PH102, 2014W, Lecture Notes: January 14, Tues, Class 3

Hydrogen Atom in (r, θ, ϕ) coordinates and (l, m_l) orbital quantization

Objectives:

- Express the time independent Schrodinger Equation for the hydrogen atom in (r, θ, ϕ)
- Apply the separation of variables method to come up with three equations.
- Understand what three quantum numbers $(n, l,\ m_l)$ represent and what combinations of quantum numbers are possible in a given n (energy) state.
- Understand the quantization of the angular momentum and the relationship between $l\ and\ m_l$.
- List degeneracies for each n state.

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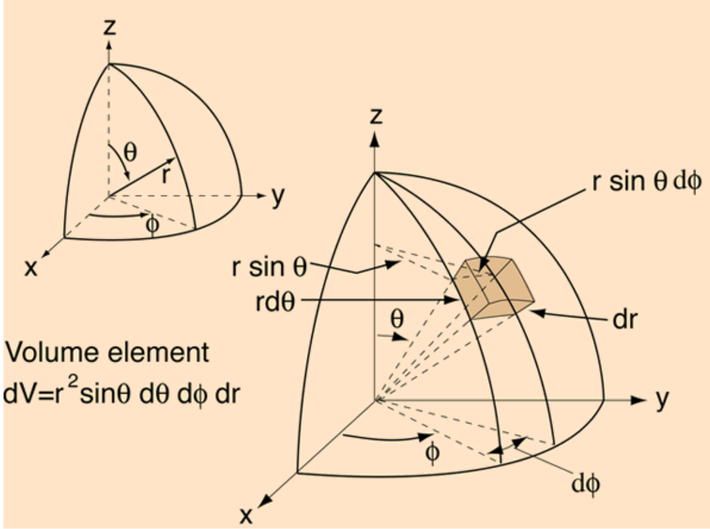
Hydrogen Atom in 3-D

The potential energy of the electron in the hydrogen atom (= Coulomb potential energy between two charges: (+*e*) of the proton and (-*e*) of the electron separated by *r*).

$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{-e^2}{r} \qquad \text{(e2.13)}$$

Since this potential has a spherical symmetry, to make solving the Schrodinger Equation easier, we choose the spherical polar coordinate system.



$$(x, y, z) \quad \leftrightarrow \quad (r, \theta, \phi)$$

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \phi = tan^{-1}\dfrac{y}{x} \\ \theta = cos^{-1}\dfrac{z}{r} \end{cases}$$

$$\begin{cases} x = rsin\theta cos\phi \\ y = r\ sin\theta sin\ \phi \\ z = rcos\theta \end{cases}$$

The time independent Schrodinger Equation for the hydrogen atom (an electron + a proton)

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E\ \psi(\vec{x}) \qquad \text{(e2.14)}$$

∇^2 can be expressed as follows:

In (x, y, z),

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In (r, θ, ϕ),

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

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

In (x, y, z), the time independent Schrodinger Equation (e2.14) becomes

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi\ (x, y, z) + \ U(x, y, z)\psi\ (x, y, z) = -\frac{2mE}{\hbar^2}\psi\ (x, y, z)$$

In (r, θ, ϕ), the time independent Schrodinger Equation (e2.14) becomes

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]\psi(r, \theta, \phi) + U(r)\ \psi(r, \theta, \phi) = E\ \psi(r, \theta, \phi)$$

Then, put the partial derivertive of $\theta\ and\ \phi$ on one side and the radial partial derivertive on the other side of the equation:

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

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

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

$$\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right)\psi + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}\psi = \ \left[-\ \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \ \frac{2mr^2}{\hbar^2}\ (E - U)\right]\psi \qquad \text{(e2.15)}$$

Separation of variables
$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ → for shorthand $\psi = R\Theta\Phi$

$$\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right)R\Theta\Phi + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}R\Theta\Phi = \ \left[-\ \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \ \frac{2mr^2}{\hbar^2}\ (E - U)\right]R\Theta\Phi$$

$$\frac{\partial \psi}{\partial r} = \ \Theta\Phi\frac{\partial R}{\partial r}$$

$$\frac{\partial \psi}{\partial \theta} = R\Phi\frac{\partial \Theta}{\partial \theta}$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} = R\Theta\frac{\partial^2 \Phi}{\partial \phi^2}$$

After substituting $\psi(r,\theta,\phi) with\ R(r)\Theta(\theta)\Phi(\phi)$, (e2.15) becomes:

$$R\Phi\,\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right)+R\Theta\frac{1}{sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2mr^2}{\hbar^2}\,(E-U)\,R\Theta\Phi \qquad \text{(e2.16)}$$

Divide (e2.16) by $R\Theta\Phi$

$$\frac{1}{\Theta}\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2mr^2}{\hbar^2}\,(E-U)=C\ \text{(Constant)} \qquad \text{(e2.17)}$$

