

Lecture Notes: January 20, Fri, Class 5

Schrodinger Equation for the Hydrogen Atom

Objectives:

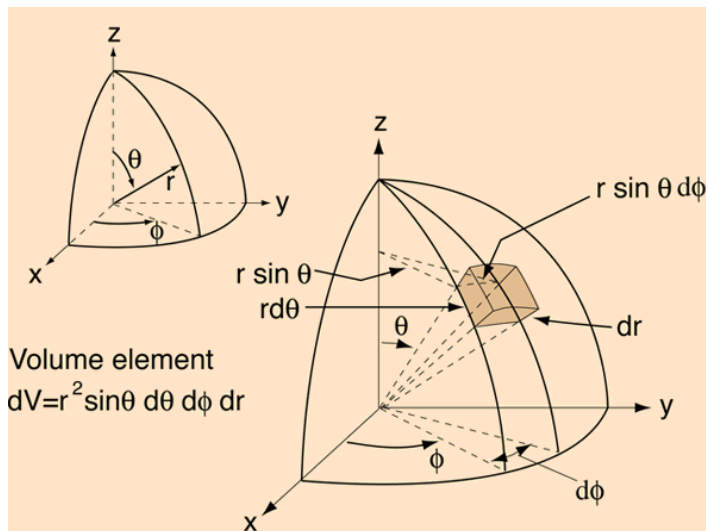
- Express the time independent Schrodinger Equation for the hydrogen atom in (r, θ, ϕ)
- Apply the separation of variables method to come up with three equations.
- Understand what three quantum numbers (n, l, m_l) represent and what combinations of quantum numbers are possible in a given n (energy) state.
- Understand the quantization of the angular momentum and the relationship between l and m_l .

Hydrogen Atom in 3-D

The potential energy of the electron in the hydrogen atom (= Coulomb potential energy between two charges: $(+e)$ of the proton and $(-e)$ of the electron separated by r).

$$U(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r} \quad (5.1)$$

Since this potential has a spherical symmetry, to make solving the Schrodinger Equation easier, we choose the spherical polar coordinate system.



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

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

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

The time independent Schrodinger Equation for the hydrogen atom (an electron + a proton)

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x}) \quad (5.2)$$

∇^2 can be expressed as follows:

In (x, y, z) ,

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

In (r, θ, ϕ) ,

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

In (x, y, z) , the time independent Schrodinger Equation (5.2) becomes

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

In (r, θ, ϕ) , the time independent Schrodinger Equation (5.2) becomes

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

Then, put the partial derivatives in θ and ϕ on one side and the radial partial derivative on the other side of the equation:

$$\csc\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \psi + \csc^2\theta \frac{\partial^2}{\partial \phi^2} \psi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) \right] \psi \quad (5.3)$$

Separation of variables

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

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

After substituting $\psi(r, \theta, \phi)$ with $R(r)\Theta(\theta)\Phi(\phi)$, (5.3) becomes:

$$R\Phi \csc\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + R\Theta \csc^2\theta \frac{\partial^2 \Phi}{\partial \phi^2} = -\Theta\Phi \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) R\Theta\Phi \quad (5.4)$$

Divide (5.4) by $R\Theta\Phi$

$$\frac{1}{\Theta} \csc\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C \text{ (Constant)} \quad (5.5)$$

Consider C is $-l(l+1)$, then each side of the equation (5.5) should be the same constant of $-l(l+1)$.

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \rightarrow (5.6)a \\ \frac{1}{\Theta} \csc\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \rightarrow (5.6)b \end{cases}$$

Divide both sides of (5.6)b by $\csc^2\theta$ (or multiply $\sin^2\theta$ since $\csc\theta = \frac{1}{\sin\theta}$)

$$\frac{1}{\Theta} \sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = -l(l+1) \sin^2\theta \quad (5.7)$$

Arrange (5.7) to separate the partial derivative of θ and that of $\phi \rightarrow$ (5.8)

$$\begin{aligned} \frac{1}{\Theta} \sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + l(l+1) \sin^2\theta &= -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} \quad (5.8) \\ &= m_l^2 \text{ (another constant)} \end{aligned}$$

Three equations can be derived from the time independent Schrodinger Equation (5.3)

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

Azimuthal Equation

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

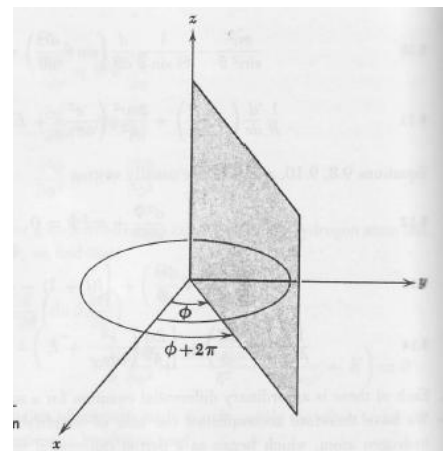
Solution: $\Phi(\phi) = A e^{im_l\phi}$

Since ϕ and $\phi + 2\pi$ represent the same meridian plane.

