto \rho^{l} \qquad \text{vanishes at } r=0 \text{ unless } l=0}$$

at very large r (large ρ)

$$\boxed{R_{nl} \propto \rho^{n-1} e^{-\rho}}$$

Normalization

$$\int_0^{2\pi}\int_0^{\pi} |Y_{lm}|^2 \sin\theta \, d\theta \, d\varphi =$$

$$\int_0^{\infty} |R_{nl}|^2 r^2 \, dr = 1$$

other Key quantities related to radial wave functions

- radial probability ~~distribution~~ density
- Some ~~[illegible]~~ helpful expectation values

$$\iint_{\theta\varphi} |R_{nl}(r)|^2 |Y_{lm}(\theta,\varphi)|^2 r^2 \sin\theta \, d\theta \, d\varphi \propto \boxed{r^2 |R_{nl}(r)|^2}$$

$$\langle r \rangle \equiv \langle n,l|\hat{r}|n,l\rangle = a_\mu \frac{n^2}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right]$$

"size of the atom"

$$\langle r^2 \rangle = a_\mu^2 \frac{n^4}{Z^2}\left[1 + \frac{3}{2}\left(1 - \frac{l(l+1) - 1/3}{n^2}\right)\right]$$

$$\langle r^3 \rangle = a_\mu^3 \frac{n^6}{Z^3}\left[1 + \frac{27}{8}\left(1 - \frac{(35/27 + 10(l+2)(l-1)/9)}{n^2} + \frac{(l+2)(l+1)l(l-1)}{9n^4}\right)\right]$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_\mu n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_\mu^2 n^3 (l+\frac{1}{2})}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_\mu^3 n^3 l (l+\frac{1}{2})(l+1)}$$

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Energies

$E_n \rightarrow$ ind. of l, m

due to funny result for $1/r$ potential

due to rotational symmetry of $V(r)$

$$E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{\hbar^2} = -\frac{Z^2}{n^2} hc R_\infty \times \left(\frac{\mu}{m_e}\right)$$

can also be expressed as

$$E_n = -\frac{1}{2}\mu c^2 \left(\frac{Z\alpha}{n}\right)^2$$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}$

is the fine structure constant

$$\boxed{\alpha = \left(\frac{e^2}{4\pi\varepsilon_0 d}\right) \Big/ \left(\frac{hc}{\lambda}\right)}$$ for $\lambda = 2\pi d$

also, compare energy of elementary dipoles (magnetic + electric) at equivalent distance $\bar{r}$

$$\alpha^2 = \left(\frac{\mu_0 \mu_B^2}{4\pi \bar{r}^3}\right) \Big/ \left(\left(\frac{e a_0}{2}\right)^2 \Big/ 4\pi\varepsilon_0 \bar{r}^3\right)$$ w/ $\mu_B = \frac{e\hbar}{2m_e}$

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Angular wf's

$$Y_{\ell m}(\theta,\varphi) = \underbrace{P_\ell^m(\cos\theta)}\, e^{im\theta}$$

see Foot table 2.1 for some explicit $Y_{\ell m}$ wfs

$\rightarrow$ eigenstate of $\underline{\hat{L}^2, \hat{L}_z}$

associated (generalized) Legendre polynomial of degree ℓ and order m

$\hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m}$

$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$

parity transformation

$\hat{r} \to -\hat{r}$, such that $\theta \to \pi - \theta$ and $\varphi \to \varphi + \pi$

under parity transformation $\quad Y_{\ell m}(\pi-\theta, \varphi+\pi) = (-1)^\ell Y_{\ell m}(\theta,\varphi)$

parity of the states $\psi_{n\ell m}$ is given by $(-1)^\ell$

A note on notation

principal quantum number $\quad n = 1, 2, 3, \ldots$

orbital quantum number $\quad \ell = 0, \ldots, n-1$

w/ $\ell = 0 \Rightarrow$ "s" orbital sharp

$\ell = 1 \Rightarrow$ "p" orbitals principal

$\ell = 2 \Rightarrow$ "d" orbitals diffuse

$\ell = 3 \Rightarrow$ "f" orbitals fine

$\ell = 4 \Rightarrow$ "g" orbitals

$\downarrow$ alphabetical from here

$1S_{1/2} \Rightarrow$ $(n,\ell) = (1,0$

$3P \Rightarrow (n,\ell) = (3,1$

taking into account the spin of the electron $(S=\frac{1}{2})$

$n\,^{2S+1}L_J$ is the common atomic orbital notation, where we typically use L in place of ℓ, where possible angular momentum values run from $J = L+S$ to $J = L-S$, and the "$2S+1$" term is often dropped.
(only positive values)

A note on units

I'll try to use SI units throughout the course, but you may find that some of the course reference materials use alternate unit systems, such as Gaussian CGS or atomic units.

Atomic units, in particular, show up in many atomic physics references

- unit of length = the Bohr radius, $a_0 \simeq 0.5\,\text{Å}$
- unit of energy = the Hartree energy, $E_h = 2Ry = 2hc\overbrace{R_\infty}^{\text{Ryd const for } m_N = \infty}$

easy ; $m_e = 1,\ e = 1,\ \hbar = 1,\ \underset{\left(\frac{1}{4\pi\epsilon_0}\right)}{K = 1},\ c = \frac{1}{\alpha} \simeq 137$

at times, may use technical units $\begin{pmatrix}\text{mostly w/ energy} \\ \text{+ frequencies}\end{pmatrix}$

e.g. $\mu_B = e\hbar/2m_e = 9.27 \times 10^{-24}\ \frac{J}{T}$

but $\mu_B/\hbar = 2\pi \times 1.40\ \frac{\text{MHz}}{G}$

is more convenient for determining how a transition frequency will change with an applied magnetic field.

Note, Also, spectroscopy folks love wave number (cm^{-1})

$\bar{\nu} = \frac{\omega}{2\pi c}$, expressed in inverse centimeters.

Potential Energy in the Hydrogen Atom

To solve this problem, we must specify the potential energy of the electron. In an atom, the Coulomb force binds the electron to the nucleus.