Consider C is **$-l(l+1)$, then each side of the equation (e2.17) should be the same constant of $-l(l+1)$.**

$$\begin{cases}-\dfrac{1}{R}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right)-\dfrac{2mr^2}{\hbar^2}\,(E-U(r))=C=\boldsymbol{-l(l+1)\rightarrow(e2.18)a}\\ \dfrac{1}{\Theta}\dfrac{1}{sin\theta}\dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right)+\dfrac{1}{\Phi}\dfrac{1}{sin^2\theta}\dfrac{\partial^2\Phi}{\partial\phi^2}=C=\boldsymbol{-l(l+1)\rightarrow(e2.18)b}\end{cases}$$

Divide both sides of (e2.18)b by $csc^2\theta\ (or\ multiply\ sin^2\theta\ since\ csc\theta=\frac{1}{sin\theta})$

$$\frac{1}{\Theta}sin\theta\,\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-l(l+1)\,sin^2\theta \qquad \text{(e2.19)}$$

Arrange (e2.19) to separate $the\ partial\ derivative\ of\ \theta\ and\ that\ of\ \phi$

$$\frac{1}{\Theta}sin\theta\,\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad \text{(e2.20)}$$

$$=\boldsymbol{m_l^2}\ \text{(another constant)}$$

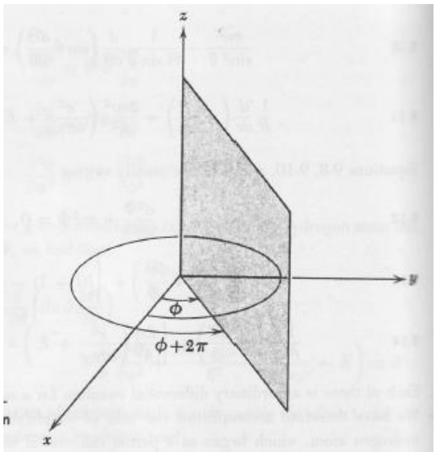
Three equations can be derived from the time independent Schrodinger Equation (e2.14)

$$\begin{cases}\dfrac{\partial^2\Phi}{\partial\phi^2}=-m_l^2\Phi\\ sin\theta\dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right)+[l(l+1)sin^2\theta-m_l^2]\Theta=0\\ \dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right)+\dfrac{2mr^2}{\hbar^2}\,(E-U(r))R\ -l(l+1)R=0\end{cases}$$

Azimuthal Equation

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

Solution: $\Phi(\phi)=A\,e^{im_l\phi}$
Boundary condition: Since $\phi\ and\ \phi+2\pi$ represent the same meridian plane. Therefore,



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

$$A\, e^{im_l\phi} = A\, e^{im_l(\phi+2\pi)} = Ae^{im_l\phi}e^{i2\pi m_l}$$

$$e^{i2\pi m_l} = 1 = cos2\pi m_l + i\, sin2\pi m_l$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, etc.$$

→ Magnetic quantum number of the hydrogen atom

Polar Equation

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

Solutions are called the associated Legendre Functions
The solutions exist only when the constant *l* is an integer equal to or greater than $|m_l|$.

That is, any given *l*, $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

- *l* is called "orbital quantum number"

Radial Equation

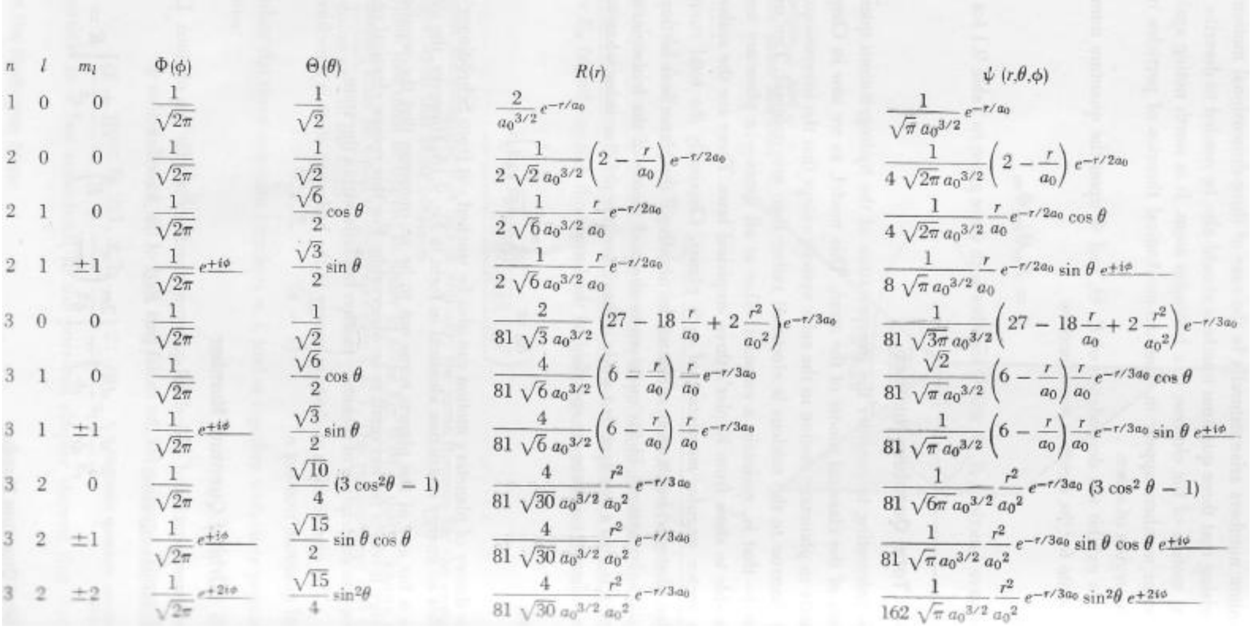
Solutions are called the associated Laguerre functions

