Recall the Bohr atom, 1912 "Old Quantum Theory"

\[ L = mvr = nh \quad ; \quad n = 1, 2, 3 \]

From de Broglie's

\[ \gamma = \frac{h}{p} \quad \Rightarrow \quad \text{i.e. photons = wave & particle} \]

Then

\[ e^- = \text{particle} + \text{wave} \]

So idea is

\[ \Delta \Gamma = n \lambda = n \frac{h}{p} \]

\[ \Gamma = \frac{1}{2\pi} \frac{h}{n} \]

\[ L = nh \quad = \text{angular momentum quantization} \]

Then From

\[ \Sigma \mathcal{F}_{\text{eff}} = -\frac{\hbar^2}{2m} \quad \Rightarrow \quad E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi \varepsilon_0 r} \]

Get

\[ \Gamma_n = \frac{4\pi \varepsilon_0 e^2}{\hbar^2} \quad ; \quad n = 1, 2, 3 \quad ; \quad j = 0.529 \quad \text{nm} \]

\[ n = \frac{e^2}{4\pi \varepsilon_0 k} \quad \Rightarrow \quad \frac{1}{n} \]

\[ E_n = \frac{-\hbar^2}{2m} \left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \frac{1}{n^2} = \frac{-13.6 \quad eV}{n^2} \]
New three great results of H-atom can be ordered stood is what began our story... 

1925 Heisenburg & Lang Fauer

Born & Jordan

Based on suggestion by de Broglie of 'wave to the wave equation'

Matrix Mechanics

Wavefunction Formalism

Boris interpretation of $\Psi$

Schrödinger recognizes

Matrix $\rightarrow$ wave are the same.

We now have!

$$\hat{H}\mid\Psi\rangle = i\hbar\frac{\partial}{\partial t}\mid\Psi\rangle$$

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi}{\partial t}$$

With this fundamental formalism will go on to have the most successful solid theory ever

Get Things "Right" better than any other theory!
The key about Hydrogen in this story is that if you have a new theory or idea of the universe—Cool.

But... you must get Hydrogen as Right & Then Because Then Thus.
Hydrogen

\[ H \Psi(x,y,z) = i\hbar \frac{\partial \Psi(x,y,z)}{\partial t} \]

As always, demand energy eigenvalue

\[ \Psi_n \equiv E_n \]

\[ \frac{\partial}{\partial t} \Psi_n = e^{\frac{i}{\hbar} E_n t} \Psi_n(x) \]

\[ \Psi_n \] guaranteed separable solns

[good basis!]

\[ \hat{H} \Psi_n = E_n \Psi_n = \text{time indep} \]

Schrödinger's

But clearly we'll need to solve this in

3-D

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi_n + V \Psi_n = E_n \Psi_n \]

3-D,

what coordinate should be used?

\[ V(r) \propto \frac{1}{r} \quad \text{so} \quad x,y,z = V(x,y,z)^{-\frac{1}{2}} \frac{1}{\sqrt{x^2 + y^2 + z^2}} \]

So spherical coords = more convenient
Spherical coods

\( r = \text{radial coord} \)
\( \sigma = \text{polar coord} \)
\( \phi = \text{azimuthal coord} \)

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

so not trivial but possible to

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

\[ \nabla^2_{r, \sigma, \phi} = \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \sigma} \frac{\partial}{\partial \sigma} \left( \sin \sigma \frac{\partial}{\partial \sigma} \right) + \frac{1}{r^2 \sin^2 \sigma} \frac{\partial^2}{\partial \phi^2} \right] \]
\[ \hat{H} \psi_n(r, \theta, \phi) = E_n \psi_n(r, \theta, \phi) \]

\[ -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi_n = E_n \psi_n \]

We will recognize this to make life easier!

But we will need to understand angular momentum.
Real H-atom

Can we make a \( \hat{L} \)?

well \( \hat{L} = \vec{p} \times \vec{r} \); \( \hat{\vec{r}} = \vec{r} \)

\[ \text{so } \hat{\vec{p}} = -i \hbar \frac{\partial}{\partial \vec{r}} \]

Then

\[ \hat{L} = \hat{\vec{L}} \]

\[ \hat{L} = (\hat{\vec{p}}_z - \hat{\vec{p}}_y) \hat{\imath} + (\hat{\vec{p}}_x - \hat{\vec{p}}_z) \hat{\jmath} + (\hat{\vec{p}}_y - \hat{\vec{p}}_x) \hat{k} \]

so

\[ \hat{L}_x = (\hat{\vec{p}}_z - \hat{\vec{p}}_y) \]

\[ \hat{L}_y = (\hat{\vec{p}}_x - \hat{\vec{p}}_z) \]

\[ \hat{L}_z = (\hat{\vec{p}}_y - \hat{\vec{p}}_x) \]
OK: so we have \( l_x, l_y, l_z \)

1st? are they Hermitian?
why --- need Hermitian \( \hat{a}'s \)

see real observables

ex: 6.1 pg 118 \( \hat{l}_z = \hat{h}_z = \) Hermitian.

