Recall the Bohr atom, 1912 "Old Quantum Theory"

$L = mvr = n\hbar$ ; $n = 1, 2, 3$

from de Broglie's

$\lambda = \frac{h}{p}$

i.e. photons = wave & particle

then

$e^- =$ particle + wave

So idea is $2\pi r_{orbit} = n\lambda = n\frac{h}{p}$

$$\underbrace{rp}_{} = \frac{h}{2\pi} n$$

$L = n\hbar$ = angular momentum quantization

Then from $\sum F_{rad} = \frac{-mv^2}{r}$ & $E_1 = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$

$$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{-mv^2}{r}$$

Get: $r_n = \frac{4\pi\varepsilon_0\hbar^2}{me^2} n^2$, $n = 1, 2, 3$ ; $= 0.529\, n^2$

$$v_n = \frac{e^2}{4\pi\varepsilon_0\hbar}\frac{1}{n}$$

$$E_n = \frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} = \frac{-13.6}{n^2}\text{ eV}$$

Solved stability & spectroscopic experiments of H-atom that could not be solved previously

How these great results of H-atom can be understood is what began our story....

1925 Heisenberg w/ hay fever

Born & Jordan

Matrix Mechanics

Schrödinger Based on suggestion by de Bye of "where is the wave equation"

(on de Broglie's $\lambda$)

Wavefunction Formalism

Born's interpretation of $\Psi$

Schrö recognizes

matrix $\rightleftarrows$ wave are the same.

we now Have!

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

With this Fundamental Formalism will go on to have the most successful 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

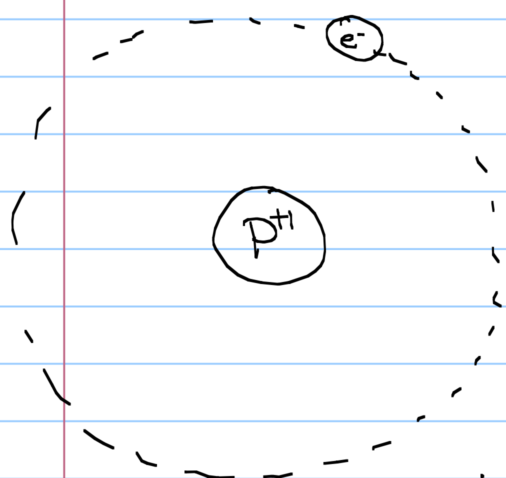
Better than

this!

Q.M.

Hydrogen

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




as always, demand energy eigen kets $\psi_n$ & $E_n$

& assume $V \neq f(t)$

so that

$$\Psi_{TOT} = e^{-i\frac{E_n t}{\hbar}} \psi_n(x)$$

& guaranteed separable solns = good Basis!

& $\hat{H}\psi_n = E_n \psi_n$ = time indep Schro

But clearly we'll need to solve this in 3-D

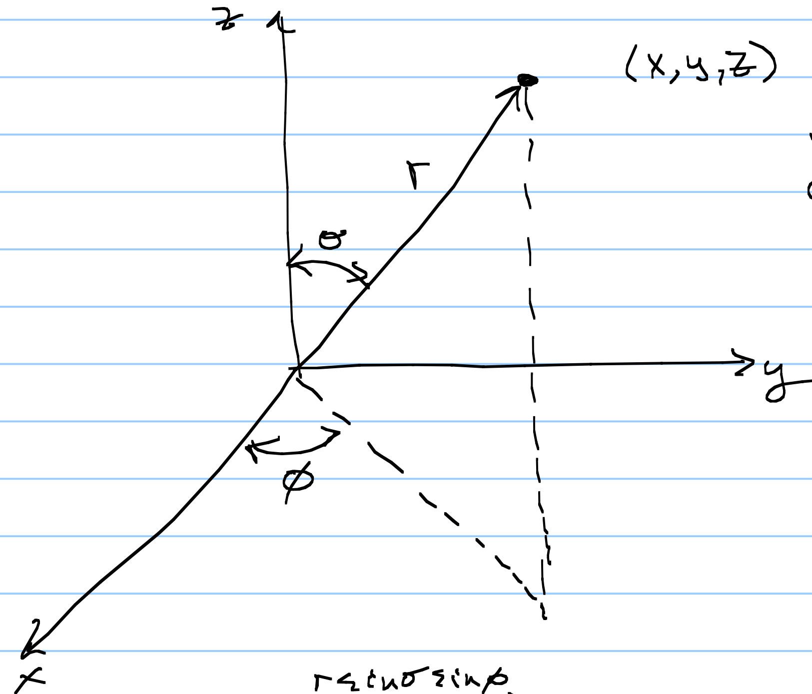
$$-\frac{\hbar^2}{2m}\nabla^2 \psi_n + V\psi_n = E_n \psi_n$$

what 3-D coordinate should be used?