- Solutions can be solved only when E is positive or has one of the following energy values

$E_n = -\frac{me^4}{32\pi\varepsilon_0^2\hbar^2}(\frac{1}{n^2})$ where *n* is an integer

→n is called the principal quantum number
This is the same as Bohr's energy levels for the hydrogen atom.

- Another condition that should be obeyed is n should be equal to or greater than *l* + 1.
  l = 0, 1, 2, …(*n*-1)



n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$
2	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$
3	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta-1)$
3	2	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	±2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

Three Quantum Numbers that describe the Hydrogen Atom:

- Principal quantum number, $n = 1, 2, 3, \ldots$
- Orbital quantum number, $l = 0, 1, 2, \ldots (n-1)$ where l =1(*s*), =2(*p*), =3(*d*), =4(*f*), *etc.*
- Magnetic quantum number, $m_l = 0, \pm1, \pm2, \ldots \pm l$

Wave function = $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l}$

where $\Theta_{l,m_l}\Phi_{m_l} = \mathbf{Y}_l^{m_l}$ (Spherical harmonics)

Symbolic designation of atomic states in hydrogen

	s *l = 0*	*p* *l =1*	*d* *l =2*	*f* *l =3*	*g* *l = 4*	*h* *l =5*
n = 1	*1s*					
n = 2	*2s*	*2p*				
n = 3	*3s*	*3p*	*3d*			
n = 4	*4s*	*4p*	*4d*	*4f*		
n = 5	*5s*	*5p*	*5d*	*5f*	*5g*	
n = 6	*6s*	*6p*	*6d*	*6f*	*6g*	*6h*

The origin of angular momentum quantization

Radial Equation is

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E-\underbrace{U(r)\big)R\ -l(l}+1)R=0$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left[E-U(r)\ -\frac{l(l+1)\hbar^2}{2mr^2}\right]R=0 \quad \text{(e3.1)}$$

The total energy of the electron E = Kinetic E (radial) + Kinetic E (orbital) + $U(r)$

Put the expression of E into (e3.1), then (e3.2) becomes

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left[Kineric\ E\ (radial)+\ Kinetic\ E\ (orbital)\ -\frac{l(l+1)\hbar^2}{2mr^2}\right]R=0$$

$$Kinetic\ E\ (orbital)=\frac{l(l+1)\hbar^2}{2mr^2}$$

The orbital kinetic energy of the electron = $\frac{1}{2}m\,v_{orbital}^2\ =\frac{L^2}{2mr^2}$
The angular momentum L of the electron = $L=mv_{orbital}r$ → $v_{orbital}=\ \frac{L}{mr}$

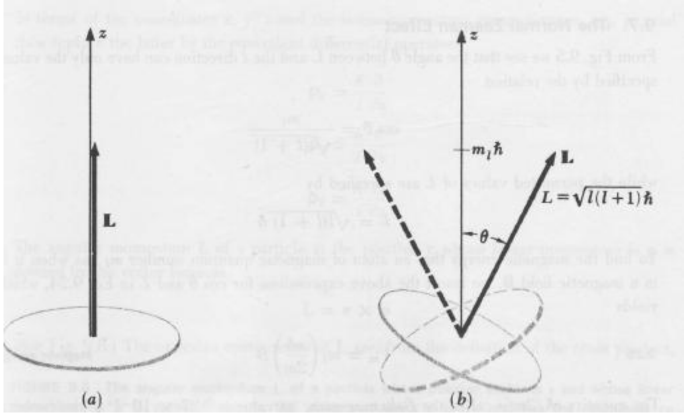
$$\frac{L^2}{2mr^2}=\ \frac{l(l+1)\hbar^2}{2mr^2}$$