2nd? how well can we measure \( l_x, l_y, l_z \) ?
classically no big deal

\[
\hat{l} = l_x \hat{x} + l_y \hat{y} + l_z \hat{z}
\]
can measure by all simultaneously

But the answer to this in Q.M. must ask about commutation?

\( l_x \hat{a} \hat{b} \) commute, then

they share some eigenfunctions
& eigenfunctions carry eigen-
values of \( a \& b \) definitively

\( l_x \hat{a} \hat{b} \) do not commute
\( \hat{a} \hat{b} \) cannot be measured simultaneously
So investigate

\[ [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \]

\[ [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \]

\[ [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \]

\[ \hat{L}_x, \hat{L}_y, \hat{L}_z \] Do not commute with each other.

Quantum Mechanically you cannot measure definite simultaneous eigenvalues of \( \hat{L}_x, \hat{L}_y, \hat{L}_z \)

So

\[ \hat{L}_x \psi = \hat{L}_y \psi \]
\[ \hat{L}_y \psi = \hat{L}_z \psi \]
\[ \hat{L}_z \psi = \hat{L}_x \psi \]

no such \( \psi \)

However, \( \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \), The angular momentum

will \[ [\hat{L}_x, \hat{L}_y] = 0 \]

Here's how
\[ \begin{align*}
\text{try } \quad \left[ L_x^2, L_z \right] &= \left[ L_x^2 + L_y^2 + L_z^2, L_z \right] \\
&= \left[ L_x^2, L_z \right] + \left[ L_y^2, L_z \right] + \left[ L_z^2, L_z \right] \\
&= 0 \\
\text{so } \quad L_x^2, L_z &= 0 \\
\text{and } \quad L_y^2, L_z &= 0 \\
\text{and } \quad L_z^2, L_z &= 0 \\
\text{So, } \quad \left[ L_z^2, L_z \right] &= 0 \\
\text{while } \quad L_x, L_y, L_z \quad \text{do not commute} \\
\left[ \hat{L}_z, L_z \right] &= L_x^2 + L_y^2 + L_z^2 \quad \text{commutes} \\
\text{with all } \quad \hat{L}_z 
\end{align*} \]
These relationships are true for all angular momentum.

\[ \vec{l} = \text{orbital} \]
\[ \vec{s} = \text{spin} \]
\[ \vec{J} = \text{Total angular momentum} \]

So

\[ [\vec{J}_x, \vec{J}_z] = i\hbar \vec{J}_y \]
\[ [\vec{J}_y, \vec{J}_z] = i\hbar \vec{J}_x \]
\[ [\vec{J}_x, \vec{J}_y] = i\hbar \vec{J}_z \]

So... Best you can hope to know simultaneously definitively about angular momentum.

In QM, we shared eigenvectors \( \frac{1}{2} \rightarrow \) Schrödinger UP is \( \vec{J}^2 \) a magnitude \( \vec{J}_x, \vec{J}_y, \vec{J}_z \) projection onto of the axes

We usually by convention chose to look for max \( \sin \theta \)

That is smallest \( \theta \) of \( \vec{J}_x^2 \vec{J}_z = 0 \).
So, if we have angular momentum, the Best \( \ell \) will
\[
\ell^2 \psi = \ell^2 \psi
\
\text{since } [\hat{l}_z, \hat{l}^2] = 0
\
\hat{l}_z \psi = \ell \hat{l}_z \psi
\]

So, The next is to find the simultaneous eigenfunction & eigenvalues of \( \hat{l}_z \) & \( \hat{l}^2 \)

To do that, you do it the same old way

D) Find \( \hat{l}_z \) & \( \hat{l}^2 \)

D) Then solve eigenvalue problems

Okay: \( \hat{l}_z = \hat{x} \partial_y - \hat{y} \partial_x \) in cartesian coordinates

\[
= \partial_x \psi
\]

\[
= -i \kappa \frac{\partial}{\partial \phi} \text{ in spherical coordinates!}
\]

