APPLICATION
OF
SCHRODINGER EQUATION
TO UNDERSTAND THE HYDROGEN ATOM

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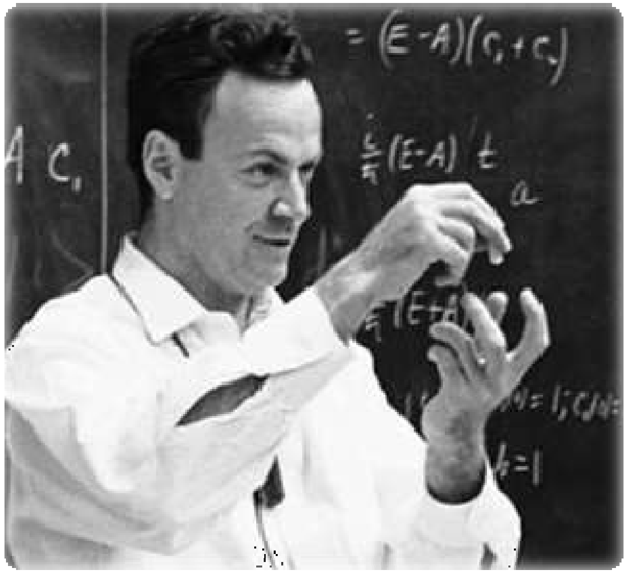
“I think I can safely say that nobody understands quantum mechanics.”

Ch. 6, “Probability and Uncertainty”

–Richard Feynman



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- Schrödinger time independent equation.
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- Solution of the Schrödinger Equation to the Hydrogen Atom.
- Solutions to radial, angular and azimuthal equation.
- Quantum Numbers.
- Normalized Spherical Harmonics

The whole aim of this project is to convert ...

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Into

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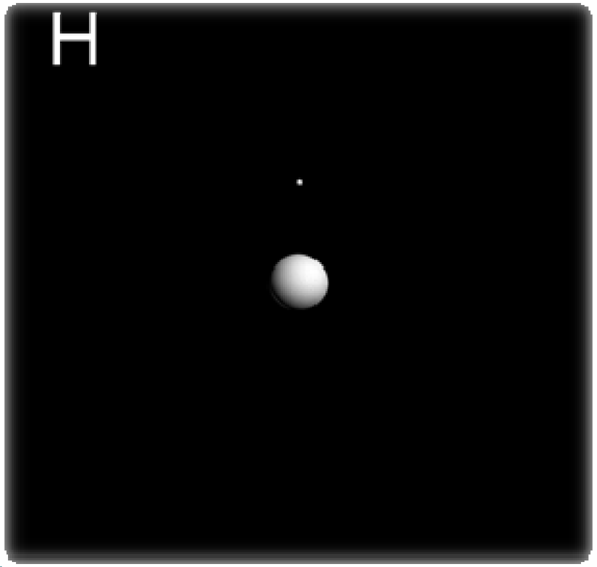
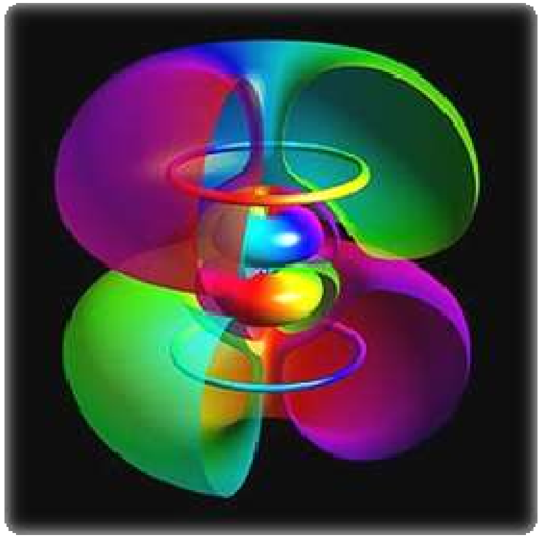




- **WAVE FUNCTION AND IT'S PHYSICAL SIGNIFICANCE (ψ)**

Max Born

The physical significance or interpretation of $|\psi|^2$ or $\psi\,\psi^*$ was given by Max Born in 1927.

