Chapter 6 – The Hydrogen Atom

Background: We have discussed the PIB, HO, and the energy of the RR model. In this chapter, we will discuss the wavefunctions of the RR, the H-atom, and atomic orbitals.

* A single particle moving under a central force – adopted from Scott Kirby's notes
  http://web.umr.edu/~pchem/qchem/pdf/qchem.lecture15.fall2002.pdf

- such a system depends only on the distance and the not the direction and is spherically symmetric
- the potential energy is dependent only on position, $\hat{V} = V(r)$
  - -- in terms of spherical coordinates: $\left(\dfrac{\partial V}{\partial \theta}\right)_{r,\phi} = \left(\dfrac{\partial V}{\partial \phi}\right)_{r,\theta} = 0$
- the Hamiltonian:

$$\hat{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

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

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}\right]$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{2mr^2}\hat{L}^2 + V(r)$$

- we have shown that the angular momentum is conserved
- in order to be able to obtain definite values of both the energy and the angular momentum simultaneously we need to see if the Hamiltonian and our angular momentum operator commute

$$\left[\hat{H},\hat{L}^2\right] = \left[\hat{K},\hat{L}^2\right] + \left[\hat{V},\hat{L}^2\right]$$

$$\left[\hat{K},\hat{L}^2\right] = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{2mr^2}\hat{L}^2\right)\hat{L}^2 - \hat{L}^2\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{2mr^2}\hat{L}^2\right)$$

$$\left[\hat{K},\hat{L}^2\right] = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi}\hat{L}^2 + \frac{1}{2mr^2}\hat{L}^2\hat{L}^2 + \hat{L}^2\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} - \hat{L}^2\frac{1}{2mr^2}\hat{L}^2$$

since the angular momentum operator is dependent of r the kinetic and angular momentum operators commute

$$\left[\hat{V},\hat{L}^2\right] = 0$$

The same can be said about the angular momentum and potential operators – therefore, the Hamiltonian and angular momentum operators commute – so we can measure both the angular momentum and the energy of any given state simultaneously

- Is our one particle description applicable to the H-atom

-- as we know there are two particles involved in hydrogen: a proton & an Electron

-- as it stands we would have two sets of coordinates (one for particle) to describe this sytem

-- let's look at the reduced mass:

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{\left(9.109\times10^{-31}kg\right)\left(1.673\times10^{-27}kg\right)}{\left(9.109\times10^{-31}kg\right)+\left(1.673\times10^{-27}kg\right)} = 9.1094\times10^{-31}kg \sim 0.9995 m_e$$

--- this indicates that we will loose little accuracy by approximating our H-atom as have the proton fixed at the origin

--- in other words we can treat our H-atom a single particle system

* Schrödinger Eqn for the H-atom

- our model will be a proton fixed at the nucleus interacting with an electron which has a mass m_e and separated from the proton by a distance of r
- recall the Coulombic potential: $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$ where e is the charge of the electron/proton and ε_0 is the permittivity of free space
- our Hamiltonian becomes:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

- the Schrödinger eqn

$$\hat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right)-\frac{e^2}{4\pi\varepsilon_0 r}\right]\psi = E\psi$$

say we multiply thru by $2\mathrm{m_e}r^2$ and move all terms to one side of the eqn

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi - \hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]\psi - 2\mathrm{m_e}r^2\left[\frac{e^2}{4\pi\varepsilon_0 r}+E\right]\psi = 0$$

-- the wavefunction will have dependents r, θ, and ϕ: ψ(r, θ, ϕ)

-- we can once again invoke separation variables: ψ(r, θ, ϕ) = R(r)Y(θ, ϕ)

--- then we can separate the r terms from those possessing θ & ϕ

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

$$-2\mathrm{m_e}r^2\left[\frac{e^2}{4\pi\varepsilon_0 r}+E\right]R(r)Y(\theta,\phi)=0$$

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

$$-\frac{2\mathrm{m_e}r^2}{R(r)Y(\theta,\phi)}\left[\frac{e^2}{4\pi\varepsilon_0 r}+E\right]R(r)Y(\theta,\phi)=0$$

Since these terms are independent of each other we can separate our SE into 2

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

$$-\frac{2\mathrm{m_e}r^2}{R(r)}\left[\frac{e^2}{4\pi\varepsilon_0 r}+E\right]R(r)=0$$

$$\frac{-\hbar^2}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)-\frac{2\mathrm{m_e}r^2}{R(r)}\left[\frac{e^2}{4\pi\varepsilon_0 r}+E\right]R(r)=0$$

$$\rightarrow -\frac{1}{R(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{2\mathrm{m_e}r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)\right]R(r)=-\beta$$

$$\frac{\hbar^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]Y(\theta,\phi)=\beta$$

$$\rightarrow \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\left(\frac{\partial^2 Y}{\partial\phi^2}\right)+\beta\sin^2\theta Y=0$$

