The Hydrogen Atom In Its Full Quantum Mechanical Glory

\[ U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \Rightarrow \text{More complicated form of } U \text{ than box} \]

By example of particle in 3D box, need to use seperation of variables \((x, y, z)\) to derive 3 independent differential eqns.

This approach will get very ugly since we have a "conjoined triplet"

To simplify the situation, use appropriate variables

Independent Cartesian \((x, y, z)\) \(\rightarrow\) Inde. Spherical Polar \((r, \theta, \phi)\)

Instead of writing Laplacian \(\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\), write

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

TISE for \(\psi(x, y, z) = \psi(r, \theta, \phi)\) becomes

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

!!!! fun!!!!
**Spherical Polar Coordinate System**

\[ x = r \sin \theta \cos \phi \]
\[ y = r \sin \theta \sin \phi \]
\[ z = r \cos \theta \]

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

**Volume Element dV**

\[ dV = (r \sin \theta d\phi)(r d\theta)(dr) = r^2 \sin \theta dr d\theta d\phi \]
\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U(r)) \psi(r, \theta, \phi) = 0
\]

Try to free up last term from all except $\phi$

This requires multiplying thruout by $r^2 \sin^2 \theta \Rightarrow$

\[
\sin^2 \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) \psi = 0
\]

For Separation of Variables, Write $\psi(r, \theta, \phi) = R(r). \Theta(\theta). \Phi(\phi)$

Plug it into the TISE above & divide thruout by $\psi(r, \theta, \phi) = R(r). \Theta(\theta). \Phi(\phi)$

\[
\frac{\partial \Psi(r, \theta, \phi)}{\partial r} = \Theta(\theta). \Phi(\phi) \frac{\partial R(r)}{\partial r}
\]

\[
\frac{\partial \Psi(r, \theta, \phi)}{\partial \theta} = R(r) \Phi(\phi) \frac{\partial \Theta(\theta)}{\partial \theta}
\]

\[
\frac{\partial \Psi(r, \theta, \phi)}{\partial \phi} = R(r) \Theta(\theta) \frac{\partial \Phi(\phi)}{\partial \phi}
\]

Note that:

\[
\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) = 0
\]

Rearrange by taking the $\phi$ term on RHS

\[
\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) = -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2}
\]

LHS is fn. of $r, \theta$ & RHS is fn of $\phi$ only, for equality to be true for all $r, \theta, \phi$

\[
\Rightarrow \text{LHS} = \text{constant} = \text{RHS} = m_i^2
\]
Now go break up LHS to separate the $r$ & $\theta$ terms.....

$LHS: \frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left( E + \frac{ke^2}{r} \right) = m_i^2$

Divide Thruout by $\sin^2 \theta$ and arrange all terms with $r$ away from $\theta \Rightarrow$

\[
\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left( E + \frac{ke^2}{r} \right) = \frac{m_i^2}{\sin^2 \theta} - \frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right)
\]

Same argument : LHS is fn of $r$, RHS is fn of $\theta$, for them to be equal for all $r, \theta$

$\Rightarrow$ \[ LHS = \text{const} = RHS = l(l+1) \] What do we have after shuffling!

\[
\frac{d^2 \Phi}{d \phi^2} + m_i^2 \Phi = 0 \ldots (1)
\]

\[
\frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d \Theta}{d \theta} \right) + \left[ l(l+1) - \frac{m_i^2}{\sin^2 \theta} \right] \Theta(\theta) = 0 \ldots (2)
\]

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{\partial R}{\partial r} \right) + \left[ \frac{2mr^2}{\hbar^2} \left( E + \frac{ke^2}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0 \ldots (3)
\]

These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

All we need to do now is guess the solutions of the diff. equations

Each of them, clearly, has a different functional form
Solutions of The S. Eq for Hydrogen Atom

The Azimuthal Diff. Equation:

\[ \frac{d^2\Phi}{d\phi^2} + m_i^2\Phi = 0 \]

Solution: \( \Phi(\phi) = A e^{im_i\phi} \) but need to check "Good Wavefunction Condition"

Wave Function must be Single Valued for all \( \phi \Rightarrow \Phi(\phi) = \Phi(\phi + 2\pi) \)

\[ \Rightarrow \Phi(\phi) = A e^{im_i\phi} = A e^{im_i(\phi + 2\pi)} \Rightarrow m_i = 0, \pm 1, \pm 2, \pm 3, \ldots \text{(Magnetic Quantum #)} \]