1. ψ^2 or $\psi\psi^*$ represents probability per unit volume, of finding a particle described by a wave function at a perticular point (x,y,z) at time 't' in that volume.

   i.e. $\psi^2 = \frac{p}{dV}$

IMPORTANT CHARACTERISTICS OF A WAVE FUNCTION ASSOCIATED WITH WAVE

1. Wave function should be normalised. i.e. it should satisfy the following condition:

   $$\int_{-\infty}^{\infty} \psi^2 dx\ dy\ dz = 1$$

2. Wave function should be finite. ∞ probability has no meaning.

3. It should have a single value. (as at perticular point probability can have only one value.

SCHRODINGER TIME INDEPENDENT EQUATION

Schrodinger used analogy of stationary waves on string for matter waves.

For a particle having position coordinates (x,y,z) and having wave function ψ equation of matter wave is

$$\frac{d^2\psi}{dt^2} = u^2\nabla^2\psi \quad , \quad \text{where } \nabla^2 = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)$$

= Laplacian Operator

The solution of this equation is given as,

$$\psi = \psi_0 e^{-i\omega t}$$, where $\omega = 2\pi\nu$ and $u = \nu\lambda$

Double differentiating and substituting in above equation we get,

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0$$

On further simplification we get,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Where,

h	=	Planck's constant
m	=	mass of particle
E	=	total energy of particle
V	=	potential energy of particle

Application of the Schrödinger Equation to the Hydrogen Atom

- The approximation of the potential energy of the electron-proton system is electrostatic:

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

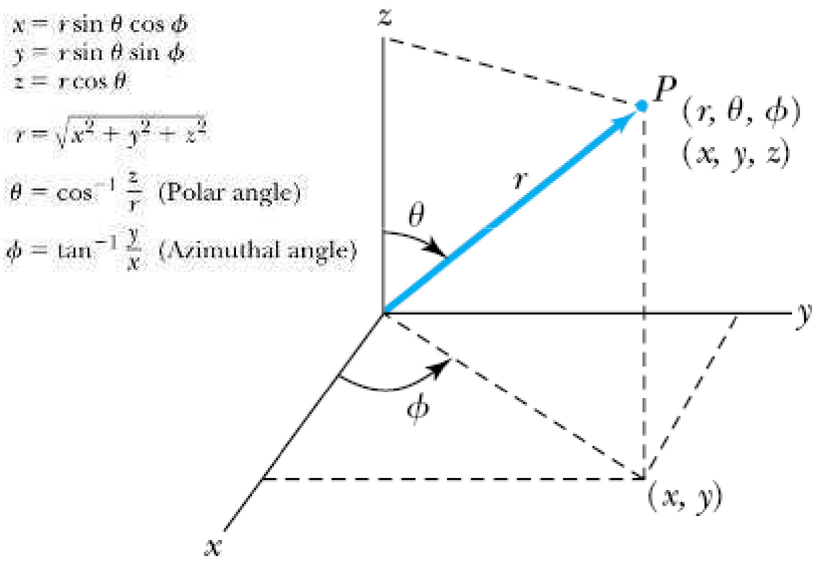
- Rewrite the three-dimensional time-independent Schrödinger Equation.

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

- For Hydrogen-like atoms (He^+ or Li^{++})
- Replace e^2 with Ze^2 (Z is the atomic number).
- Use appropriate reduced mass μ.

Application of the Schrödinger Equation

- The potential (central force) $V(r)$ depends on the distance r between the proton and electron.



Transform to spherical polar coordinates because of the radial symmetry.

Insert the Coulomb potential into the transformed Schrödinger equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0$$

Application of the Schrödinger Equation

- The wave function ψ is a function of r, θ, ϕ .
  1. Equation is separable.
  2. Solution may be a product of three functions.

$$\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)$$

- We can separate Equation into three separate differential equations, each depending on one coordinate: r, θ, or ϕ .

Solution of the Schrödinger Equation for Hydrogen

- Substitute into Equation and separate the resulting equation into three equations: $R(r)$, $f(\theta)$, and $g(\phi)$.

Separation of Variables

- The partial differential equations of $R(r)$, $f(\theta)$, and $g(\phi)$ are

$$\frac{\partial \psi}{\partial r} = fg\frac{\partial R}{\partial r} \qquad \frac{\partial \psi}{\partial \theta} = Rg\frac{\partial f}{\partial \theta} \qquad \frac{\partial^2 \psi}{\partial \phi^2} = Rf\frac{\partial^2 g}{\partial \phi^2}$$

- Substitute them into main equation

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V) - \frac{\sin\theta}{f}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial \phi^2}$$

- Multiply both sides by $r^2 \sin^2\theta / Rfg$

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rfg = 0$$

Solution of the Schrödinger Equation

- Only r and θ appear on the left side and only ∅ appears on the right side of Equation.
- The R.H.S. of equation is function of ∅ .
- The L.H.S. is function of r and θ.
- This implies ONLY ONE THING
- Each side needs to be equal to a constant for the equation to be true.