-- the R(r) term is called the radial equation and will be addressed later

-- the Y(θ, ϕ)is the angular momentum dependence and we will now solve this \ system

* Wave Functions of the Rigid Rotator & Spherical Harmonics

- once again we need to use separation of variables: $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$
- if we substitute and divide this relationship into our SE:

$$\frac{1}{\Theta(\theta)\Phi(\phi)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)\Phi(\phi)+\left(\frac{\partial^2}{\partial\phi^2}\right)\Theta(\theta)\Phi(\phi)+\beta\sin^2\theta\Theta(\theta)\Phi(\phi)\right]=0$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\frac{1}{\Phi(\phi)}\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)+\beta\sin^2\theta=0$$

- As always we can separate these two equations into their independent components:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\frac{1}{\Phi(\phi)}\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)+\beta\sin^2\theta=0$$

$$-m^2+m^2=0$$

$$\frac{1}{\Phi(\phi)}\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)=-m^2$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta=m^2$$

- Let's look at phi first:

$$\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)=-m^2\Phi(\phi)\rightarrow\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)+m^2\Phi(\phi)=0$$

-- we have seen the solution to this equation many times – however, we must take into consideration that these are spherical coordinates and what that means for our wavefunction

$$\Phi(\phi)=A_m e^{im\phi}\quad \Phi(\phi)=A_{-m}e^{-im\phi}$$

--- to be single valued we need to set $\Phi(\phi)=\Phi(\phi+2\pi)$ since phi is the component that circle the z-axis and so it will be at the same exact place for ϕ & $\phi+2\pi$

$$A_m e^{im(\phi+2\pi)}=A_m e^{im\phi}\quad A_{-m}e^{-im(\phi+2\pi)}=A_{-m}e^{-im\phi}$$

for these relationships to be true $e^{\pm i2m\pi}=1$ with $m=0,\pm1,\pm2,\ldots$

--- Normalization of phi leads to $N=\frac{1}{\sqrt{2\pi}}\quad\therefore\quad\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$

- Theta's Turn

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta=m^2$$

we rearrange the equation:

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

Now, we change the variables: $x=\cos\theta,\ \Theta(\theta)=P(x)$

$dx=-\sin\theta d\theta\rightarrow\frac{dx}{-\sin\theta}=d\theta$ or $\frac{1}{d\theta}=\frac{-\sin\theta}{dx}$

where $0\le\theta\le\pi\rightarrow-1\le x\le1$ and $\sin^2\theta=1-\cos^2\theta=1-x^2$

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

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

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

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

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

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

-- due to the continuity of theta – we have a quantization constraint for β

$\beta=l\left(l+1\right)$ where $l=0,1,2,\ldots$ and $m=0,\pm1,\pm2,\ldots$

-- therefore we also have quantization of energy:

$$\beta=\frac{2IE}{\hbar^2}\rightarrow E=\frac{\hbar^2}{2I}\beta=\frac{\hbar^2}{2I}l\left(l+1\right)\ \ l=0,1,2,\ldots\quad |m|\leq l$$

this is very similar to rigid rotator: $E=\dfrac{\hbar^2}{2I}J\left(J+1\right)\ \ J=0,1,2,\ldots$

-- our P(x) is actually a set of polynomials called Legendre (lə′zhän·drə) polynomials, $P_l^{|m|}(x)$, which arise from central force problems in classical physics

$$P_l^{|m|}(x)=(1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l^0(x)=P_l^{|m|}(\cos\theta)$$

---- the first few $P_l^0(x)$

$$P_0^0(x)=1\quad P_1^0(x)=x=\cos\theta\quad P_2^0(x)=\frac{1}{2}\left(3x^2-1\right)=\frac{1}{2}\left(3\cos\theta^2-1\right)$$

---- Application of our formula for the first few $P_l^1(x)$

$$P_1^1(x)=(1-x^2)^{1/2}\frac{d}{dx}P_1^0(x)=(1-x^2)^{1/2}\frac{d}{dx}x=(1-x^2)^{1/2}=(1-\cos^2)^{1/2}=\sin\theta$$

$$P_2^1(x)=(1-x^2)^{1/2}\frac{d}{dx}P_2^0(x)=(1-x^2)^{1/2}\frac{d}{dx}\left[\frac{1}{2}\left(3x^2-1\right)\right]=(1-x^2\theta)^{1/2}\bullet3x=3\sin\theta\cos\theta$$

$$P_2^2(x)=(1-x^2)^{2/2}\frac{d^2}{dx^2}P_2^0(x)=(1-x^2)\frac{d^2}{dx^2}\left[\frac{1}{2}\left(3x^2-1\right)\right]=3\sin^2\theta$$