The Polar Diff. Eq:

\[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m_i^2}{\sin^2 \theta} \right] \Theta(\theta) = 0 \]

Solutions: go by the name of "Associated Legendre Functions"

only exist when the integers \( l \) and \( m_i \) are related as follows

\( m_i = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l \); \( l \) = positive number

\( l \): Orbital Quantum Number

For \( l = 0, m_i = 0 \Rightarrow \Theta(\theta) = \frac{1}{\sqrt{2}} \)

For \( l = 1, m_i = 0, \pm 1 \Rightarrow \text{Three Possibilities for the Orbital part of wavefunction} \)

\[ [l = 1, m_i = 0] \Rightarrow \Theta(\theta) = \frac{\sqrt{6}}{2} \cos \theta \]
\[ [l = 1, m_i = \pm 1] \Rightarrow \Theta(\theta) = \frac{\sqrt{3}}{2} \sin \theta \]

\[ [l = 2, m_i = 0] \Rightarrow \Theta(\theta) = \frac{\sqrt{10}}{4} (3\cos^2 \theta - 1) \ldots \text{and so on and so forth (see book)} \]
Solutions of The S. Eq for Hydrogen Atom

The Radial Diff. Eqn: \[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{\partial R}{\partial r} \right) + \left[ \frac{2m}{\hbar^2} \left( E + \frac{k^2}{2} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0 \]

**Solutions**: Associated Laguerre Functions \( R(r) \), Solutions exist only if:

1. \( E > 0 \) or has negative values given by \( E = -\frac{k^2}{2a_0} \left( \frac{1}{n^2} \right) \); \( a_0 = \frac{\hbar^2}{mk^2} = \) Bohr Radius

2. And when \( n = \) integer such that \( l = 0, 1, 2, 3, 4, ..., (n-1) \)

\( n = \) principal Quantum \# or the "big daddy" quantum \#

To Summarize: The hydrogen atom is brought to you by the letters

\[
\begin{align*}
n &= 1, 2, 3, 4, 5, ..., \infty \\
l &= 0, 1, 2, 3, ..., (n-1) \\
m_l &= 0, \pm 1, \pm 2, \pm 3, ..., \pm l
\end{align*}
\]

Quantum \# appear only in Trapped systems

The Spatial Wave Function of the Hydrogen Atom

\[ \Psi(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm_l}(\theta) \cdot \Phi_{m_l}(\phi) = R_{nl}Y_l^{m_l} \) (Spherical Harmonics) \]
Radial Wave Functions & Radial Prob Distributions

\[ R(r) = \begin{cases} 
\frac{2}{a_0^{3/2}} e^{-r/a} & \text{for } n=1 \\
\frac{1}{2\sqrt{2}a_0^{3/2}} (2 - \frac{r}{a_0}) e^{\frac{r}{2a_0}} & \text{for } n=2 \\
\frac{2}{81\sqrt{3}a_0^{3/2}} (27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}) e^{\frac{r}{3a_0}} & \text{for } n=3
\end{cases} \]

\[
\begin{align*}
n=1 & \rightarrow \text{K shell} & l=0 & \rightarrow s(\text{harp}) \text{ sub shell} \\
n=2 & \rightarrow \text{L Shell} & l=1 & \rightarrow p(\text{principal}) \text{ sub shell} \\
n=3 & \rightarrow \text{M shell} & l=2 & \rightarrow d(\text{diffuse}) \text{ sub shell} \\
n=4 & \rightarrow \text{N Shell} & l=3 & \rightarrow f(\text{fundamental}) \text{ ss} \\
\text{......} & \text{......} & l=4 & \rightarrow g \text{ sub shell} \\
\text{......} & \text{......}
\end{align*}
\]
Symbolic Notation of Atomic States in Hydrogen

\[
l \rightarrow \begin{array}{cccccc}
    & s (l = 0) & p (l = 1) & d (l = 2) & f (l = 3) & g (l = 4) \\
    \downarrow \ & 1 & 1s & 2 & 2s & 2p \\
    \downarrow \downarrow \ & 3 & 3s & 3p & 3d \\
    \downarrow \downarrow \downarrow \ & 4 & 4s & 4p & 4d & 4f \\
    \downarrow \downarrow \downarrow \downarrow \ & 5 & 5s & 5p & 5d & 5f & 5g
\end{array}
\]

Note that:

- \( n = 1 \) non-degenerate system
- \( n > 1 \) are all degenerate in \( l \) and \( m_l \).