  Set the constant $-m_\ell^2$ equal to the right side of Equation

$$\frac{d^2 g}{d\phi^2} = -m_\ell{}^2 g$$ --------- azimuthal equation

- It is convenient to choose a solution to be

$$e^{im_\ell \phi}$$

Solution of the Schrödinger Equation

- $e^{im_\ell \phi}$ satisfies equation for any value of m_ℓ.
- The solution be single valued in order to have a valid solution for any Φ , which is

$$g(\phi) = g(\phi + 2\pi) \longrightarrow e^{0} = e^{2\pi i m_\ell}$$

$$g(\phi = 0) = g(\phi = 2\pi)$$

- m_ℓ to be zero or an integer (positive or negative) for this to be true.
- Set the left side of eqn equal to $-m_\ell^2$ and rearrange it.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}(E - V) = \frac{m_\ell^{\,2}}{\sin^2\theta} - \frac{1}{f \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial f}{\partial \theta}\right)$$

- Everything depends on r on the left side and θ on the right side of the equation.

Solution of the Schrödinger Equation

- Set each side equal to constant $\ell(\ell + 1)$.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R=0$$

----Radial equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^{\,2}}{\sin^2\theta}\right]f=0$$

----Angular equation

$$\frac{d^2g}{d\phi^2}=-m_\ell^{\,2}g$$

----Angular equation

- Schrödinger equation has been separated into three ordinary second-order differential equations each containing only one variable.

Solution of the Radial Equation

- The radial equation is called the **associated Laguerre equation** and the *solutions R* that satisfy the appropriate boundary conditions are called *associated Laguerre functions*.
- Assume the ground state has $\ell = 0$ and this requires $m_\ell = 0$.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}(E-V)R=0$$

- The derivative of $r^2\frac{dR}{dr}$ yields two terms.

  Write those terms and insert in equation

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0$$

Solution of the Radial Equation

- Try a solution $R = Ae^{-r/a_0}$
  A is a normalized constant.
  a_0 is a constant with the dimension of length.
  Take derivatives of *R* and insert them into Eqn

$$\left(\frac{1}{a_0{}^2} + \frac{2\mu}{\hbar^2}E\right) + \left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0$$

- To satisfy this Eqn for any *r* is for each of the two expressions in parentheses to be zero.
  Set the second parentheses equal to zero and solve for a_0.

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

  Set the first parentheses equal to zero and solve for *E*.

$$E = -\frac{\hbar^2}{2\mu a_0{}^2} = -E_0$$

  Both equal to the Bohr result.

Quantum Numbers

- The appropriate boundary conditions to and (7.11) leads to the following restrictions on the quantum numbers ℓ and m_ℓ:
  - $\ell = 0, 1, 2, 3, \ldots$
  - $m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, . \ell ., \ell - 1, \ell$
  - $|m_\ell| \leq \ell$ and $\ell < 0$.

- The predicted energy level is

$$E_n = -\frac{E_0}{n^2}$$

Hydrogen Atom Radial Wave Functions

- First few radial wave functions $R_{n\ell}$

Table 7.1 Hydrogen Atom Radial Wave Functions

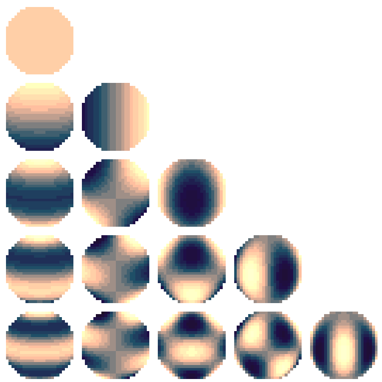
n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

- Subscripts on R specify the values of n and ℓ.