--- Normalizing these obnoxious polynomials

$$\int_{-1}^{1}P_l^{|m|}(x)P_n^{|m|}(x)dx=\frac{2}{2l+1}\frac{\left(l+|m|\right)!}{\left(l-|m|\right)!}\delta_{\text{ln}}\quad or\quad N_{lm}=\sqrt{\frac{2l+1}{2}\frac{\left(l-|m|\right)!}{\left(l+|m|\right)!}}$$

-- Putting it all together – Spherical Harmonics:

$$Y_l^m(\theta,\phi)=\Theta(\theta)\Phi_m(\phi)=\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)\frac{1}{\sqrt{2\pi}}e^{im\phi}=\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

where $l=0,1,2,\dots$ and $m=0,\pm1,\pm2,\dots$

--- let's get a few spherical harmonics:

$$Y_0^0=\sqrt{\frac{2\bullet0+1}{4\pi}\frac{(0-|0|)!}{(0+|0|)!}}P_0^0(\cos\theta)e^{i\bullet0\bullet\phi}=\sqrt{\frac{1}{4\pi}}$$

$$Y_1^0=\sqrt{\frac{2\bullet1+1}{4\pi}\frac{(1-|0|)!}{(1+|0|)!}}P_1^0(\cos\theta)e^{i\bullet0\bullet\phi}=\sqrt{\frac{3}{4\pi}}\cos\theta$$

* Angular Momentum & Quantum Numbers

$$\hat{L}^2Y_l^m(\theta,\phi)=\hbar^2l(l+1)Y_l^m(\theta,\phi)\qquad l=0,1,2$$

- I will leave it to you prove the above relationship to yourself
- this is the same *l* that you learned in genchem – and it is called the angular momentum quantum number since it arises when we apply the angular momentum operator twice
- in chapter 5, we showed $\hat{H}=\frac{\hat{L}^2}{2I}\quad\therefore\quad\hat{H}Y_l^m(\theta,\phi)=\frac{\hbar^2l(l+1)}{2I}Y_l^m(\theta,\phi)\quad l=0,1,2$

  and hence the energy values are given by: $E=\frac{\hbar^2l(l+1)}{2I}$

* The Three Components of Angular Momentum do not play nice together

- they cannot be measured simultaneously
- recall the angular momentum operator by components:

$$\hat{L}_x=y\hat{p}_z-z\hat{p}_y=-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\rightarrow-i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta}-\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y=z\hat{p}_x-x\hat{p}_z=-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial x}\right)\rightarrow-i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z=x\hat{p}_y-y\hat{p}_x=-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\rightarrow-i\hbar\frac{\partial}{\partial\phi}$$

-- $\hat{L}_ze^{im\phi}=-i\hbar\frac{\partial}{\partial\phi}e^{im\phi}=-i\hbar(im)e^{im\phi}=\hbar me^{im\phi}$

--- since the Legendre component of the spherical harmonic has no ϕ dependency: $\hat{L}_zY_l^m(\theta,\phi)=m\hbar Y_l^m(\theta,\phi)$

--- therefore the spherical harmonics are also eigenfunctions of the z-component of the angular momentum operator

-- it turns out that the spherical harmonics are not eigenfunctions of the x- and y-components of the angular momentum operator

- time to prove $|m| \le l$
  - $\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)$ & $\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$ $l = 0,1,2$
  - Also, by definition: $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \rightarrow \hat{L}^2 - \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2$
  - $\left(\hat{L}^2 - \hat{L}_z^2\right) Y_l^m(\theta,\phi) = \left[l(l+1) - m^2\right]\hbar^2 Y_l^m(\theta,\phi) = \left(\hat{L}_x^2 + \hat{L}_y^2\right) Y_l^m(\theta,\phi)$
  - since $\hat{L}_x^2 + \hat{L}_y^2$ is a sum of two squares, $\left[l(l+1) - m^2\right]\hbar^2 \ge 0 \rightarrow l(l+1) \ge m^2$
  - finally, since l and m are both integers $|m| \le l \;\therefore\; m = 0, \pm 1, \pm 2, \ldots \pm l$
    - which is what we can the magnetic quantum number

* Finally the Hydrogen Atomic Orbitals

- The radial component is:

$$-\frac{h^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{h^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r} - E\right]R = 0$$

  - the solution is:

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{m_e e^4}{32\varepsilon_0^2 \hbar^2 n^2} \quad n = 1, 2, 3, \ldots$$

  - recall Bohr radius is $a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$
  - so then the energy can also be written as

$$E_n = -\frac{e^4}{8\pi\varepsilon_0 a_0 n^2} \quad n = 1, 2, 3, \ldots$$

- a consequence of solving this radial component is “n” which must satisfy the condition $n \ge l + 1$ or $0 \le l \le n - 1$ $\quad l = 0, 1, 2, \ldots \rightarrow n = 1, 2, 3, \ldots$
  - this should look familiar as the principle quantum number
- the results for $R_{nl}(r)$:

$$R_{nl}(r) = -\left(\frac{(n-l-1)!}{2n\left[(n+1)!\right]^3}\right)^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n+1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