So \( \hat{l}_z \psi = \ell \hat{l}_z \psi \) since we know \( \hat{l}_z \)
eigenvalue = projection of angular momentum \( \hat{l} \)
eigenvalues = angular momentum \( \ell \) units = every sec...
\[ \psi = \psi_0 \psi(r) = \text{separable ans"ate} \]

\[ -i \hbar \frac{\partial \psi}{\partial t} = \mathbf{p} \cdot \mathbf{p} \psi(r) \]

or

\[ \sum \frac{\partial \psi}{\partial r} = \mathbf{p} = i \hbar \mathbf{e} \cdot \mathbf{p} \]

\[ \psi(r) = e^{i \mathbf{p} \cdot \mathbf{r}} \quad \text{constant} \quad \psi(r) \]

\[ \text{Norm} e^{i \mathbf{e} \cdot \mathbf{r}} \]

\[ \text{Some sum} \]

\[ \text{Later} \]

\[ \psi_p (\rho) = e^{i \mathbf{e} \cdot \mathbf{r}} \]

Better... little complications

in spherical coordinates

\[ \psi_p (\rho \pm 2\pi) = \psi_p (\rho) \]

So we need

\[ e^{i \mathbf{e} \cdot (\rho \pm 2\pi)} = e^{i \mathbf{e} \cdot \mathbf{r}} \]

or

\[ e^{i \mathbf{e} \cdot 2\pi} = e^{i \mathbf{e} \cdot \mathbf{r}} \]

\[ e^{2\pi i \mathbf{e} \cdot \mathbf{r}} = 1 \]

\[ 2\pi i \mathbf{e} \cdot \mathbf{r} = 1 \]

\[ \cos (2\pi i \mathbf{e} \cdot \mathbf{r}) + i \sin (2\pi i \mathbf{e} \cdot \mathbf{r}) = 1 \]

So \( \mathbf{e} \) has to be \( \mathbf{e} = 0, \pm \mathbf{e}, \pm 2\mathbf{e}, \ldots \)

So proj of \( \mathbf{L} \) = Quantized!
\[ l^2_{\ell, \ell_\nu, \nu} \psi = \ell^2 \psi \quad \text{again, } l^2 \text{ eigenvalue} \]

so expect \( \ell^2 \)

\[-\hbar^2 \left[ \frac{1}{\sin \sigma} \frac{\partial}{\partial \sigma} \left( \sin \sigma \frac{\partial}{\partial \sigma} \right) + \frac{\ell^2}{\sin^2 \sigma} \right] \psi = \ell^2 \mathcal{L}(\ell \psi) \psi \]

**Recall also need**

\[ l^2 \psi = m^2 \psi \]

(Can show)

\[ \psi(\ell, \sigma) = \sum_{m} e^{i m \ell} (\ell, \sigma) \]

\[ \sum_{m} e^{i m \ell} (\ell, \sigma) = \begin{cases} \begin{array}{cc}
\sqrt{\frac{1}{2\ell+1}} & \text{for } m \geq 0 \\
\sqrt{\frac{1}{2\ell+1}} & \text{for } m \leq 0
\end{array}
\end{cases} \]

\[ \frac{1}{\sin \sigma} \frac{\partial}{\partial \sigma} \left( \sin \sigma \frac{\partial}{\partial \sigma} \right) \psi = \frac{m+m}{m} \psi \]

\[ \psi = (-1)^m \]

\[ \text{for } m \geq 0 \]

\[ \text{already got!} \]

\[ \psi = (-1)^m \psi \]

\[ \text{for } m \leq 0 \]

\[ \text{restricts } \psi \text{'s} \]

\[ \text{associated Legendre Polynomials} \]

\[ A, \ell P = P^m_{\ell} (x) = (1-x^2)^{\frac{m}{2}} \left( \frac{d}{dx} \right)^m P^m_{\ell} (x) \]

\[ P^0_0 (\cos \sigma) = 0 \]

\[ P^1_0 (\cos \sigma) = \sin \sigma \quad P^1_1 (\cos \sigma) = \cos \sigma \]

\[ P^2_2 (\cos \sigma) = 3 \sin^2 \sigma \quad P^1_0 (\cos \sigma) = 3 \cos \sigma (3 \cos^2 \sigma - 1) \]

\[ P^0_1 (\cos \sigma) = 1 \quad P^2_0 (x) = \frac{1}{2} (3 x^2 - 1) \]

\[ P^1_1 (x) = \frac{1}{2} (5 x^3 - 3 x) \]