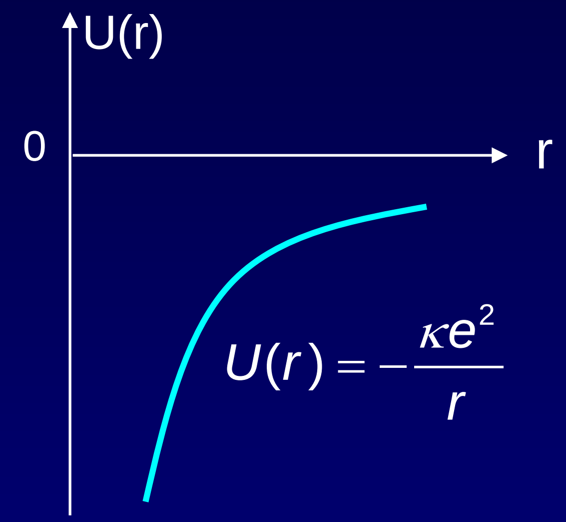
This problem does not separate in Cartesian coordinates, because we cannot write $U(x,y,z) = U_x(x)+U_y(y)+U_z(z)$. However, we can separate the potential in spherical coordinates (r,θ,ϕ), because:

$$U(r,\theta,\phi) = U_r(r) + U_\theta(\theta) + U_\phi(\phi)$$

$$-\frac{\kappa e^2}{r} \qquad\qquad 0 \qquad\qquad 0$$

Therefore, we will be able to write:

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$$

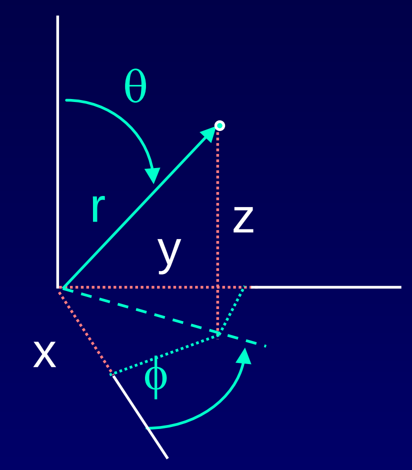


$$\kappa = \frac{1}{4\pi\varepsilon_0} = 9\times10^9\ \text{Nm}^2/\text{C}^2$$

Supplement: Potential Energy in the Hydrogen Atom

Time Independent Schrodinger's Equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2-\frac{\kappa e^2}{r}\right]\psi(\vec{r})=E\psi(\vec{r})$$



In Cartesian Coordinates:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{\kappa e^2}{r}\right]\psi(\vec{r})=E\psi(\vec{r})$$

In Spherical Coordinates:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial^2}{\partial r}+\underbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{\boxed{\hat{L}^2}}\right)-\frac{\kappa e^2}{r}\right]\psi(\vec{r})=E\psi(\vec{r})$$

This is SEPARABLE! (thankfully!!)

Supplement: Potential Energy in the Hydrogen Atom

In Spherical Coordinates:

$$\left[-\frac{\hbar^2}{2mr^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial^2}{\partial r}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)-\frac{\kappa e^2}{r}\right]\psi(\vec{r})=E\psi(\vec{r})$$

Let's separate the *r* dependence from the *θ* and *φ* dependences. Write

$$\psi(\vec{r})=R(r)Y(\theta,\phi)$$

same

Plug this into TI-SEQ. Divide by *RY*. Multiply by $-2mr^2/\hbar^2$

$$\underbrace{\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left(\frac{\kappa e^2}{r}+E\right)\right]}_{\text{Only depends on } r}=\underbrace{-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]}_{\text{Only depends on } \theta \text{ and } \varphi}$$

Therefore each side equals a constant, $l(l+1)$, ***l*** must be 0, 1, 2, ...

This comes from solving diff eq for Y.

Supplement: Potential Energy in the Hydrogen Atom

$$\underbrace{\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left(\frac{\kappa e^2}{r}+E\right)\right]}_{\text{Only depends on } r}=\underbrace{-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]}_{\text{Only depends on } \theta \text{ and } \varphi}$$

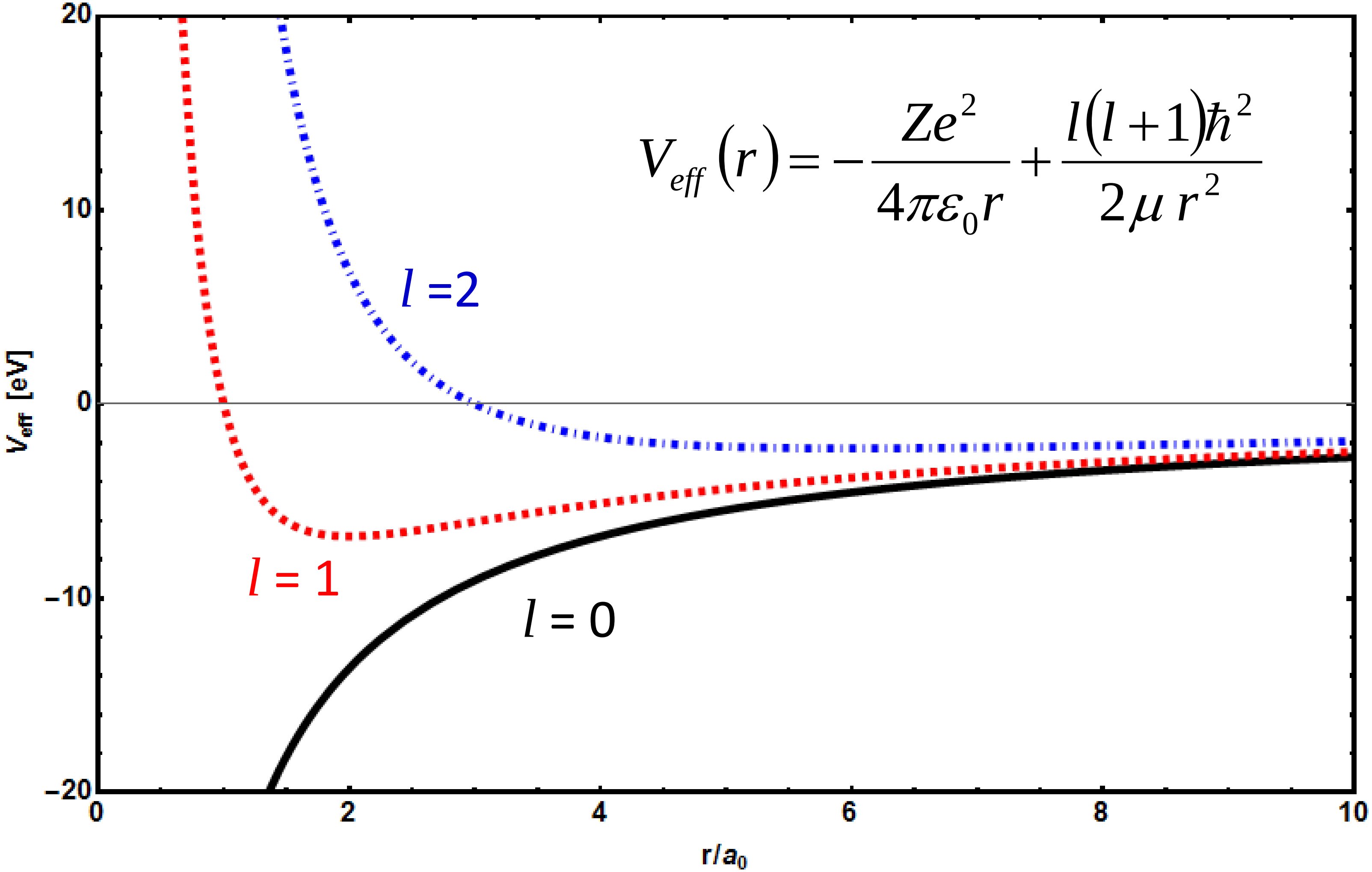
Therefore each side equals a constant, $l\left(l+1\right)$, $\boldsymbol{l}$ must be 0, 1, 2, ...