Solution of the Angular and Azimuthal Equations

- The solutions for Azimuthal equation are $e^{im_\ell \phi}$ or $e^{-im_\ell \phi}$.
- Solutions to the angular and azimuthal equations are linked because both have m_ℓ.
- Group these solutions together into functions.

$$Y(\theta, \phi) = f(\theta) g(\phi)$$ ---- spherical harmonics

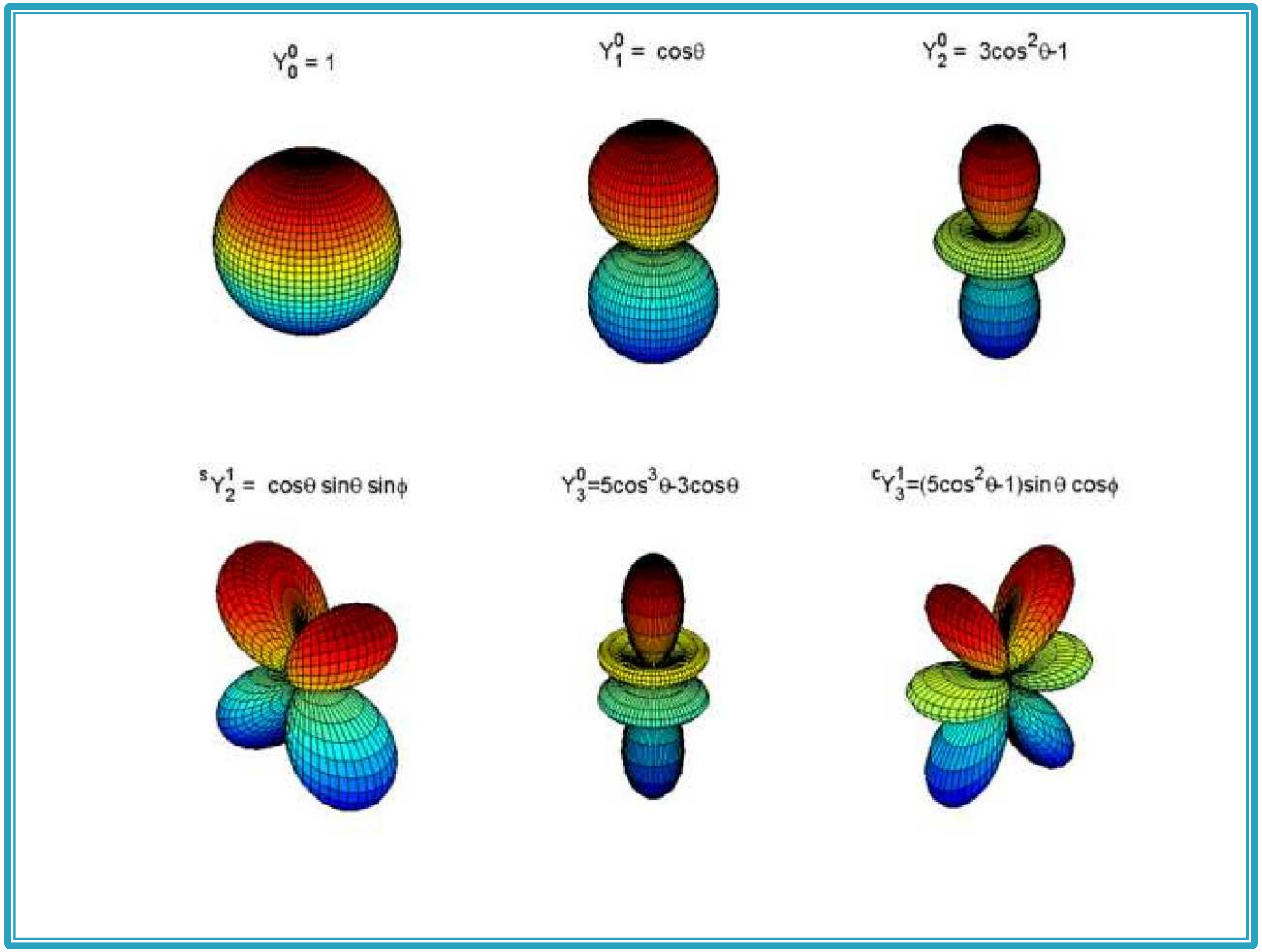


Normalized Spherical Harmonics

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Normalized Spherical Harmonics



Solution of the Angular and Azimuthal Equations

- The radial wave function R and the spherical harmonics Y determine the probability density for the various quantum states. The total wave function $\psi(r,\theta,\phi)$ depends on n, ℓ, and m_ℓ. The wave function becomes

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta,\phi)$$

Quantum Numbers

The three quantum numbers:

- n Principal quantum number
- ℓ Orbital angular momentum quantum number
- m_ℓ Magnetic quantum number

The boundary conditions:

- $n = 1, 2, 3, 4, . . .$ Integer
- $\ell = 0, 1, 2, 3, . . . , n - 1$ Integer
- $m_\ell = -\ell, -\ell + 1, . . . , 0, 1, . . . , \ell - 1, \ell$ Integer

The restrictions for quantum numbers:

- $n > 0$
- $\ell < n$
- $/m_\ell| \leq \ell$

Principal Quantum Number n

- It results from the solution of $R(r)$ because $R(r)$ includes the potential energy $V(r)$.
  The result for this quantized energy is

$$E_n = \frac{-\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative means the energy E indicates that the electron and proton are bound together.

