PH102, 2012W, Lecture Notes: January 15, 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.
- Come up with the normalization condition for a spherically symmetric potential in (r, θ, ϕ).
- Recognize characteristics of radial and angular probability densities using n, l, m_l.
- Extend the Schrodinger Equation solutions of the hydrogen atom to the hydrogenlike atoms.

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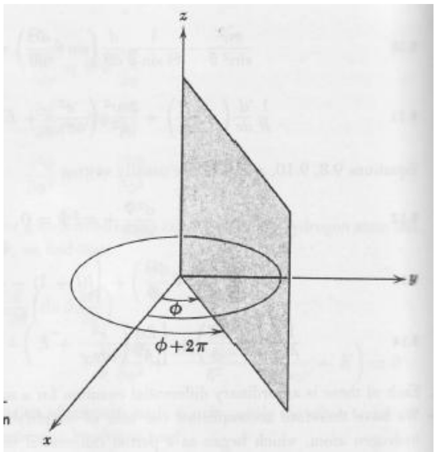
In the last class, we learned that the time independent Schrodinger Equation for a hydrogen atom in a Coulomb potential can be turned into three equations after the separation of variable method as follows:

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

Azimuthal Equation

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



Solution: $\Phi(\phi) = A\ e^{i m_l \phi}$

Boundary condition: Since $\phi\ and\ \phi + 2\pi$ represent the same meridian plane. Therefore,

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

$$A\ e^{i m_l \phi} =\ A\ e^{i m_l (\phi + 2\pi)} = A e^{i m_l \phi} e^{i 2\pi m_l}$$

$$e^{i 2\pi m_l} = 1 = cos2\pi m_l +\ i\ sin2\pi m_l$$

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

→ 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

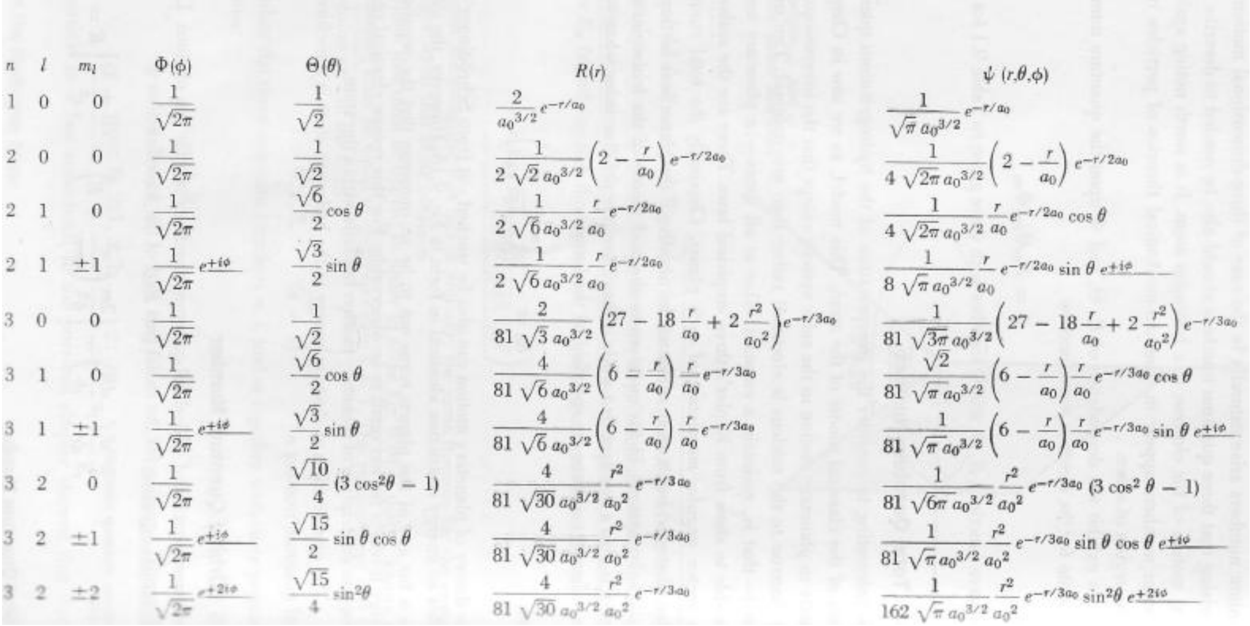
- Solutions can be solved only when E is positive or has one of the following energy values

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

→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, $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

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

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

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

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 = $\frac{1}{2}m\,v_{orbital}^2 = \frac{L^2}{2mr^2}$

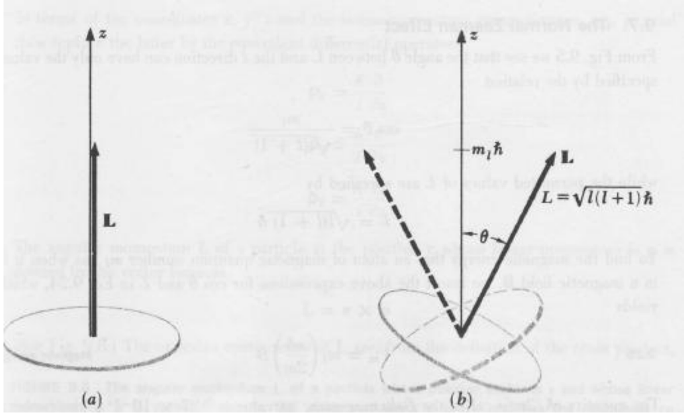
The angular momentum L of the electron = $L = mv_{orbital}r$ → $v_{orbital} = \frac{L}{mr}$