This comes from solving diff eq for Y.

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)=-\frac{2mr^2}{\hbar^2}\left(\frac{\kappa e^2}{r}+E\right)R(r)+l\left(l+1\right)R(r)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}=-l\left(l+1\right)Y(\theta,\phi)$$

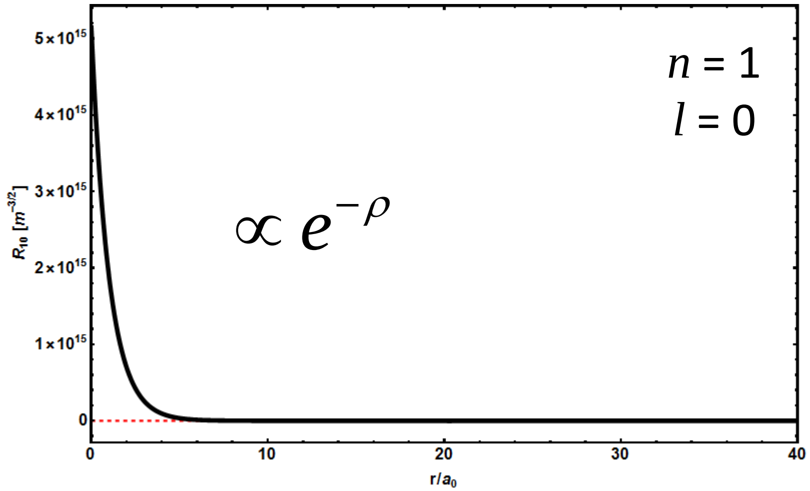
Effective radial potential



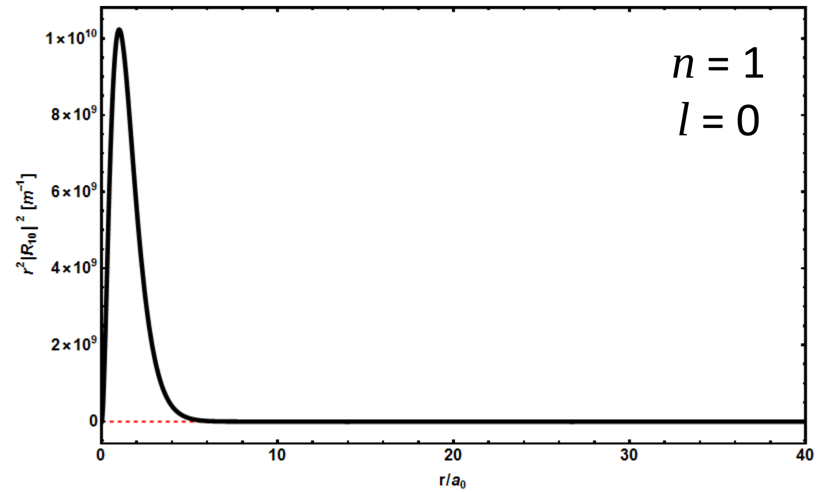
$$V_{eff}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Radial wave functions R_{nl}

Radial wave function



Radial probability density



$$\rho \equiv Zr / na_{\mu}$$

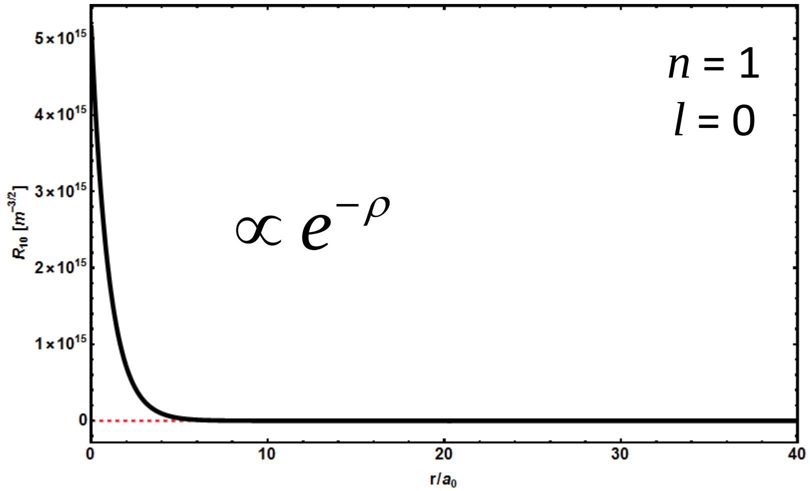
$$R_{nl}(\rho) \propto \left(\frac{\rho}{r}\right)^{3/2} e^{-\rho} \rho^{l} L_{n-l-1}^{2l+1}(2\rho)$$

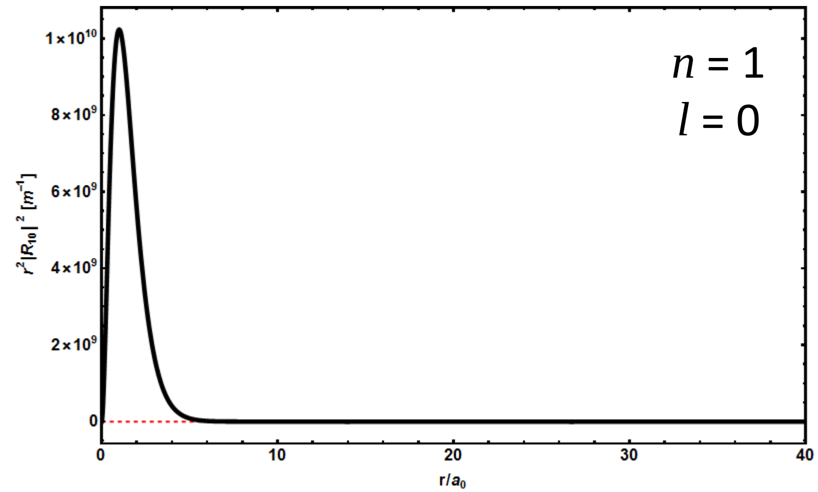
$$\int_0^{\infty} |R_{nl}|^2 r^2 dr = 1$$