All states have **same energy**

But different spatial configuration

\[
E = -\frac{ke^2}{2a_0} \left( \frac{1}{n^2} \right)
\]
Facts About Ground State of H Atom

\[ n = 1, \ l = 0, \ m_l = 0 \Rightarrow R(r) = \frac{2}{a_0^{3/2}} e^{-r/a}; \ \Theta(\theta) = \frac{1}{\sqrt{2\pi}}; \ \Phi(\phi) = \frac{1}{\sqrt{2}} \]

\[ \Psi_{100}(r, \theta, \phi) = \frac{1}{a_0 \sqrt{\pi}} e^{-r/a} \]......look at it carefully

1. Spherically symmetric \( \Rightarrow \) no \( \theta, \phi \) dependence (structure)

2. Probability Per Unit Volume: \( |\Psi_{100}(r, \theta, \phi)|^2 = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a}} \)

Likelihood of finding the electron is same at all \( \theta, \phi \) and depends only on the radial separation (r) between electron & the nucleus.

3. Energy of Ground State = \( -\frac{ke^2}{2a_0} = -13.6eV \)

Overall The Ground state wavefunction of the hydrogen atom is quite \textit{boring}

Not much chemistry or Biology could develop if there was only the ground state of the Hydrogen Atom!

\textbf{We need structure, we need variety, we need some curves!}
Interpreting Orbital Quantum Number ($l$)

Radial part of S.Eqn: \[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( E + \frac{ke^2}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0
\]

For H Atom: \( E = K + U = K_{\text{RADIAL}} + K_{\text{ORBITAL}} - \frac{ke^2}{r} \); substitute this form for \( E \)

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ K_{\text{RADIAL}} + K_{\text{ORBITAL}} - \frac{\hbar^2 l(l+1)}{2m r^2} \right] R(r) = 0
\]

Examine the equation, if we set \( K_{\text{ORBITAL}} = \frac{\hbar^2 l(l+1)}{2m r^2} \) then get a diff. eq. in \( r \)

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ K_{\text{RADIAL}} \right] R(r) = 0 \quad \text{which depends only on radius } r \text{ of orbit}
\]

Further, we also know that \( K_{\text{ORBITAL}} = \frac{1}{2} m v_{\text{orbit}^2} \); \( \vec{L} = \vec{r} \times \vec{p} \); \( |L| = m v_{\text{orbit}} r \implies K_{\text{ORBITAL}} = \frac{L^2}{2mr^2} \)

Putting it all together: \( K_{\text{ORBITAL}} = \frac{\hbar^2 l(l+1)}{2m} = \frac{L^2}{2mr^2} \implies \text{magnitude of Ang. Mom} |L| = \sqrt{l(l+1)} \hbar \)

Since \( l = \text{positive integer} = 0, 1, 2, 3 \ldots (n-1) \Rightarrow \text{angular momentum} |L| = \sqrt{l(l+1)} \hbar = \text{discrete values} \)

\[ |L| = \sqrt{l(l+1)} \hbar \quad \text{QUANTIZATION OF Electron's Angular Momentum} \]
\[ \mathbf{\tilde{L}} = \mathbf{\tilde{r}} \times \mathbf{\tilde{p}} \] (Right Hand Rule)

Classically, direction & Magnitude of \( \mathbf{\tilde{L}} \) always well defined

QM: Can/Does \( \mathbf{\tilde{L}} \) have a definite direction? Proof by Negation:

Suppose \( \mathbf{\tilde{L}} \) was precisely known/defined (\( \mathbf{\tilde{L}} \parallel \mathbf{\hat{z}} \))

Since \( \mathbf{\tilde{L}} = \mathbf{\tilde{r}} \times \mathbf{\tilde{p}} \Rightarrow \) Electron MUST be in x-y orbit plane

\[ \Rightarrow \Delta z = 0 \; ; \; \Delta p_z \Delta z \sim \hbar \Rightarrow \Delta p_z \sim \infty; \; E = \frac{p^2}{2m} \sim \infty \; !!! \]

So, in Hydrogen atom, \( \mathbf{\tilde{L}} \) can not have precise measurable value

Uncertainty Principle & Angular Momentum : \[ \Delta L_z \Delta \phi \sim \hbar \]

Arbitrarilily picking \( Z \) axis as a reference direction:

\( \mathbf{\tilde{L}} \) vector spins around \( Z \) axis (precesses).

