Welcome back to PHY 3305

<u>Today's Lecture:</u> Hydrogen Atom Part I

John von Neumann 1903 - 1957



One-Dimensional Atom

To analyze the hydrogen atom, we must solve the Schrodinger equation for the Coulomb potential energy of the proton and electron. c^2

$$U(r) = -\frac{e}{4\pi\epsilon_0 r}$$

The Schrödinger equation will look like -

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - \frac{e^2}{4\pi\epsilon_0 x}\psi(x) = E\psi(x)$$

The wave function solving this equation must meet two criteria:

ψ(x) must fall to zero as x approaches infinity
 ψ(x) must be zero at x = 0, so the LHS remains finite at zero.

Any ideas on the solution?

$$\psi(x) = Axe^{-bx}$$

where

$$b = \frac{me^2}{4\pi\epsilon_0\hbar^2} = \frac{1}{a_0} \qquad a_0 = \text{Bohr Radius}$$
$$E = -\frac{\hbar^2 b^2}{2m} = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2}$$
$$n = 1, 2, 3, \dots$$

How do we find the constant A?

$$\int_0^\infty |\psi(x)|^2 \, dx = A^2 \int_0^\infty x^2 e^{-2x/a_0} \, dx = 1$$

A handy integral -

$$\int_0^\infty x^n e^{-cx} \, dx = \frac{n!}{c^{n+1}}$$

Substituting

$$A^2 \frac{2!}{(2/a_0)^3} = 1 \longrightarrow A = 2a_0^{-3/2}$$

Angular Momentum of Classical Orbits

Classically, the angular momentum of a planet is given by

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

The direction of the angular momentum is perpendicular to the plane of the orbit.

The energy and angular momentum remains constant.



In this example, the planetary orbits have the same energy but differing angular momentum.

To describe the angular momentum vector, we need three numbers (L_x , L_y , L_z).

Angular Momentum in Quantum Mechanics

The angular momentum properties of a 3-D wave function are described by two quantum numbers.

Angular Momentum Quantum Number: *l*

determines the length of the angular momentum vector

$$|\vec{L}| = \sqrt{\ell(\ell+1)}\hbar$$
 $(\ell = 0, 1, 2, ...)$

Magnetic Quantum Number: m

$$L_z = m_\ell \hbar$$
 $(m_\ell = 0, \pm 1, \pm 2, \dots \pm \ell)$

Note: for each value of $\ell,$ there are $2\ell+1 {\rm possible}$ values of m_ℓ

Example: Angular Momentum

Compute the length of the angular momentum vectors that represent the orbital motion of an electron in a quantum state with

$$\ell = 1$$
 and $\ell = 2$

Case: $\ell = 1$ $|\vec{L}| = \sqrt{1(1+1)}\hbar = \sqrt{2}\hbar$ Case: $\ell = 2$

$$|\vec{L}| = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$$

What are the possible z components of the angular momentum vector that represent the orbital angular momentum state with $\ell = 2$?

The possible m_{ℓ} values for $\ell = 2$ are +2, +1, 0, -1, -2.

Thus, the z components are -

$$L_z = m_\ell \hbar$$

$$L_z = 2\hbar, \hbar, 0, -\hbar, -2\hbar$$

Examine angular momentum for case $\ell=2$



The angle between L and the polar axis is given by

$$\cos\theta = \frac{L_z}{|\vec{\mathbf{L}}|} = \frac{m_l}{\sqrt{l(l+1)}}$$

This demonstrates an aspect of quantum mechanics known as

spatial quantization. Only certain orientations of angular momentum vectors are allowed.

Notes:

- In classical angular momentum, we needed 3 numbers to provide an exact location.
- Quantum angular momentum is described by only 2 numbers.
- Something is missing from our description. We cannot identify a vector in three-space with 2 numbers.
- This missing component is related to the uncertainty principle.

Hydrogen Atom in 3D

The 3D Schroedinger Equation in Cartesian coordinates:

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

Normal method to solve this, is to replace a function of 3 variables with the product of 3 functions each with 1 variable.

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

But,

$$U(x, y, z) = -\frac{e^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}$$

So, it's better to work in spherical coordinates. 3D Schroedinger equation in spherical coordinates.

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

Since we can define the Coulomb potential in terms of only r, the solution is separable.

