

# PH102: Interactive Lecture 5

- Topics
  - 3d Schrodinger Equation for Hydrogen atom
  - $(x, y, z) \leftrightarrow (r, \theta, \phi)$
  - Separation of variables  $R\Theta\Phi$
  - Three equations
  - Three quantum numbers
  - Wave functions
  - Quantization of angular momentum (L)

# Hydrogen atom

- Potential created by Coulomb interactions between electron ( $-e$ ) and proton ( $+e$ )

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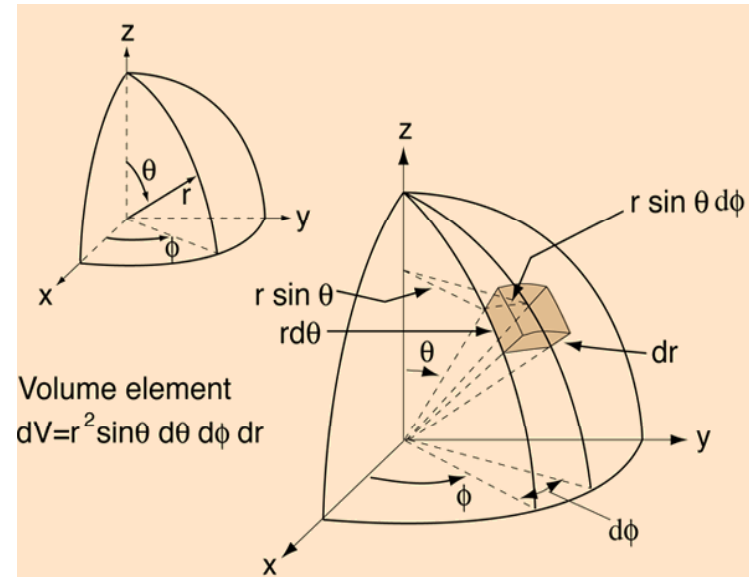
- Symmetric in  $r$
- Choose  $(r, \theta, \phi)$

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

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

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

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



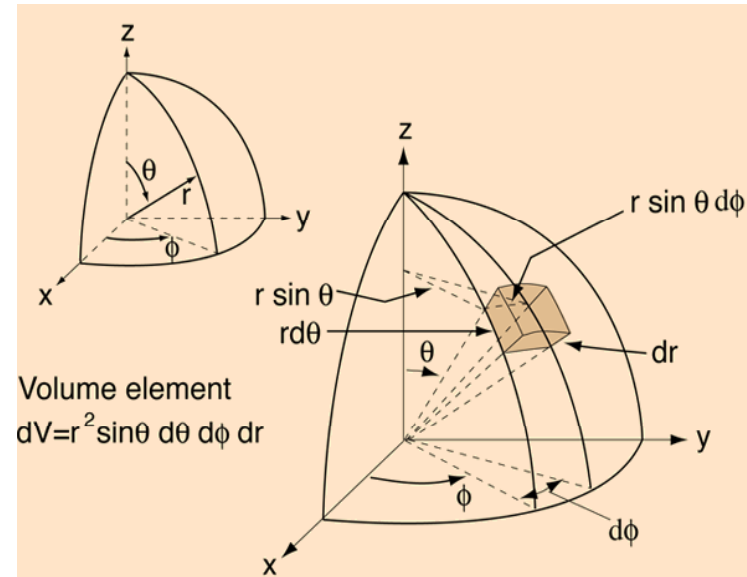
$$(x, y, z) \leftrightarrow (r, \theta, \phi)$$

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

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



# Schrodinger Equation

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

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

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

# Schrodinger Equation

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

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

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$$\begin{aligned} & \csc\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) \psi(r, \theta, \phi) + \csc^2\theta \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) \\ &= \left[ -\frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) \right] \psi(r, \theta, \phi) \end{aligned}$$

# Schrodinger Equation

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

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

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

$$\csc\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) \psi(r, \theta, \phi) + \csc^2\theta \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi)$$