Orbital Angular Momentum Quantum Number ℓ

- It is associated with the $R(r)$ and $f(\theta)$ parts of the wave function.
- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = mv_{\text{orbital}}r$.
- ℓ is related to L by $L = \sqrt{\ell(\ell+1)}\hbar$.
- In an $\ell = 0$ state, $L = \sqrt{0(1)}\hbar = 0$

It disagrees with Bohr's semiclassical "planetary" model of electrons orbiting a nucleus $L = n\hbar$.

Orbital Angular Momentum Quantum Number ℓ

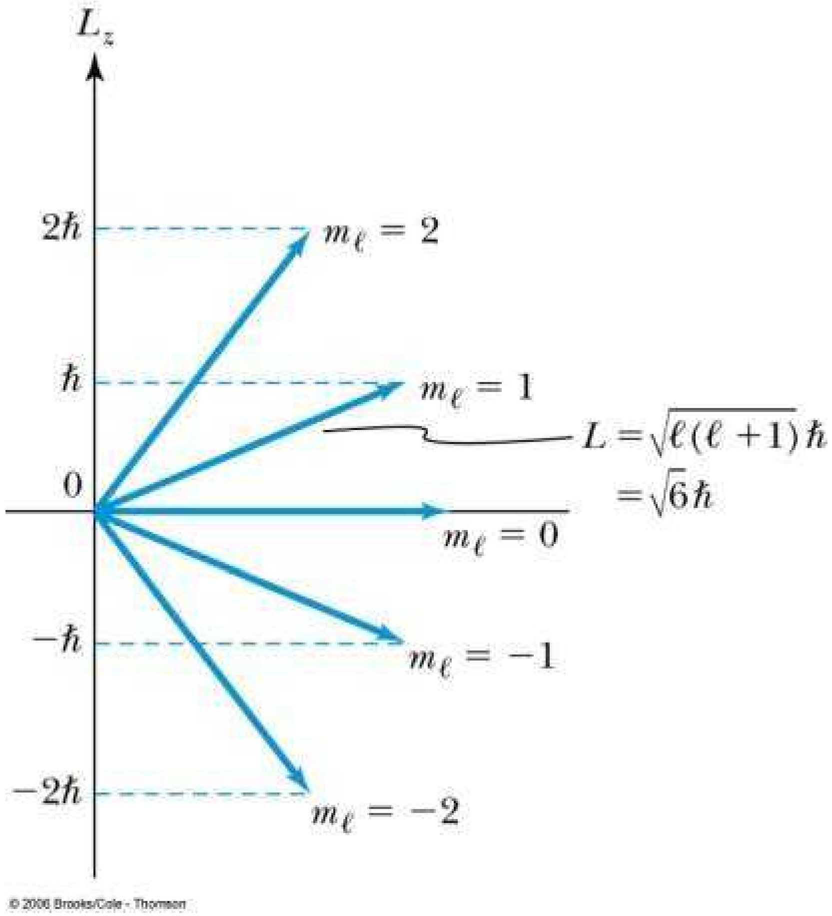
- A certain energy level is **degenerate** with respect to ℓ when the energy is independent of ℓ.
- Use letter names for the various ℓ values.
  - $\ell =$ 0 1 2 3 4 5 . . .
  - Letter = *s* *p* *d* *f* *g* *h* . . .
- Atomic states are referred to by their n and ℓ.
- A state with $n = 2$ and $\ell = 1$ is called a $2p$ state.
- The boundary conditions require $n > \ell$.

Magnetic Quantum Number m_ℓ

- The angle Φ is a measure of the rotation about the z axis.
- The solution for g(Φ) specifies that m_ℓ is an integer and related to the z component of L.

$$L_z = m_\ell \hbar$$

- The relationship of L, L_z, ℓ, and m_ℓ for $\ell = 2$.
- $L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$ is fixed because L_z is quantized.
- Only certain orientations of $\vec{L}$ are possible and this is called space quantization.