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

R(r) = radial function
 $\Theta(\theta)$ = polar function
 $\Phi(\phi)$ = azimuthal function



The quantum state of a particle that moves in a potential energy that depends only on r can be described by angular momentum quantum numbers ℓ and m_ℓ .

The polar and azimuthal solutions are given by combinations of standard trigonometric functions. The remaining radial function is obtained by solving

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) + \frac{\hbar^2 \ell (\ell + 1)}{2mr^2} R(r) + U(r) R(r) = E R(r)$$

KE_{rad} **KE**_{rot} **PE**

Note: Classical mechanics gives us $KE = L^2/2I$ and the moment of inertia (I) for a point particle is mr^2 .

If you were to solve this equation, three quantum numbers emerge from the solution.

n	principle quantum number	I, 2, 3
-	angular momentum quantum number	0, I, 2, (n-I)
m	magnetic quantum number	$0, \pm 1, \pm 2, \pm (n-1)$

The principle quantum number determines the quantized energy levels.

$$E = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

Question

Of the following sets of quantum numbers for an electron in a spherically symmetric potential, which is possible?

A)
$$n = 5$$
, $l = 3$, $m_l = -3$
B) $n = 3$, $l = 3$, $m_l = -2$
C) $n = 5$, $l = -3$, $m_l = 2$
D) $n = 3$, $l = 2$, $m_l = -3$
E) $n = 4$, $l = 5$, $m_l = -2$

The solutions of the 3D SWE, complete quantum numbers, can be written as

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

n	1	m	<i>R</i> (<i>r</i>)	$\Theta(\theta)$	Φ(φ)	
1	0	0	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	Ground state (n=1; l = 0; m _l = 0)
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$(n=2; l = 0, 1; m_l = 0, \pm 1)$
2	1	±1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\mp \frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	
3	0	0	$\frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	
3	1	0	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	
3	1	±1	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\mp \frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	
3	2	0	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	$(n=3; l=0, 1, 2; m_l=0, \pm 1, \pm 2)$
3	2	±1	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\mp \sqrt{\frac{15}{4}} \sin \theta \cos \theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$]/
3	2	±2	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$	¥

What is a degeneracy?

When different wave functions have the same energy, it is known as a degeneracy and the energy levels for which it is true are said to be degenerate.

In $our/example, \theta, he) = 2Rleyel (hose <math>a, he) = 4$

n	1	m	<i>R</i> (<i>r</i>)	$\Theta(\theta)$	Φ(φ)	
1	0	0	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	Ground state (n=1; l = 0; m _l = 0)
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$(n=2; l = 0, 1; m_l = 0, \pm 1)$
2	1	±1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\mp \frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	
3	0	0	$\frac{2}{(2-r)^{2/2}}\left(1-\frac{2r}{2}+\frac{2r^{2}}{2r^{2}}\right)e^{-r/3a_{0}}$	1	1	

If different combinations of quantum numbers have exactly the same energy, why list them separately?

- The different levels are not precisely degenerate. They are separated by a small (~10⁻⁵ eV) energy difference.
- 2. The intensity of individual transitions between levels depends on the quantum numbers.
- 3. Each set of quantum numbers corresponds to a very different wave function and therefore represents a very different state of motion of the electron.

These states have different spacial probability distribution functions for locating the electron, and thus can affect many atomic properties (i.e. the way two atoms form molecular bonds).

What quantities do each of the 3 quantum numbers we discussed quantize?

n	energy
I	length of the angular momentum vector
mı	z-component of the angular momentum

Re-examine angular momentum for case $\ \ell=2$

Angular Momentum: $L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$



Vector L cannot point directly along the z-axis!

- This means that the vector L must have either an x- or y-component (or both).
- The classical orbit cannot lie in the xy plane!

The orbital plane is restricted to a few discrete angles.

What are the quantum numbers for the ground state of the hydrogen atom?

$$n = 1, l = 0$$
 and $m_l = 0$

Calculate the magnitude of the angular momentum for the ground state of a hydrogen atom.

$$L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{0}\hbar = 0$$

Note: The ground state of hydrogen has ZERO angular momentum. A classical particle can not orbit unless it has angular momentum. Apparently, a quantum particle does not have this requirement. The end (for today)