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

Separation of variables

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

$$\begin{aligned} \frac{\partial \psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} \\ \frac{\partial \psi}{\partial \theta} &= R\Phi \frac{\partial \Theta}{\partial \theta} \\ \frac{\partial^2 \psi}{\partial \phi^2} &= R\Theta \frac{\partial^2 \Phi}{\partial \phi^2} \end{aligned}$$

# Schrodinger Equation

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

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

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

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

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

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

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

# Schrodinger Equation


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

Angular part

Radial part

# Schrodinger Equation

$$\underbrace{\frac{1}{\sin\theta} \csc\theta \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \csc^2\theta \frac{\partial^2\psi}{\partial\phi^2}}_{\text{Angular part}} = \underbrace{-\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r))}_{\text{Radial part}} = C \text{ (Constant)}$$

  
 **$-l(l+1)$**

# Schrodinger Equation

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

Angular part

↓  
 $-l(l+1)$

Radial part

↓  
 $-l(l+1)$

↓  
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# Schrodinger Equation

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

Angular part

↓  
-l(l+1)

Radial part

↓  
-l(l+1)

↓  
-l(l+1)

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \csc\theta \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \end{cases}$$

# Schrodinger Equation

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$$\begin{aligned} \frac{1}{\Theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) + l(l+1)\sin^2\theta &= -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} \\ &= m_l^2 \text{ (another constant)} \end{aligned}$$

# Schrodinger Equation

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

# Schrodinger Equation

$$\left\{ \begin{array}{ll} \frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi & \text{Azimuthal Equation} \\ \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta}{\partial \theta} \right) + [l(l+1)\sin^2\theta - m_l^2]\Theta = 0 & \text{Polar Equation} \\ \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} (E - U(r))R - l(l+1)R = 0 & \text{Radial Equation} \end{array} \right.$$

# Azimuthal Equation

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

Wave function

Boundary condition

Quantization

# Azimuthal Equation

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

Wave function  $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

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# Azimuthal Equation

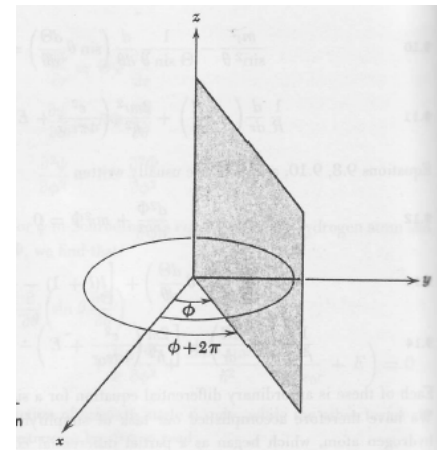
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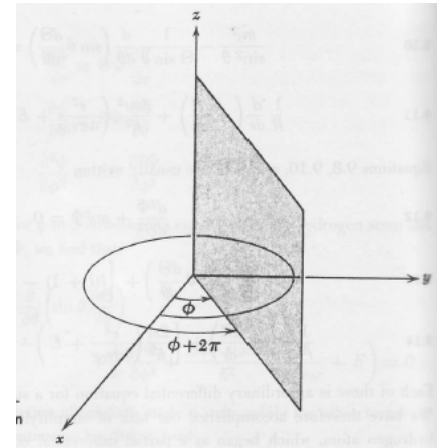
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Boundary condition

$$\begin{aligned}\Phi(\phi) &= \Phi(\phi + 2\pi) \\ A e^{im_l \phi} &= A e^{im_l(\phi + 2\pi)} = A e^{im_l \phi} e^{i2\pi m_l} \\ e^{i2\pi m_l} &= 1 = \cos 2\pi m_l + i \sin 2\pi m_l\end{aligned}$$

Quantization



# Azimuthal Equation

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

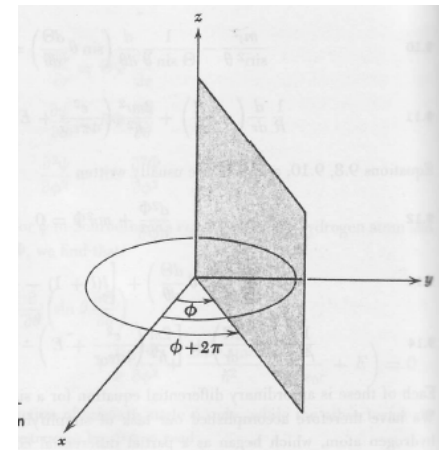
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Quantization

