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Quantum Theory of Hydrogen Atom

We have already learnt about Schrödinger equation. Now we shall apply this to the **simplest physical system containing interaction potential** one can think: The **Hydrogen Atom with 1 proton, 1 electron and the electrostatic/ coloumb potential holding them together.**

The potential energy in this case is:

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

It is actually the attractive potential between charges of +vely charged nucleus and –vely chargred electron separated by distance **r** .

The potential experienced by the electron in hydrogen atom is an example of **central potential** as the potential energy experienced by the electron depends only on distance from a single point (nucleus).

Notice that the potential is expressed in term of **r.** This **r** can be expressed in terms of x, y and z coordinates and the problem can be solved

here $\mathbf{r}^2 = x^2+y^2+z^2$

But this will make the problem complicated.

We will take an alternative approach. The motion of electrons in H atom can be considered as a series of concentric spheres. As the potential is spherically symmetric, spherical polar coordinates can be used to solve this problem.

We are going to solve 3D Schrödinger equation as we are conidering H atom as sphere. So we need 3 quantum numbers to describe the electron (remember 3 quantum number in 3D Box problem)

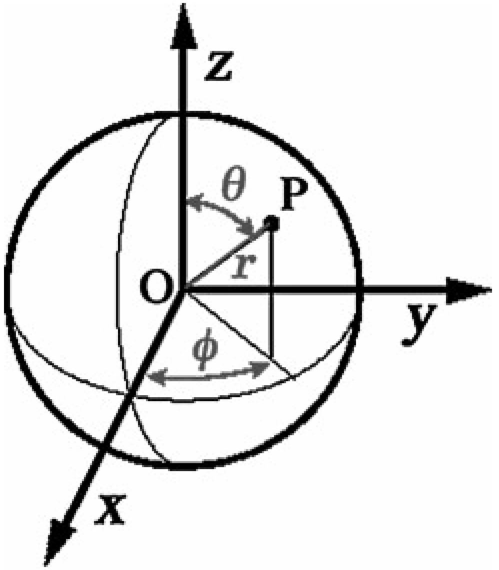
In spherical polar coordinate, a point P (expreesed as (x,y,z) in Cartesian Coordinate) is expressed as (r, θ , φ)

Here, **r** is the length of radius vector from origin (nucleus) to a point (electron) , θ is the angle vector between the radius vector and z axis. The third coordinate φ is the angle between the projection of the radius vector on the xy plane and the x axis

$$r = \sqrt{x^2 + y^2 + z^2}.$$

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right).$$

$$\varphi = \tan^{-1}\left(\frac{y}{x}\right).$$



So we can now express x, y and z as

$$x = r\sin\theta\cos\varphi \qquad y = r\sin\theta\sin\varphi \qquad z = r\cos\theta\,.$$

The time independent 3D Schrödinger equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

m is reduced mass of the system

In spherical polar coordinate it can be written as

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

Now putting the value of potential V and multiplying both side by $r^2\sin^2\theta$ we finally obtain

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{\partial^2\psi}{\partial\varphi^2} + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = 0\,.$$

Though the last equation, a partial differential equation, looks a bit complicated, it can be solved easily by the technique called separation of variable.

Let us assume **$\psi(r, \theta,\phi) = R(r)Y(\theta,\phi)$**

Whether our assumption is right or not can be checked when we shall obtain final result.

Now bringing r dependent part in one side and angular momentum dependent to other and then divivding by **ψ** we obtain:

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2mr^2}{\hbar^2}(E-V(r))R\right]=-\frac{O^{QM}_{\theta\phi}Y(\theta,\phi)}{Y(\theta,\phi)}=\lambda$$

Where **λ** is a constant

- Radial equation:

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

- Angular equation:

$$-\frac{O_{\theta\phi}^{QM}Y(\theta,\phi)}{Y(\theta,\phi)}=\frac{-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi)}{Y(\theta,\phi)}=\lambda$$

Or,

$$-\frac{\partial^2 Y}{\partial\phi^2}=\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta}+\lambda\sin^2\theta Y$$

Again we assume that: $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$

Putting this in angular equation we obtain:

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

m^2 I a constant.

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2\Phi(\phi)=0$$

From this equation we get the idea of azimuthal angle.

Here, boundary condition $\Phi(\phi+2\pi)=\Phi(\phi)$

We obtain solution:

$$\Phi(\phi) = e^{im\phi}$$

Using boundary condition:

$$\Phi(\phi + 2\pi) = e^{im(\phi+2\pi)} = \Phi(\phi) = e^{im\phi}$$

$$e^{2\pi im} = 1$$

So, m = 0, ±1, ±2….This I called magnetic quantum numbers

This is a Quantization Condition

Angular Wave Function

$$L^2 = \frac{\hbar}{i}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Angular Momentum $\vec{L} = (L_x, L_y, L_z)$

$$L^2 Y_{lm}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta,\phi) \qquad L_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi)$$

with $\ell = 0,1,2,\ldots$ and $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$