Therefore,

$$\begin{aligned} \Phi(\phi) &= \Phi(\phi + 2\pi) \\ A e^{im_l\phi} &= A e^{im_l(\phi+2\pi)} = A e^{im_l\phi} e^{i2\pi m_l} \\ e^{i2\pi m_l} &= 1 = \cos 2\pi m_l + i \sin 2\pi m_l \\ m_l &= 0, \pm 1, \pm 2, \pm 3, \text{ etc.} \end{aligned}$$

\rightarrow 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 , $m_l = 0, \pm 1, \pm 2, \dots \pm l$

- 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

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

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

Therefore, three quantum numbers are:

- 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, $m_l = 0, \pm 1, \pm 2, \dots \pm l$

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

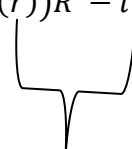
where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

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

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


$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left[E - U(r) - \frac{l(l+1)\hbar^2}{2mr^2} \right] R = 0 \quad (5.10)$$

The total energy of the electron $E = \text{Kinetic } E \text{ (radial)} + \text{Kinetic } E \text{ (orbital)} + U(r)$

Put the expression of E into (5.10), then (5.10) becomes

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

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

The orbital kinetic energy of the electron $= \frac{1}{2} m v_{\text{orbital}}^2 = \frac{L^2}{2mr^2}$

The angular momentum L of the electron $= L = m v_{\text{orbital}} r \rightarrow v_{\text{orbital}} = \frac{L}{mr}$

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

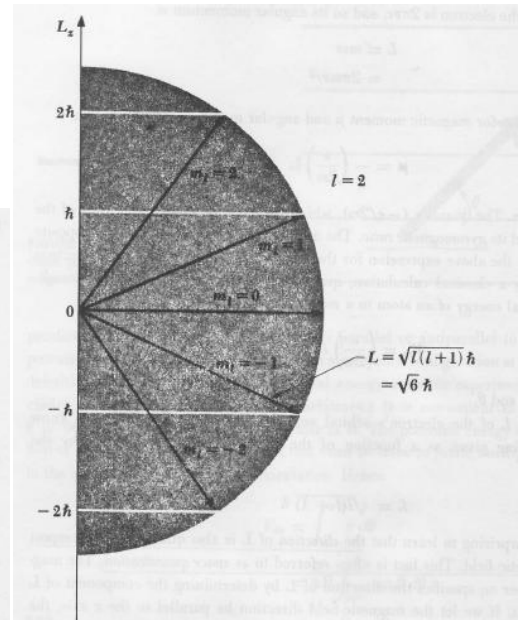
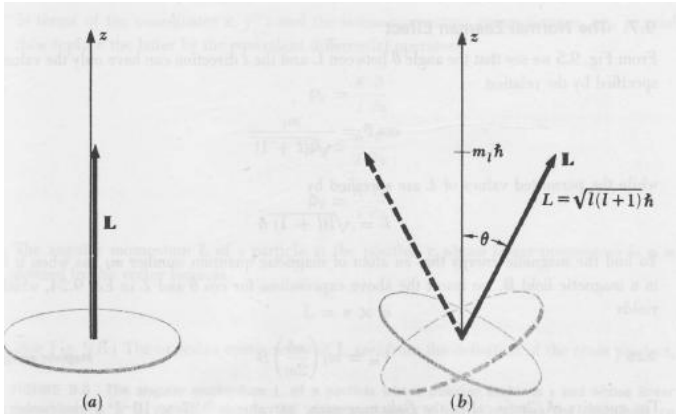
$$L^2 = l(l+1)\hbar^2$$

$L = \sqrt{l(l+1)}\hbar \rightarrow$ Electron angular momentum L is quantized

Angular momentum L is defined as a vector $L = r \times p$

- 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 L_z .



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