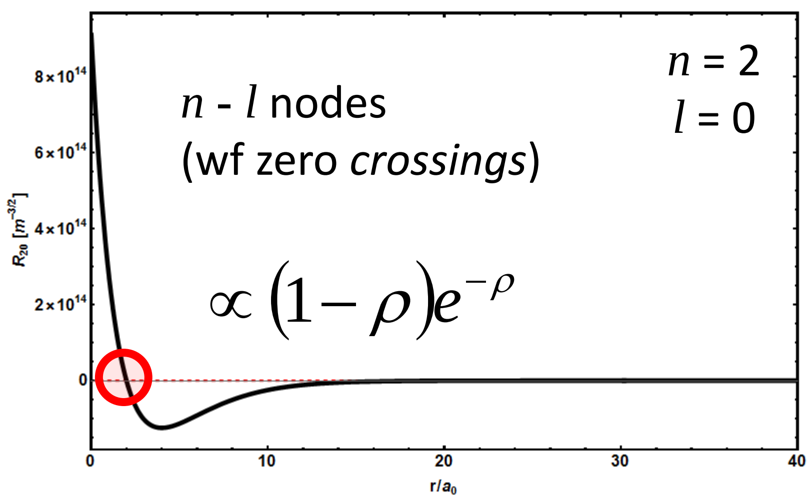
for increasing n

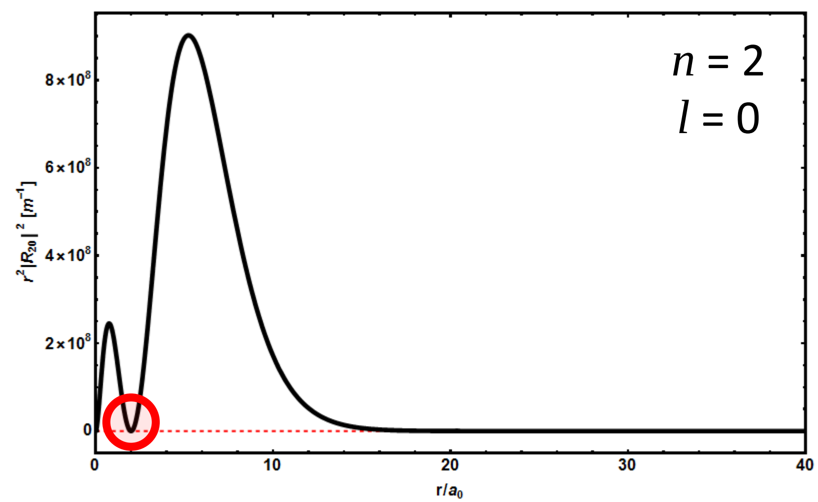
Radial wave functions R_{nl}

Radial wave function | Radial probability density





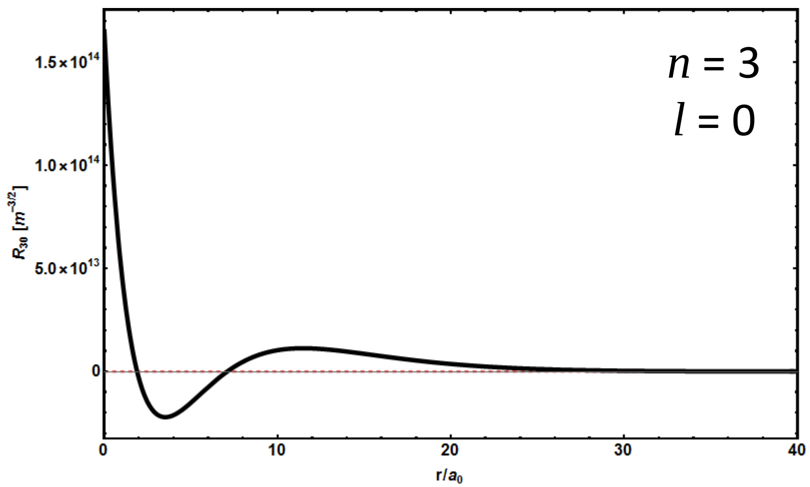


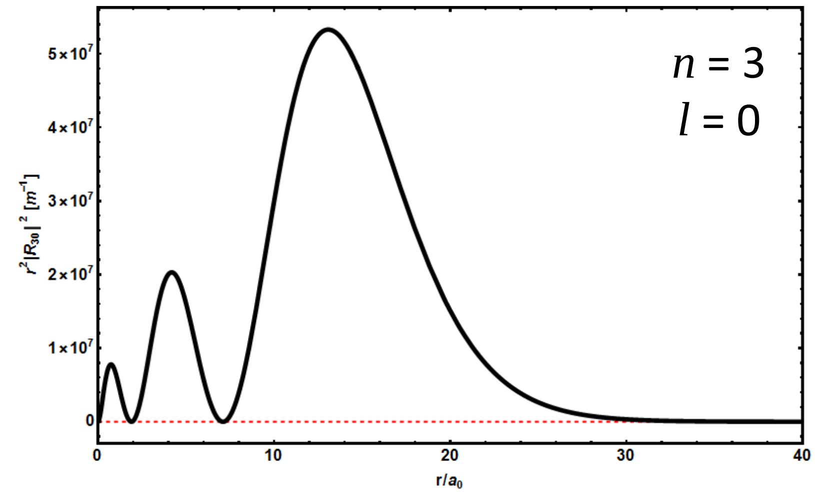


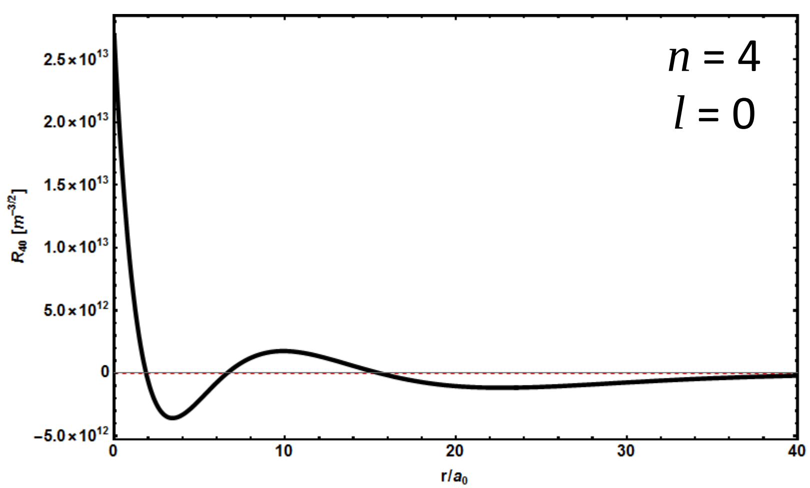
for increasing n