- Spherical Harmonics

$$Y_{lm}(\theta,\phi)$$

- Solutions:

$$Y_{00}=\sqrt{\frac{1}{4\pi}}$$

$$Y_{11}=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$

$$Y_{10}=-\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,-1}=\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

$$\int_{\Omega}\left|Y_{lm}(\theta,\phi)\right|^2 d\Omega=1$$

$$\int_{\Omega}Y_{lm}^{*}Y_{l'm'}d\Omega=\delta_{ll'}\delta_{mm'}$$

- The Radial Part

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

↓

$$-\frac{\hbar^2}{2m}\left(R''+\frac{2}{r}R'\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}R=ER$$

- At r→ infinity, R(r) → 0
- Trial solution:

$$R(r)=Ae^{-r/a}$$

→

$$R'=-\frac{A}{a}e^{-r/a}=-\frac{R}{a}$$

$$R''=\frac{A}{a^2}e^{-r/a}=\frac{R}{a^2}$$

- From the previous slide, we obtain

$$-\frac{\hbar^2}{2m}\left(\frac{1}{a^2}-\frac{2}{ar}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}=E$$

must hold for all values of r

prefactor for 1/r

$$\frac{\hbar^2}{ma}-\frac{Ze^2}{4\pi\varepsilon_0}=0$$

→ gives idea of length scale parameter

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2 m}$$

→ Bohr radius

- Solutions for energy

$$E = -\frac{\hbar^2}{2ma} = -Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}$$

Ground state in Bohr model (n=1)

Quantum Numbers

1. Principal Q. N. n gives total energy
2. Orbital or azimuthal Q. N. l gives the angular momentum . It can vary from 0 to n-1

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

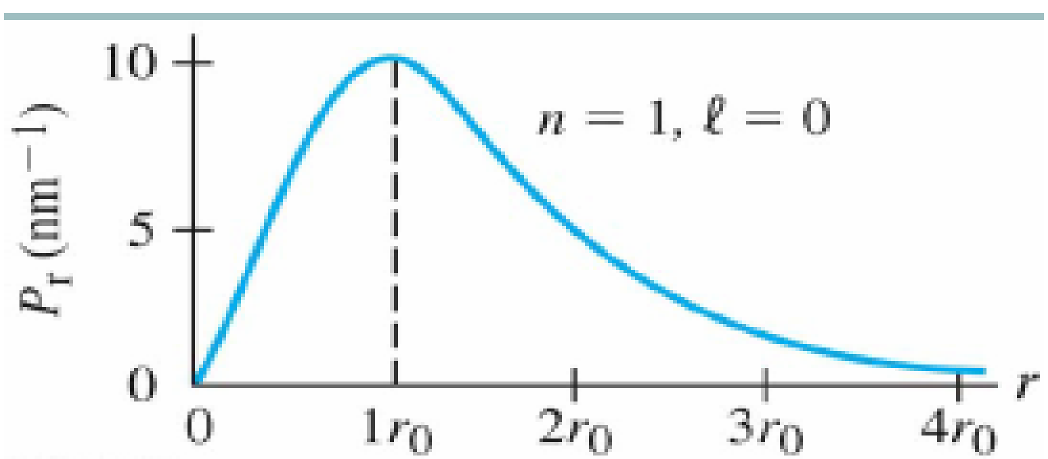
3. The magnetic Quantum number m (values from –l to +l)

$$L_z = m_\ell \hbar$$

- Hydrogen atom wave function for ground state:

$$\psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}}$$

- The probability of finding an electron in a volume dV is given by expression $|\psi|^2 dV$
- Radial probability distribution
- Spherical shell of thickness dr, inner radius r and outer radius r + dr. Hence, $dV = 4\pi r^2 dr$, or, density $|\psi|^2 dV = |\psi|^2 4\pi r^2 dr$, the radial probabilty ditribution $P = 4\pi r^2 |\psi|^2$



Orbitals: Represents the 3D space where the probability of finding electron maximum

Probability to find an electron at a point r at time t = $|\psi(\mathbf{r}, t)|^2$

Different radial wave function:

$n = 1$	$\ell = 0$	$R_{10} = \frac{2}{\sqrt{a^3}} e^{-\rho}$
$n = 2$	$\ell = 0$	$R_{20} = \frac{1}{\sqrt{2a^3}} \left(1 - \frac{\rho}{2}\right) e^{-\rho/2}$
	$\ell = 1$	$R_{21} = \frac{1}{2\sqrt{6a^3}} \rho e^{-\rho/2}$
$n = 3$	$\ell = 0$	$R_{30} = \frac{2}{3\sqrt{3a^3}} \left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right) e^{-\rho/3}$
	$\ell = 1$	$R_{31} = \frac{8}{27\sqrt{6a^3}} \rho \left(1 - \frac{\rho}{6}\right) e^{-\rho/3}$
	$\ell = 2$	$R_{32} = \frac{4}{81\sqrt{30a^3}} \rho^2 e^{-\rho/3}$

- Reference:
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- Molecular Quantum Mechanics, Atkins and Friedman
- Perturbation theory note by Chris-Kriston kylaris
- http://hitoshi.berkeley.edu/221A/variational.pdf