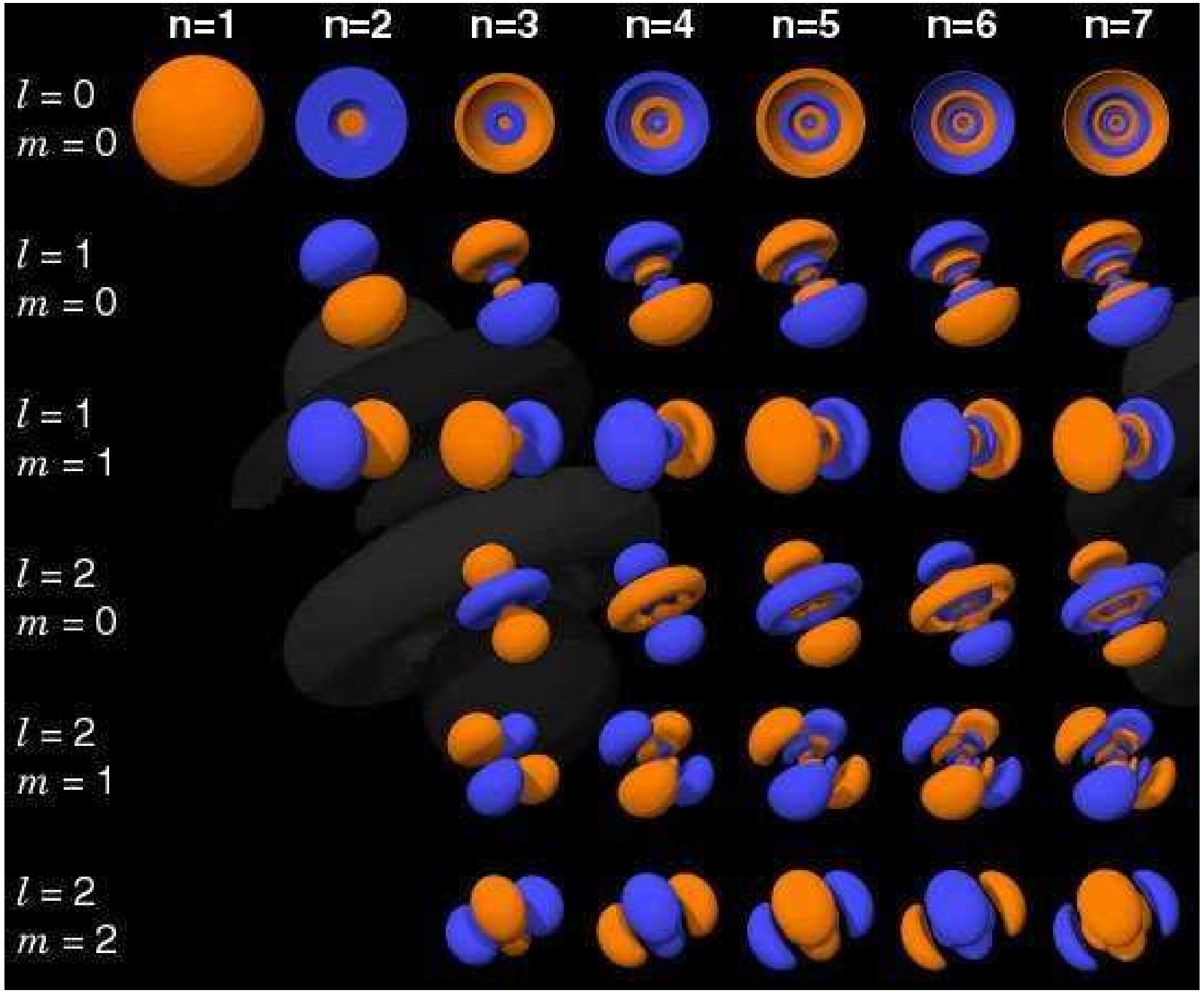
Magnetic Quantum Number m_ℓ

- Quantum mechanics allows $\vec{L}$ to be quantized along only one direction in space. Because of the relation $L^2 = L_x^2 + L_y^2 + L_z^2$ the knowledge of a second component would imply a knowledge of the third component because we know $\vec{L}$.

- We expect the average of the angular momentum components squared to be $\langle L_x^{\ 2} \rangle = \langle L_y^{\ 2} \rangle = \langle L_z^{\ 2} \rangle$.

$$\langle L^2 \rangle = 3\langle L_z^{\ 2} \rangle = \frac{3}{2\ell+1} \sum_{m_\ell=-\ell}^{\ell} m_\ell^{\ 2}\hbar^2 = \ell(\ell+1)\hbar^2$$

Hydrogen Orbitals



Thank You!!!