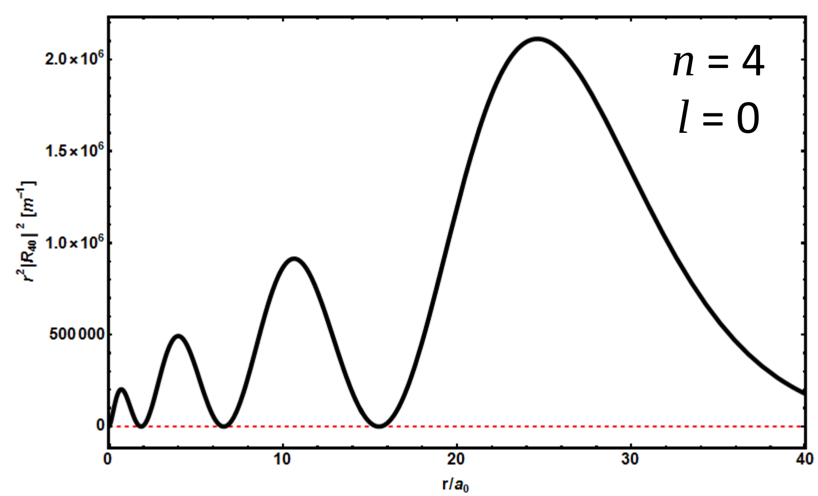
Radial wave functions R_{nl}

Radial wave function	Radial probability density





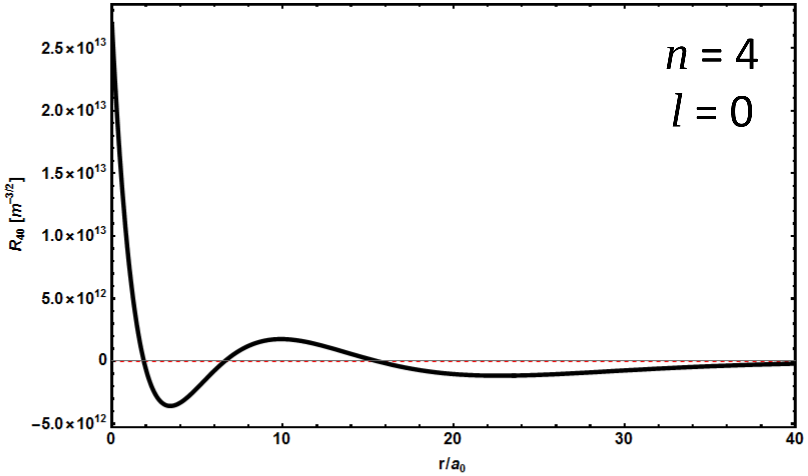




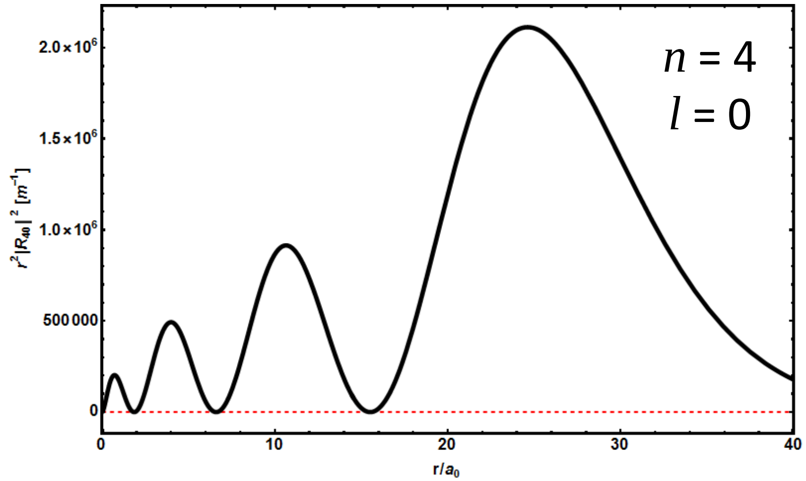
for increasing *l*

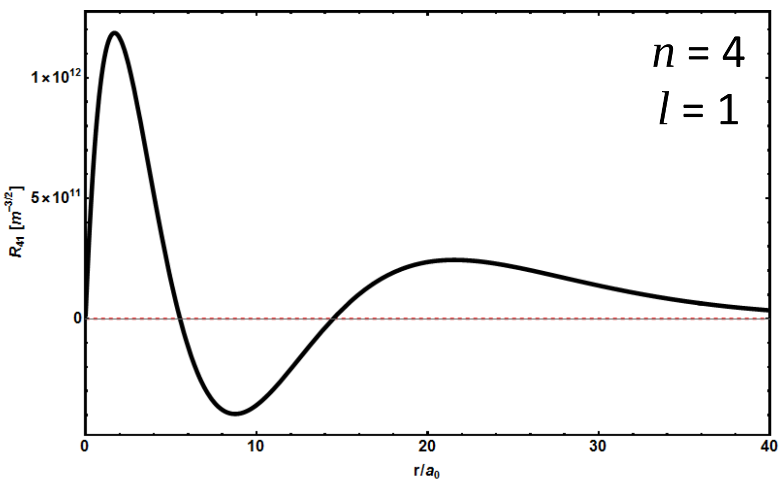
Radial wave functions R_{nl}

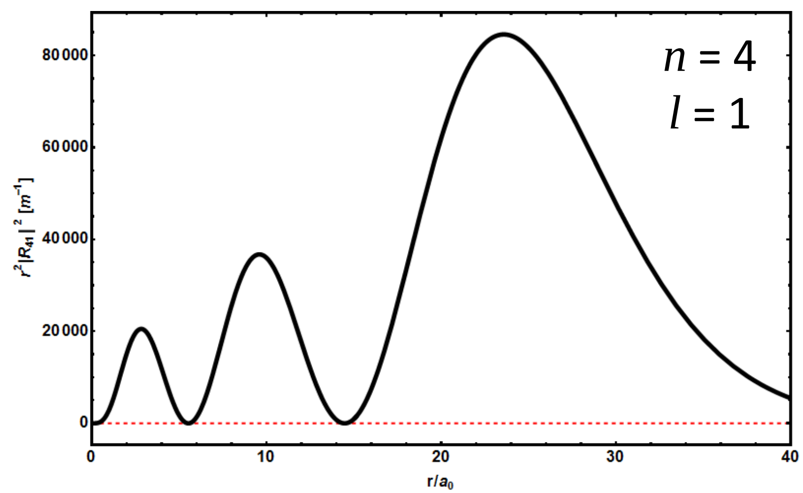