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



# Azimuthal Equation

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

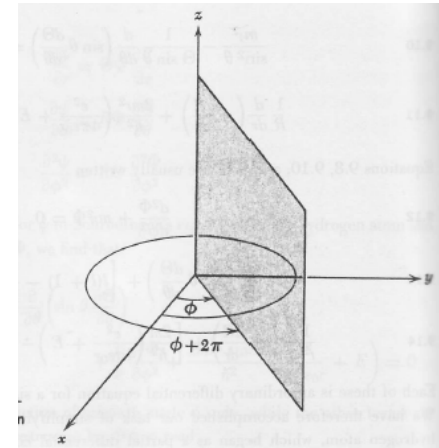
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Quantization

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



**Magnetic quantum number**

# 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: Associated Legendre Functions

Quantization

any given  $l$ ,  $m_l$  values can be  $0, \pm 1, \pm 2, \dots, \pm l$

→ **Orbital quantum number**

# Radial Equation

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

Solutions: associated Laguerre functions

Quantization:

$$E_n = - \frac{me^4}{32\pi \epsilon_0^2 \hbar^2} \left( \frac{1}{n^2} \right) \text{ where } n \text{ is an integer}$$

$n \rightarrow$  **Principal quantum number**

$$l = 0, 1, 2, \dots, (n-1)$$

# Solutions

- Principal quantum number,  $n = 1, 2, 3, \dots$
- Orbital quantum number,  $l = 0, 1, 2, \dots (n - 1)$  where  $l = 1(s), = 2(p), = 3(d), = 4(f), \text{ etc.}$
- Magnetic quantum number,  $m_l = 0, \pm 1, \pm 2, \dots \pm l$

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

$$\text{where } \Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l} \text{ (Spherical harmonics)}$$

# Symbolic designation of atomic states

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

# Origin of angular momentum quantization

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

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

# Origin of angular momentum quantization

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$$E = \text{Kinetic E (radial)} + \text{Kinetic E (orbital)} + U(r)$$

# Origin of angular momentum quantization

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

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

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

# Origin of angular momentum quantization

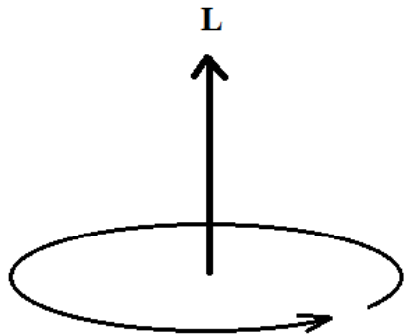
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$$\text{Kinetic E (orbital)} = \frac{l(l+1)\hbar^2}{2mr^2}$$



