Modern Physics

Lecture 24

The Hydrogen Atom

- Application of the Schrödinger Equation to the Hydrogen Atom
- Solution of the Schrödinger Equation for Hydrogen atom
- Quantum Numbers
- Energy Levels etc.

What is Hydrogen Atom and Hydrogen like Atom

Application of the Schrödinger Equation to the Hydrogen Atom

The three-dimensional time-independent Schrödinger Equation.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+V\psi(x,y,z)=E\psi(x,y,z)$$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]=(E-V)\psi(x,y,z)$$

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

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

What is the nature of the potential
Which coordinate system to apply

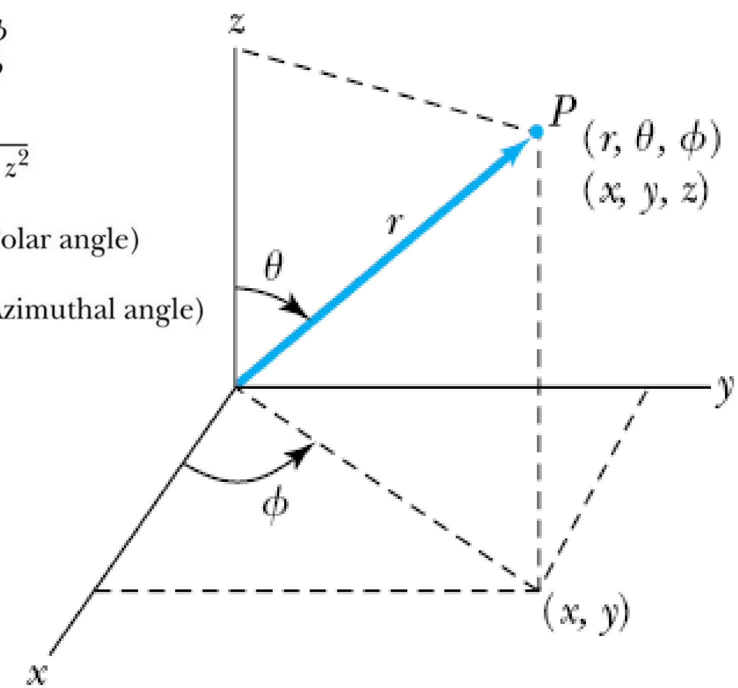
The potential (central force) $V(r)$ depends on the distance r between the proton (or nucleus) and electron.

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

Transform to spherical polar coordinates because of the radial symmetry.

Insert the Coulomb potential into the transformed Schrödinger equation.

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$
$$\phi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$



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

.... (1)

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

The wave function ψ is a function of r, θ, and φ.

Equation 1 is separable.

Solution may be a product of three functions.

$$\psi(r,\theta,\phi)=R(r)f(\theta)g(\phi) \qquad \text{.......................} \ (2)$$

We can separate the basic Schrodinger equation into three separate differential equations, each depending on one coordinate: r, θ, or φ .

This means substitution of equation 2 into equation 1 and separation of variables will result into the three equations: $R(r)$, $f(\theta)$, and g(φ).

Separation of Variables

The derivatives from Eq 2 $\psi = Rfg$

$$\frac{\partial \psi}{\partial r} = fg \frac{\partial R}{\partial r} \qquad \frac{\partial^2 \psi}{\partial r^2} = fg \frac{\partial^2 R}{\partial r^2}$$

$$\frac{\partial \psi}{\partial \theta} = Rg \frac{\partial f}{\partial \theta} \qquad \frac{\partial^2 \psi}{\partial \theta^2} = Rg \frac{\partial^2 f}{\partial \theta^2}$$

$$\frac{\partial \psi}{\partial \phi} = Rf \frac{\partial f}{\partial \phi} \qquad \frac{\partial^2 \psi}{\partial \phi^2} = Rf \frac{\partial^2 f}{\partial \phi^2}$$

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

Substitute them into equation 1

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

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

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

……………………… (3)

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

- Only r and θ appear on the left side and only φ appears on the right side of Eq (3)

- 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 Eq (3)

This means

$$\frac{d^2 g}{d\varphi^2}=-m_l^2 g$$ -------- **azimuthal equation**

- Therefore solution will be $e^{im_l\varphi}$ …………………… (4)

- $e^{im_l\varphi}$ satisfies Eq (4) for any value of m_ℓ.
- The solution must be single valued for any φ, this means

$$g(\varphi) = g(\varphi + 2\pi)$$

$$g(\varphi = 0) = g(\varphi = 2\pi) \longrightarrow e^0 = e^{2\pi i m_l}$$

- ***m*<u>$_\ell$</u> <u>to be zero or an integer (positive or negative) for this to be true.</u>**

This means, $m_l = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots.$

We start from Eq (4) again

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

Set the left side of Eq (4) equal to $-m_\ell^2$.

