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 $l\ and\ m_l$.

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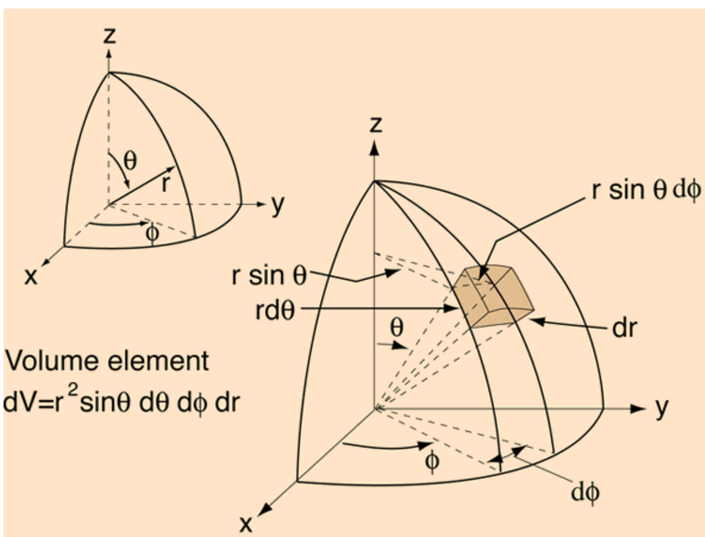
Hydrogen Atom in 3-D
The potential energy of the electron in the hydrogen atom (= Coulomb potential energy between two charges: (+*e*) of the proton and (-*e*) of the electron separated by *r*).

$$U(x) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad (5.1)$$

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



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

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

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

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

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

∇^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),

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

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 derivertivees in θ *and* ϕ on one side and the radial partial derivertive on the other side of the equation:

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

Separation of variables
$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ → for shorthand $\psi = R\Theta\Phi$

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

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

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

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

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

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

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

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

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

Arrange (5.7) to separate *the partial derivative of* θ *and that of* ϕ → (5.8)

$$\frac{1}{\Theta}\sin\theta\,\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad (5.8)$$

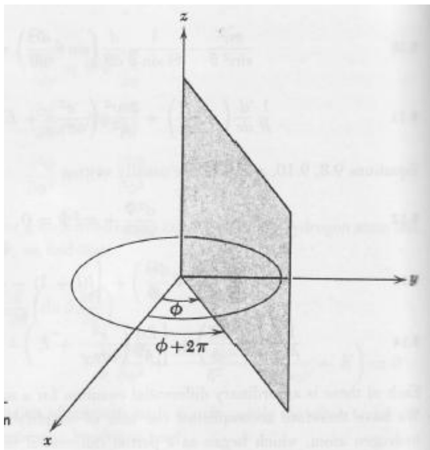
$$=m_l^2\ \text{(another constant)}$$

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

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

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,

$$\Phi(\phi)=\Phi(\phi+2\pi)$$

$$A\,e^{im_l\phi}=A\,e^{im_l(\phi+2\pi)}=Ae^{im_l\phi}e^{i2\pi m_l}$$

$$e^{i2\pi m_l}=1=\cos2\pi m_l+i\sin2\pi m_l$$

$$m_l=0,\pm1,\pm2,\pm3,etc.$$

→ 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 *values can be* $0, \pm1, \pm2, \pm l$

- *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

$$E_n = -\frac{me^4}{32\pi\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right)$$ where *n* 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, …(*n*-1)

Therefore, three quantum numbers are:

- Principal quantum number, $n = 1, 2, 3, ...$
- Orbital quantum number, $l = 0, 1, 2, ... (n-1)$ where *l* =1*(s)*, =2*(p)*, =3*(d)*, =4*(f)*, *etc.*
- Magnetic quantum number, $m_l = 0, \pm1, \pm2, ... \pm l$

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

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

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

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

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

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

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

The orbital kinetic energy of the electron = $\frac{1}{2}m\ v_{orbital}^2\ = \frac{L^2}{2mr^2}$
The angular momentum L of the electron = $L = mv_{orbital}r$ → $v_{orbital}\ =\ \frac{L}{mr}$

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

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

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

Angular momemtum L is defined as a vector L = r x 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 Lz.