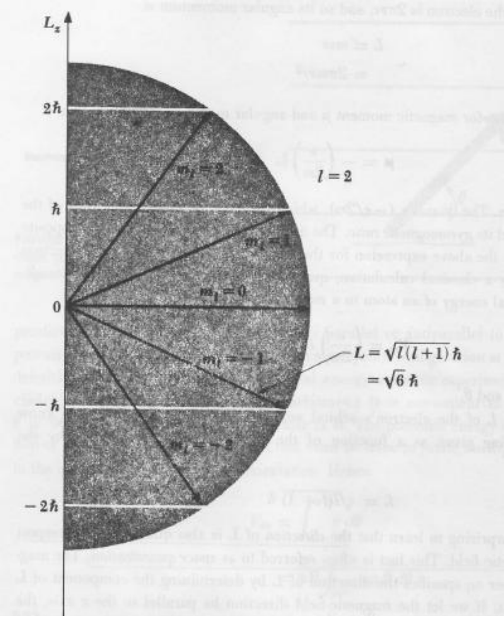
$$L^2=\ l(l+1)\hbar^2$$

$L=\ \sqrt{l(l+1)}\hbar$ → Electron angular momentum L is quantized

Angular momemtum L is defined as a vector L = r x p

- L is perpendicular to the plane in which the rotational motion takes place and follows the right hand rule.
- The amount is quantized and determined by the orbital angular quantum number, l. $L=\sqrt{l(l+1)}\hbar$
- The direction is also quantized and determined by the $m_l\ value$ with respect to the external magnetic field. The magnetic quantum number m_l specifies the direction of L determining the component of L in the magnetic field direction. If the magnetic field direction is parallel to the z-axis, then the component of L on the z-axis would be $L_z=\ m_l\hbar$.
- L can never be parallel to the z-axis because the amount of L is always greater than the largest m_l value allowed.
- Uncertainty principle explains the relationship between L and Lz.

- 



Three quantum numbers are defined so that the resulting wave functions can satisfy the Schrodinger Equation:

- Principal quantum number, n
- Orbital quantum number, l,
- Magnetic quantum number, m_l

where

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\ \hbar^2}\right)\left(\frac{1}{n^2}\right) =$$
$$-\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$L^2 = l(l+1)\hbar^2$$
$$L_z = m_l\hbar$$

where Bohr radius $a_0 = \frac{4\pi\varepsilon_0\ \hbar^2}{me^2}$= 0.053 nm or 0.53 A; and
Hydrogen atom’s ground state energy, $E_1 = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right) = -13.6\ eV$

Wave function = $\psi(r,\theta,\phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}\mathbf{Y}_l^{m_l}$

where $\Theta_{l,m_l}\Phi_{m_l}$= $\mathbf{Y}_l^{m_l}$ (Spherical harmonics)

These relationships can be simply written using operator notations:

$$\mathbf{H}\psi_{n,l,m_l} = \boldsymbol{E_n}\psi_{n,l,m_l}$$
$$\mathbf{L^2}\psi_{n,l,m_l} = \boldsymbol{l(l+1)}\hbar^{\mathbf{2}}\psi_{n,l,m_l}$$
$$\mathbf{L_z}\psi_{n,l,m_l} = \boldsymbol{m_l}\hbar\psi_{n,l,m_l}$$

Note. These equations can be applied to all systems where the Hamiltonian (H = T+V) has a spherical symmetry (remember that the hydrogen atom's potential energy has a spherical symmetry). In such a case, the wave function, ψ_{n,l,m_l}, is an eigenfunction of **H, $\mathbf{L^2}, \mathbf{L_z}$ and $\boldsymbol{E_n, L^2, and\ L_z}$ are all quantized.**

Degeneracies in the Hydrogen Atom

According to the rules related to the three quantum numbers above, the following states (wave functions) are possible in each energy level:

n	l	m_l	E_n(eV)	$\|L\|$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2^2)	2s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		
3	0	0	-1.51	0	0	ψ_{300}	$R_{30}\mathbf{Y}_0^0$	9 (=3^2)	3s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{31-1}	$R_{31}\mathbf{Y}_1^{-1}$		3p
		0			0	ψ_{310}	$R_{31}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{311}	$R_{31}\mathbf{Y}_1^1$		
	2	-2		$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}	$R_{32}\mathbf{Y}_2^{-2}$		3d
		--1			$-\hbar$	ψ_{32-1}	$R_{32}\mathbf{Y}_2^{-1}$		
		0			0	ψ_{320}	$R_{32}\mathbf{Y}_2^0$		
		1			$+\hbar$	ψ_{321}	$R_{32}\mathbf{Y}_2^1$		
		2			$+2\hbar$	ψ_{322}	$R_{32}\mathbf{Y}_2^2$		

Therefore, in the hydrogen atom, there are n^2degenerate wave functions associated with each E_n.