The \( Z \) component of \( \mathbf{\tilde{L}} \)

\[ |L_z| = m_i \hbar; \; \; m_i = \pm 1, \pm 2, \pm 3... \pm l \]

Note : \( |L_z| < |L| \) (always)

since \( m_i \hbar < \sqrt{l(l+1)} \hbar \)

It can never be that \( |L_z| = m_i \hbar = \sqrt{l(l+1)} \hbar \)

(breaks Uncertainty Principle)

So you see, the dance has begun!

\[ |L| = \sqrt{6} \hbar \]

\[ L_z = 2 \hbar \]
\[ L_z = \hbar \]
\[ L_z = 0 \]
\[ L_z = -\hbar \]
\[ L_z = -2 \hbar \]

\( l = 2 \)

\( L_z = 2 \hbar \)
L=2, m_l=0,±1, ± 2 : Pictorially

\[ L = \hbar \sqrt{l(l+1)} = \hbar \sqrt{2(2+1)} = \hbar \sqrt{6} \]

Sweeps Conical paths of different \( \vartheta \): \( \cos \vartheta = L_Z/L \) and average

\[ \langle L_X \rangle = 0 \]
\[ \langle L_Y \rangle = 0 \]
What’s So “Magnetic”? 

Precessing electron → Current in loop → Magnetic Dipole moment $\mu$

More in this in Tomorrow’s lecture when we look at Energy States
Radial Probability Densities

\[ \Psi(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \Phi_{n_l}(\phi) = R_{nl} Y_{lm} \]

Probability Density Function in 3D:

\[ P(r, \theta, \phi) = \Psi^* \Psi = |\Psi(r, \theta, \phi)|^2 = |R_{nl}|^2 \cdot |Y_{lm}|^2 \]

Note: 3D Volume element \( dV = r^2 \cdot \sin \theta \cdot dr \cdot d\theta \cdot d\phi \)

Prob. of finding particle in a tiny volume \( dV \) is

\[ P.dV = |R_{nl}|^2 \cdot |Y_{lm}|^2 \cdot r^2 \cdot \sin \theta \cdot dr \cdot d\theta \cdot d\phi \]

The Radial part of Prob. distribution: \( P(r)dr \)

\[ P(r)dr = |R_{nl}|^2 \cdot r^2 \cdot d\theta \int_0^{2\pi} |\Theta_{lm}(\theta)|^2 d\theta \int_0^\pi |\Phi_{n_l}(\phi)|^2 d\phi \]

When \( \Theta_{lm}(\theta) \) & \( \Phi_{n_l}(\phi) \) are auto-normalized then

\[ P(r)dr = |R_{nl}|^2 \cdot r^2 \cdot dr, \quad \text{in other words} \quad P(r) = r^2 |R_{nl}|^2 \]

Normalization Condition:

\[ 1 = \int_0^\infty r^2 |R_{nl}|^2 dr \]

Expectation Values:

\[ <f(r)> = \int_0^\infty f(r)P(r)dr \]
Ground State: Radial Probability Density

\[ P(r)dr = |\psi(r)|^2 \cdot 4\pi r^2 dr \]

\[ \Rightarrow P(r)dr = \frac{4}{a_0^3} r^2 e^{-\frac{r}{a_0}} \]

Probability of finding Electron for \( r > a_0 \)

\[ P_{r > a_0} = \int_{a}^{\infty} \frac{4}{a_0^3} r^2 e^{-\frac{r}{a_0}} dr \]

To solve, employ change of variable

Define \( z = \left[ \frac{2r}{a_0} \right] \); change limits of integration

\[ P_{r > a_0} = \frac{1}{2} \int_{2}^{\infty} z^2 e^{-z} dz \] (such integrals called Error. Fn)

\[ = \frac{1}{2} \left[ z^2 + 2z + 2 \right] e^{-z} \bigg|_{2}^{\infty} = 5e^2 = 0.667 \Rightarrow 66.7\% \]