Radial wave function



Radial probability density



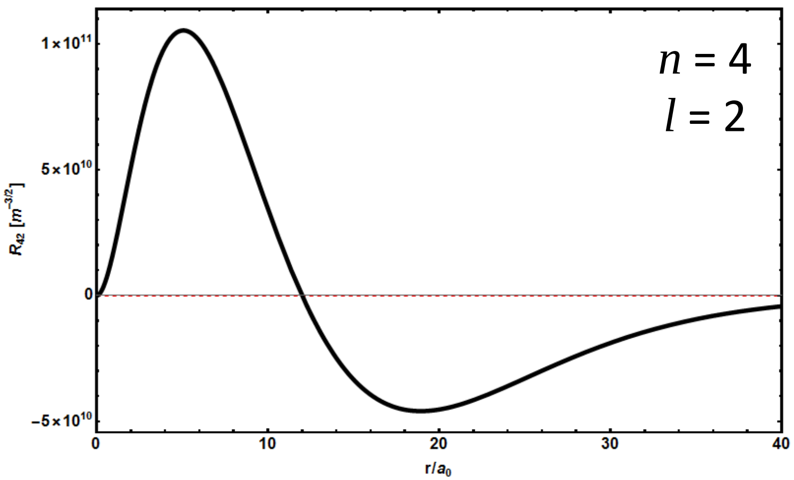


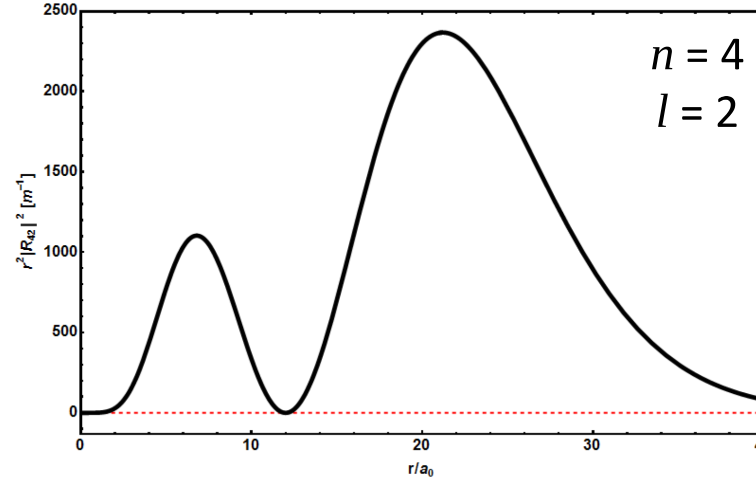


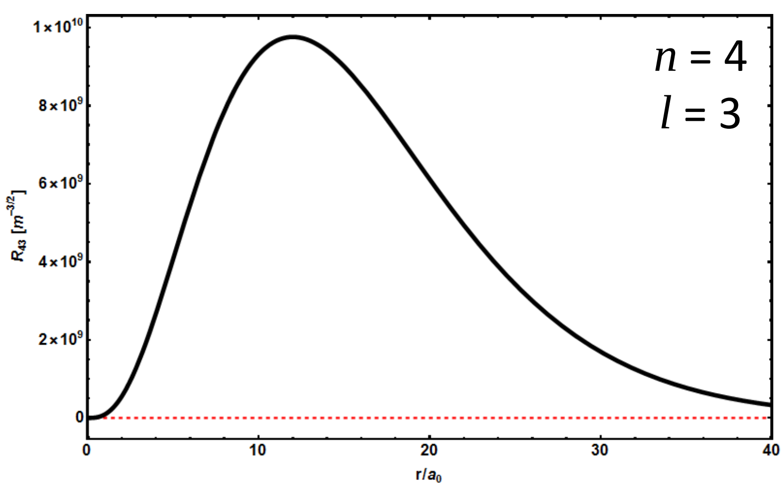
Radial wave functions R_{nl}

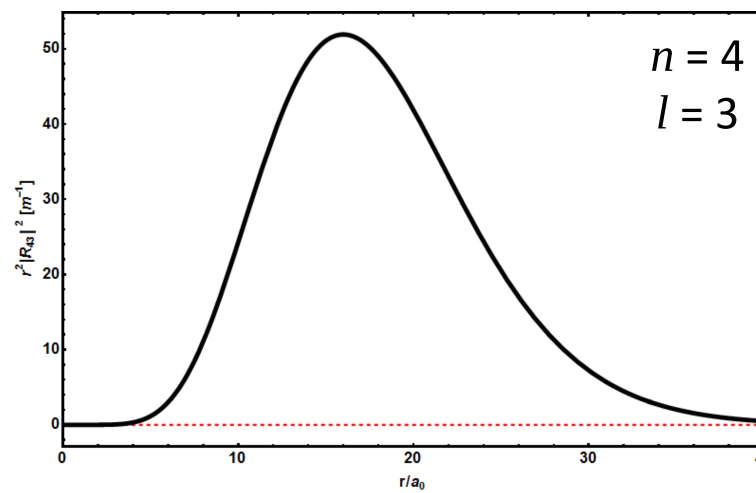
Radial wave function

Radial probability density

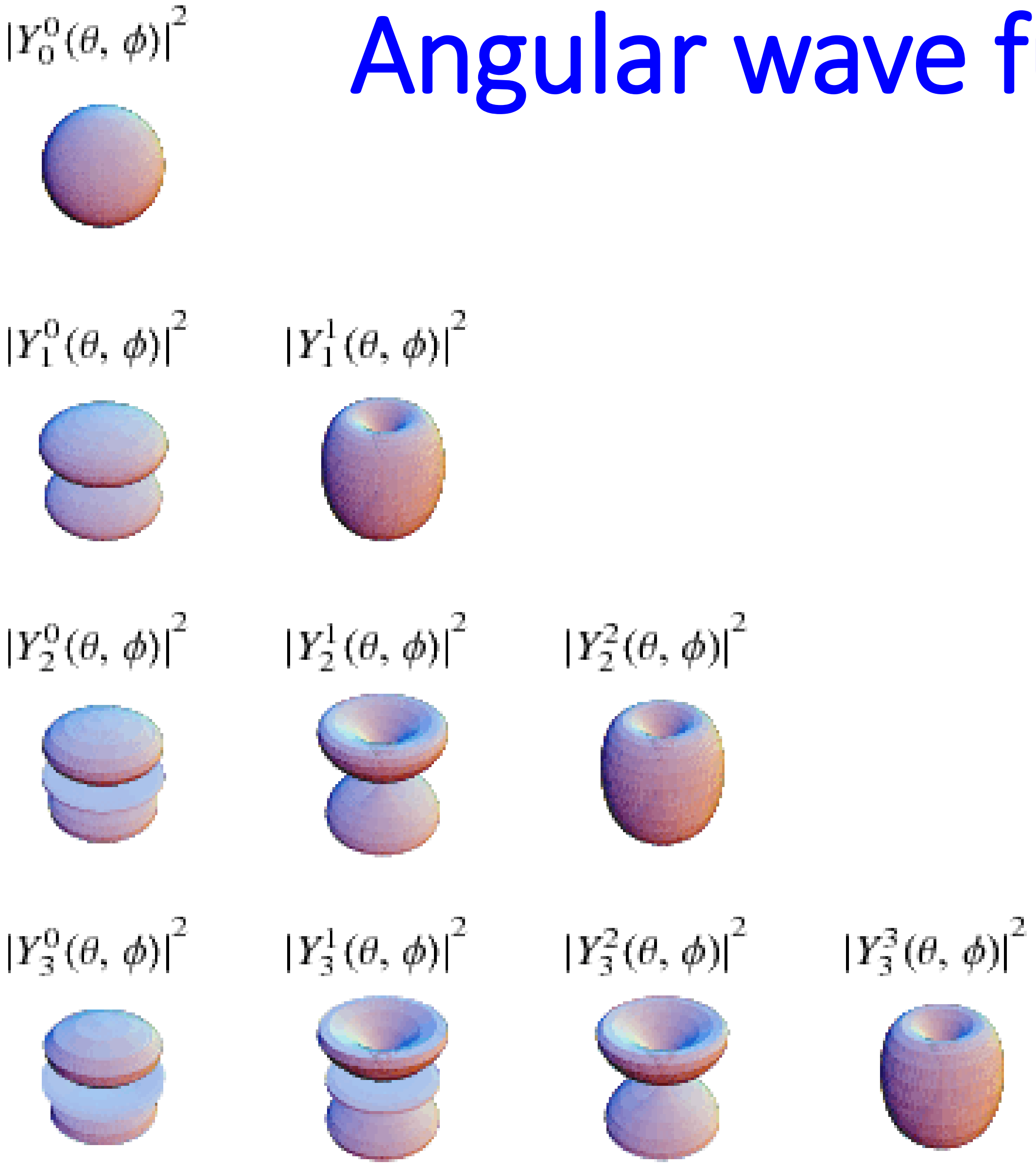