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)-\frac{2m}{\hbar^2}r^2\sin^2\theta(E-V)=-m_l^2$$

and rearrange it

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

…………………….. (5)

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

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

- Set each side of Eq (5) equal to constant **ℓ(ℓ + 1)**

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

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E-V-\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]R=0$$ **---- Radial equation**

…………… (6)

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

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]f=0$$ **---- Angular equation**

…………… (7)

Schrödinger equation has been separated into three ordinary second-order differential equations [Eq 4, 6, and 7], each containing only one variable.

After separation of variables
Three separate equations

$$\frac{d^2 g}{d\varphi^2} = -m_l^2 g$$

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

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

Solution of the Radial Equation

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

- The radial equation is called the **associated Laguerre equation** and the *solutions of R* are called *associated Laguerre functions*.

- Assume the ground state has $\ell = 0$ and $m_\ell = 0$.

  Eq (5) becomes

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

$$\frac{1}{\cancel{r^2}}\cancel{r^2}\frac{d^2R}{dr^2}+\frac{1}{r^{\cancel{2}}}2\cancel{r}\frac{dR}{dr}+\frac{2m}{\hbar^2}\left[E-\frac{e^2}{4\pi\varepsilon_0 r}\right]R=0$$

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2m}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]R=0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 8$$

- Try a solution $R = Ae^{-r/a_0}$ A is a normalization constant.
  a_0 is a constant with the dimension of length.
  Take derivatives of R and insert them into equation 8.

$$\left[\frac{1}{a_0^2} + \frac{2mE}{\hbar^2}\right] + \left[\frac{2me^2}{4\pi\varepsilon_0\hbar^2} - \frac{2}{a_0}\right]\frac{1}{r} = 0 \qquad \ldots\ldots\ldots\ldots (9)$$

- To satisfy equation 8 for any r is for each of the two expressions in parentheses has to be zero.

Setting the second parentheses equal to zero and solving for a_0 we get

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \longrightarrow \text{Bohr radius}$$

Set the first parentheses equal to zero and solve for E,

$$E = -\frac{\hbar^2}{2ma_0^2} = -E_0$$

Bohr energy

Both equal to the Bohr result.

Quantum Numbers

- Considering the solutions of equations 4, 6 and 7, the following restrictions are imposed on the quantum numbers ℓ and m_ℓ:

  $\ell = 0, 1, 2, 3, \ldots$

  $m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, \ldots \ell \ldots, \ell - 1, \ell$

  $|m_\ell| \leq \ell$.

- Also the predicted energy levels are

$$E_n = -\frac{\mathrm{m}}{2}\left(\frac{e}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2} = \frac{-E_0}{n^2} \qquad \mathrm{n} = 1,2,3\ldots..$$

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

Comparison of PIB, SHO and H Atom energy levels

Quantum Numbers

The three quantum numbers:

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

The restrictions on quantum numbers:

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

Range of the quantum numbers:

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

Hydrogen Atom Radial Wave Functions

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

$n > 0$
$\ell < n$

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 Eq (4) are $e^{im_\ell\phi}$ or $e^{-im_\ell\phi}$
- Solutions to the angular and azimuthal equations are linked because both have m_ℓ.
- We can group these solutions into functions.

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

Normalized Spherical Harmonics

$$\ell < n$$
$$|m_\ell| \le \ell$$

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	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

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 (depends on *n*, ℓ, and m_ℓ) becomes

$$\psi_{nlm_l}(r,\theta,\varphi) = R_{nl}(r)Y_{lm_l}(\theta,\varphi)$$

If $n = 1$ then what will be ℓ and m_ℓ

What will be the form of $\psi_{100} = R_{10}(r)Y_{00}(\theta,\varphi)$

Probability Density

$\boxed{\text{No definite orbits for electrons}}$

Quantum theory suggests the following things,

- No definite values of co-ordinates (r, θ and φ) for the electrons but only probabilities
- We do not consider time dependence only spatial dependence

<u>Probability of finding the electron in elemental area *dV*</u>

In spherical polar coordinate elemental area (*dV*)

$$dV = r^2 \sin\theta dr d\theta d\varphi$$

Probability of finding the particle within the region *dr* will be,

$$P(r)dr = \left|R(r)f(\theta)g(\phi)\right|^2 r^2 \sin\theta dr d\theta d\varphi$$

What will be the expectation value of 1/r for a 1s electron in the Hydrogen atom

Wave function of 1s electron is,

$$\psi = \frac{e^{-\frac{r}{a_0}}}{\sqrt{\pi} a_0^{3/2}}$$

Expectation value of 1/r is,

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \frac{1}{r} |\psi|^2 dV$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}$$

Orbital Angular Momentum Quantum Number ℓ

- Classically, the orbital angular momentum with $L = mv_{\text{orbital}}r$ is

$$\vec{L} = \vec{r} \times \vec{p}$$

- ℓ is related to L (QM) by

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

Properties of 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.
  - ℓ = 0 1 2 3 4 5 . . .
  - Letter = *s* *p* *d* *f* *g* *h* . . .