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

$$L = m v_{\text{orbital}} r \rightarrow v_{\text{orbital}} = \frac{L}{mr}$$

# Origin of angular momentum quantization

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

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

$$E = \text{Kinetic E (radial)} + \text{Kinetic E (orbital)} + U(r)$$

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

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

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

$$L = m v_{\text{orbital}} r \rightarrow v_{\text{orbital}} = \frac{L}{mr}$$

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

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

# Origin of angular momentum quantization

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

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

$$E = \text{Kinetic E (radial)} + \text{Kinetic E (orbital)} + U(r)$$

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

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

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

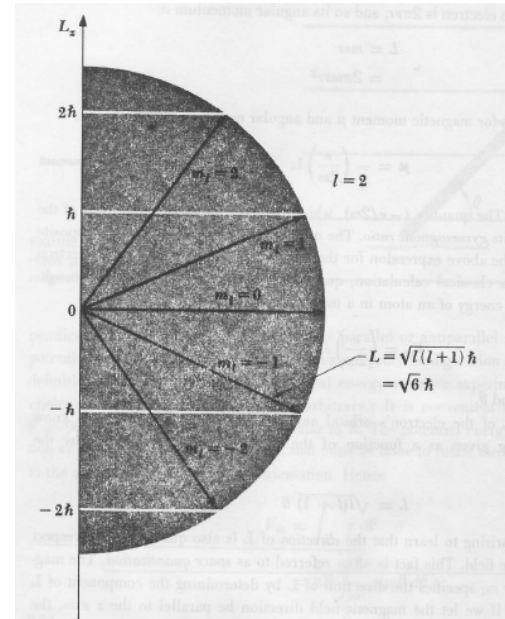
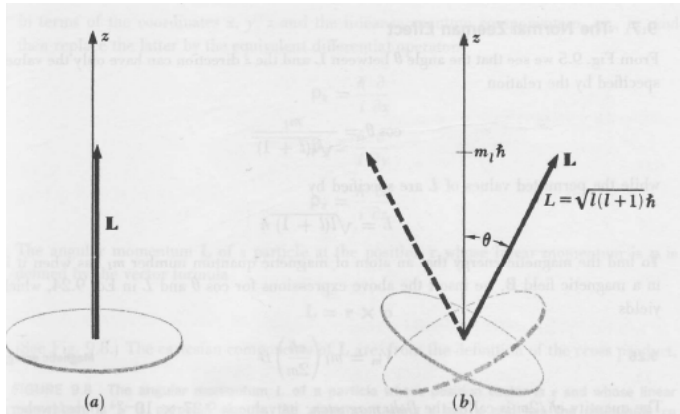
$$L = m v_{\text{orbital}} r \rightarrow v_{\text{orbital}} = \frac{L}{mr}$$

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

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

**Angular momentum is quantized**

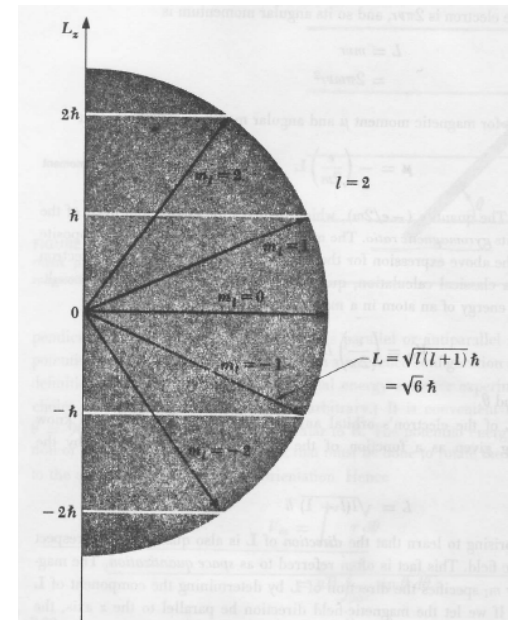
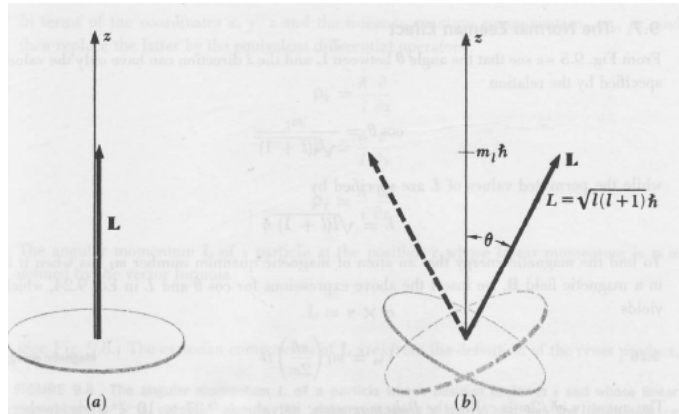
# Angular Momentum (L)



Amount =

Direction =

# Angular Momentum (L)



Amount =  $L = \sqrt{l(l+1)} \hbar$

Direction = *the  $m_l$  value* determines the direction of L