Angular wave function - Y_{lm}

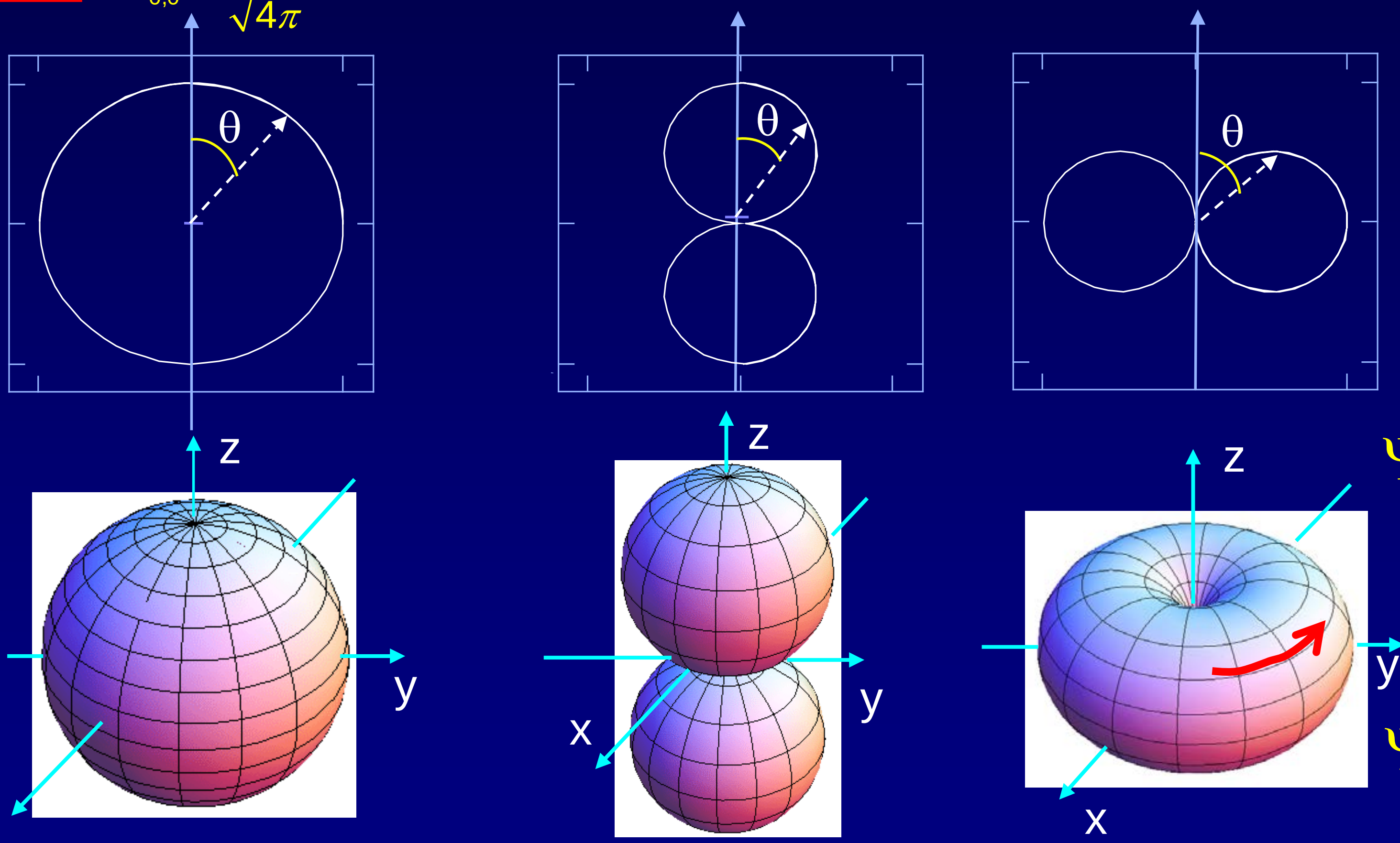


http://mathworld.wolfram.com/SphericalHarmonic.html

The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

$l = 0$ $\qquad Y_{0,0} = \dfrac{1}{\sqrt{4\pi}}$

$l = 1$ $\qquad |Y_{1,0}| \propto |\cos\theta| \qquad |Y_{1,\pm1}| \propto |\sin\theta|$