- Atomic states are referred to by their n and ℓ.
- For example a state with $n = 2$ and $\ell = 1$ is called a $2p$ state.

Classical angular momentum

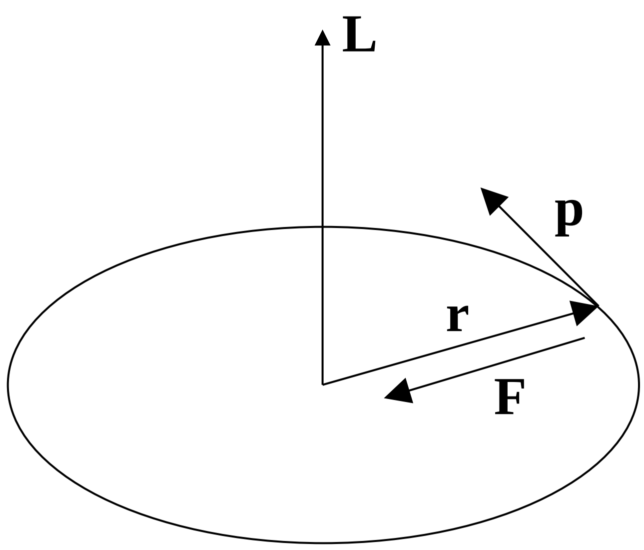
For a classical particle, the angular momentum is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

$$= L_x \mathbf{i} + L_y \mathbf{j} + L_z \mathbf{k}$$

In components

$$\boxed{\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned}}$$

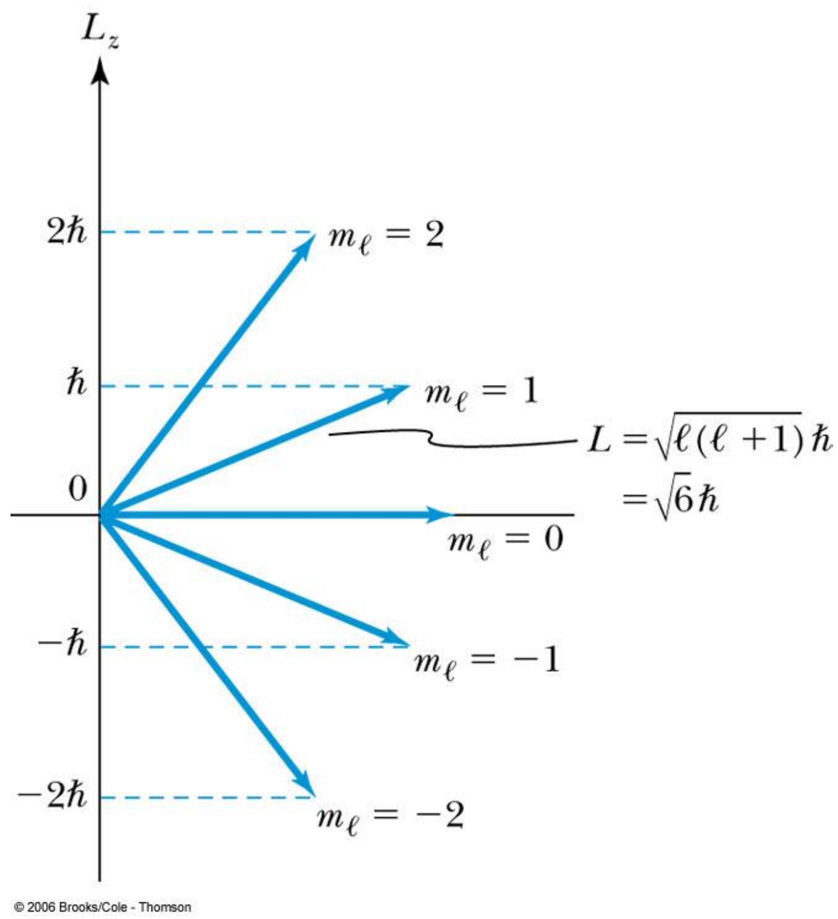


Same origin for **r** and **F**

Magnetic Quantum Number m_ℓ

- The z component of L is connected to m_l through the following relation.

$$L_z = m_l \hbar$$



- The relationship of L *and* l *is*

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

- Only certain orientations of L are possible and this is called **space quantization**.