  - where $L_{n+1}^{2l+1}\left(\frac{2r}{na_0}\right)$ are Laguerre (ləʹger) polynomials, here are the first few:

$$n = 1 \quad l = 0 \quad L_1^1 = -1$$

$$n = 2 \quad l = 0 \quad L_2^1 = -2!\left(2 - \frac{Zr}{a_0}\right)$$

$$l = 1 \quad L_3^3 = -3!$$

  - it turns out that this wavefunction is normalized –you should prove this later
- the total hydrogen atomic wavefunction, $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_l^m(\theta,\phi)$
  - these wavefunctions are orthonormal:

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} \psi^*_{n'l'm'}\left(r,\theta,\phi\right)\psi_{nlm}\left(r,\theta,\phi\right)d\phi = \delta_{n'n}\delta_{l'l}\delta_{m'm}$$

-- the first few wavefunctions where Z = atomic number

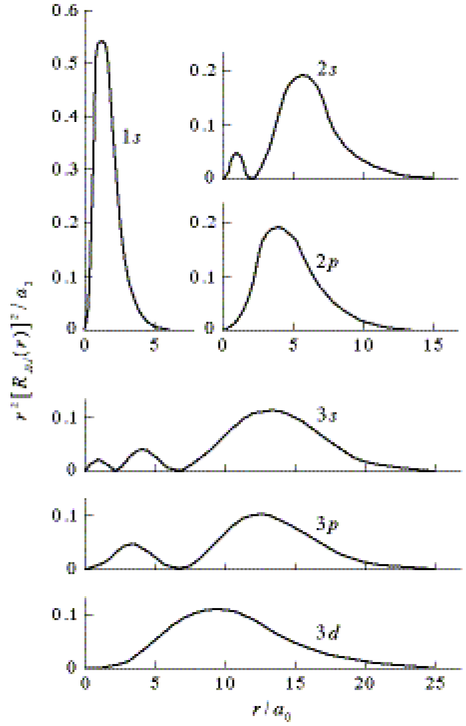
n	l	$\lvert m \rvert$	wavefunction, $\psi_{nlm}\left(r,\theta,\phi\right)$
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$
2	1	±1	$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta e^{\pm i\phi}$

* The Atomic Orbitals

- quantum numbers – a rehash
    -- n, our principle quantum number – related to size, $n = 1, 2, 3, \ldots$
    -- *l*, angular momentum quantum number – related to shape, $0 \le l \le n-1$
        --- describes the angular momentum of e- about a p+: $\lvert L \rvert = \hbar\sqrt{l\left(l+1\right)}$

Orbital	**Name**	**l**
s	sharp	0
p	principle	1
d	diffuse	2
f	fundamental	3

        --- these names come from spectroscopy
        --- higher orbitals (e.g. g & h) do not have names
    -- m, magnetic quantum number – related to direction the orbital points in, $m = -l, \ldots + l$
        --- the z-component of the angular momentum is completely specified by m: $L_z = m\hbar$
        --- the name comes from the energy of the hydrogen atom in a magnetic field
            ---- in the absence of a field 2*l* + 1
            ---- the splitting in the presence of a magnetic field is called the Zeeman effect – this will be discussed in more detail when we talk about magnetic spectroscopy
- Radial Distribution Plots
    -- describe the probabilistic location of an electron using the distance from the nucleus or radius, r



-- for the 1s: the maximum is located at a distance of r = a_0

-- in general the number of nodes for each orbital is given by n – *l* – 1 nodes

- p orbitals
  - -- m = 0 is the p_z orbital on the basis of our description where the spherical harmonic has only real components
  - -- the m = ±1 correspond to the p_x & p_y orbitals
    - --- there are both real and imaginary components for these orbitals

$$Y_1^1(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}\quad Y_1^{-1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$$

--- where the probability densities are equal:

$$\left|Y_1^1(\theta,\phi)\right|^2=\left|Y_1^{-1}(\theta,\phi)\right|^2=\frac{3}{8\pi}\sin^2\theta$$

--- these are often represented by linear combos:

$$p_x=\frac{1}{\sqrt{2}}\left(Y_1^1+Y_1^{-1}\right)=\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi\quad p_y=\frac{1}{\sqrt{2i}}\left(Y_1^1+Y_1^{-1}\right)=\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$$

- there are similar combos for the d-orbitals

* Multi-electron atoms

- we can solve the SE exactly for our single electron system but that is not the case when another electron gets involved
- we will discuss how to handle such a system in the next chapter