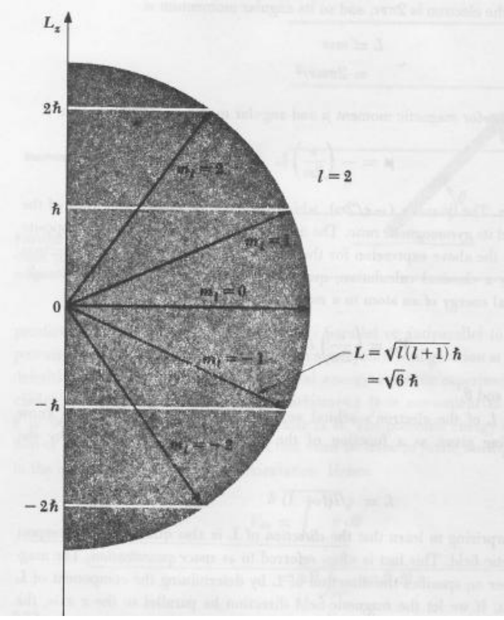
$$\frac{L^2}{2mr^2} = \frac{l(l+1)\hbar^2}{2mr^2}$$

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

$L = \sqrt{l(l+1)}\hbar$ → 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:

$$\mathbf{H}\psi_{n,l,m_l} = \boldsymbol{E_n}\psi_{n,l,m_l}$$

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

$$\mathbf{L_z}\psi_{n,l,m_l} = \boldsymbol{m_l}\hbar\psi_{n,l,m_l}$$

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)	$\lvert L\rvert$	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.

Normalization

The probability density of the hydrogen atom can be written as:

$$|\psi_{n,l,m_l}|^2 = R(r)^2\Theta(\theta)^2\Phi(\phi)^2$$

Normalization condition: $|\psi_{n,m,m_l}|^2\ over\ all\ space\ (dV = r^2 sin\theta\ drd\theta d\phi)$

$$\begin{aligned}\int |\psi_{n,l,m_l}|^2\, dV &= \int |\psi_{n,l,m_l}|^2\, r^2 sin\theta\ drd\theta d\phi \\ &= \int_0^\infty R(r)^2 r^2\, dr \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi\end{aligned}$$

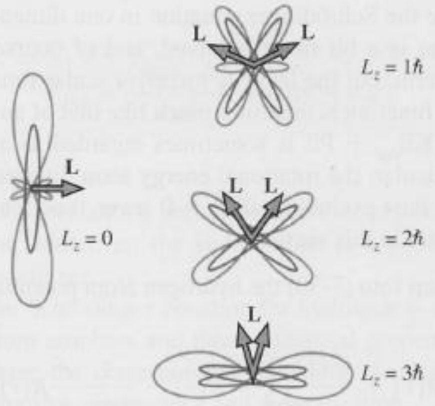
$$\begin{cases} \displaystyle\int_0^\infty R(r)^2 r^2\, dr = 1 \\ \displaystyle\int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi = 2\pi \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta = 1 \end{cases}$$

Electron whereabouts: Angular directions $(\boldsymbol{\theta}, \boldsymbol{\varphi})$
Angular Probability Density

$$\Theta(\theta)^2\Phi(\phi)^2 \equiv \mathbf{Y}_l^{m_l*}\mathbf{Y}_l^{m_l}$$

- The probability density is a diffuse cloud spread over space.
- The probability density extends farther from the origin (where the proton is) as n increases.
- The probability density should be symmetric along the ϕ axis.
- In s states where l = 0, the kinetic energy is solely radial, so the probability density is spherically symmetric. No orbital motion.
- Note that the electron is orbiting the place perpendicular to the direction of $L_z. See\ Figure\ on\ the\ right.$
- In p states where (l=1), three possible probability distributions: $L_z = 1, 0, -1$. See Figure below.
- In d states where (l=2), five possible probability distributions $L_z = 2, 1, 0, -1, -2$.

Figure 7.14 A crude correspondence to orbital motion.



- If l=0, the probability is the same in any direction.
- There is no probability at the center when $l \neq 0$. Take a look at the p, d, f orbitals as compared to s orbitals. In all $l \neq 0$ cases, as m_l increases, the probability density progressively changes from mostly along the z-axis to mostly in the xy-plane. See 7.14.
- In all $m_l \neq 0$ cases, the probability density is zero at the z-axis, suggesting that motion is more closely restricted to the xy-plane.
- All $m_l = \pm l$ cases have equatorial lobes, suggesting orbit near the xy-plane and becoming flatter as l increases.

Figure 7.13 Angular probability densities for a central force.