Length of the dashed arrow is the magnitude of Y_{lm} as a function of θ.

$$\Psi_{1,+1} \propto e^{+i(\phi-\omega t)}$$

Positive L_z

$$\Psi_{1,-1} \propto e^{+i(-\phi-\omega t)}$$

The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

$\boxed{l = 2}$

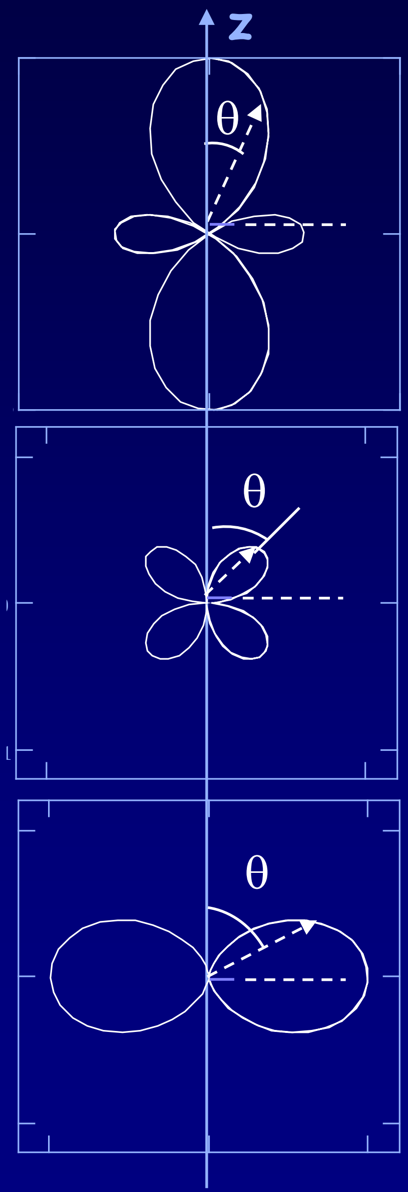
$$|Y_{2,0}| \propto \left|\left(3\cos^2\theta - 1\right)\right|$$

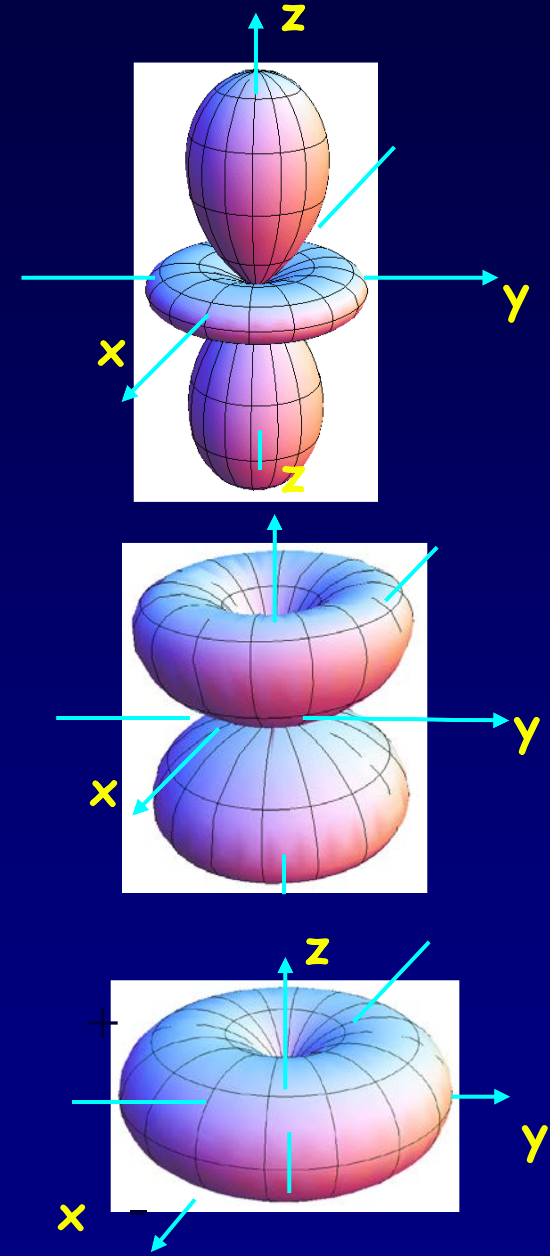
$$Y_{2,\pm1} \propto \sin\theta\cos\theta$$

$$\propto e^{\pm i\phi}$$

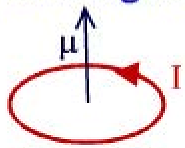
$$|Y_{2,\pm2}| \propto \left|\sin^2\theta\right|$$

$$\propto e^{\pm 2i\phi}$$





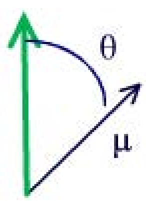
current in a loop creates/is affected by a magnetic field:



The loop has a 'magnetic moment' $\mu = IA\hat{n}$

I = current
A = loop area
$\hat{n}$ = normal to loop (using RHRule)

$\mathbf{B} = B_z\hat{z}$



$\mathbf{U} = -\mu \bullet \mathbf{B} = -\mu_z B_z$

n = "principal quantum number"

l = "total orbital angular momentum" L = r x p

m = projection of the angular momentum along z-axis

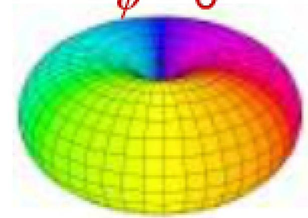
"magnetic quantum number"

Magnetic moment

$Y_{1,1}(\theta,\phi) \propto \sin(\theta)e^{+i\phi}$

$\phi = 0$

$\pi/2$



$3\pi/2$

$\phi = \pi$

$\Psi(\phi,t) \propto e^{+i\phi}\, e^{-i\omega t}$
$= e^{+i(\phi - \omega t)}$

~electron current around the z-axis

$\rightarrow L_z = \hbar$

l=1
m_l=+/- 1