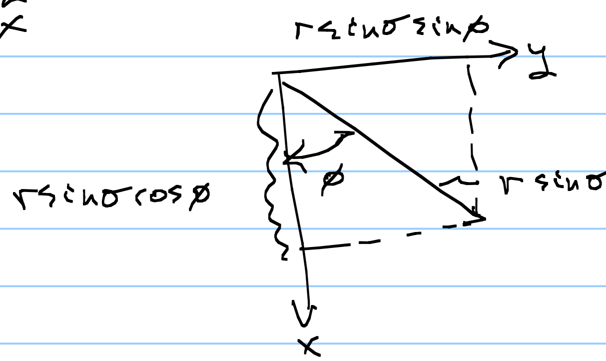
$V(r) \propto \frac{1}{r}$ so $x, y, z$ = $V(x,y,z) \propto \frac{1}{\sqrt{x^2+y^2+z^2}}$

So spherical coords = more convenient

Spherical coords




$r$ = radial coord
$\theta$ = polar coord
$\phi$ = azimuthal coord




so $x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

so not trivial but possible to go from

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

$$\Updownarrow$$

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

so $\hat{H}\psi_n(r,\theta,\phi) = E_n \psi_n(r,\theta,\phi)$

$$-\frac{\hbar^2}{2m}\nabla^2_{r,\theta,\phi}\,\psi(r,\theta,\phi) = E_n \psi_n(r,\theta,\phi)$$

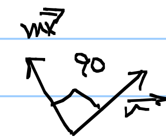
$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right]\psi_n = E_n\psi_n$$

we will regonize this to make life easier!

But we will need to understand Angular Momentum.

# Real H-atom


$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times m\vec{v} = rmv \sin\theta$




$L = rmv$

Can we make a $\hat{L}$?

well $\vec{L} = \vec{r} \times \vec{p}$ ; $\hat{x} = x$

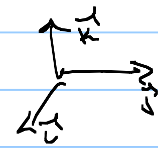
so $\hat{\vec{r}} = \hat{x}\,\hat{i} + \hat{y}\,\hat{j} + \hat{z}\,\hat{k}$

& $p_x = -i\hbar \frac{\partial}{\partial x}$

so $\vec{p} = -i\hbar\left(\frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}\right)$

Then

$$\hat{\vec{L}} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{P}_x & \hat{P}_y & \hat{P}_z \end{vmatrix}$$




$$\hat{\vec{L}} = (\hat{y}\hat{P}_z - \hat{z}\hat{P}_y)\hat{i} + (\hat{z}\hat{P}_x - \hat{x}\hat{P}_z)\hat{j} + (\hat{x}\hat{P}_y - \hat{y}\hat{P}_x)\hat{k}$$

or $L_x = (\hat{y}\hat{P}_z - \hat{z}\hat{P}_y)$

$L_y = (\hat{z}\hat{P}_x - \hat{x}\hat{P}_z)$

$L_z = (\hat{x}\hat{P}_y - \hat{y}\hat{P}_x)$

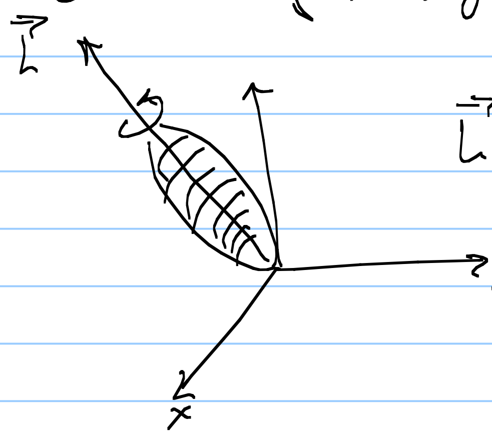
OK: so we have $\hat{L}_x, \hat{L}_y, \hat{L}_z$

1st ? are they Hermetian?
why --- need Hermetian $\hat{o}$'s
for Real observables

ex: 6.1 pg 118 $\hat{L}_z^{+} = \hat{L}_z$ = Hermetian.

2nd ? How well can we measure
$\hat{L}_x$, $\hat{L}_y$ & $\hat{L}_z$ ?

classically no big deal




$\vec{L} = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}$

can measure well simultaneously

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

If 2 $\hat{o}$'s $[\hat{A} \& \hat{B}]$ commute, then
They share same eigenfunctions
& eigenfunctions carry eigen-
values of a & b definitively

If $[\hat{A}, \hat{B}] \neq$ do not commute
$\hat{A}$ & $\hat{B}$ cannot be measure simultaneously

So investigate

$$[\hat{L}_x, \hat{L}_y] = \text{pg } 120 \text{ scherrer}$$
$$= i\hbar \hat{L}_z$$

& worse

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

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

Quantum Mechanically you cannot measure definite simultaneous eigenvalues of $L_x, L_y, L_z$

so $\cancel{\hat{L}_x \psi = l_x \psi}$

$\cancel{\hat{L}_y \psi = l_y \psi}$

$\cancel{\hat{L}_z \psi = l_z \psi}$

no such $\psi$

However: $\hat{L}^2 = L_x^2 + L_y^2 + L_z^2$, The angular momentum squared

will $\left[\hat{L}^2, \begin{matrix} L_x \\ L_y \\ L_z \end{matrix}\right] = 0$ here's how try $[L^2, L_z] = [L_x^2 + L_y^2 + L_z^2, L_z]$

$$= \underbrace{[L_x^2, L_z] + [L_y^2, L_z]}_{\substack{=0 \\ \text{pg } 121}} + \underbrace{[L_z^2, L_z]}_{\substack{(L_zL_zL_z - L_zL_zL_z)\psi \\ = L_z(L_zL_z - L_zL_z)\psi \\ = 0}}$$

so $[L^2, L_z] = 0$

$[L^2, L_x] = 0$

$[L^2, L_y] = 0$

So while $\hat{L}_x, \hat{L}_y, \hat{L}_z$ do not commute

$\hat{L}^2 = L_x^2 + L_y^2 + L_z^2$ commutes w/ all 3

Those relationships are true for all angular momentum. ....

$\vec{L}$ = orbital

$\vec{S}$ = spin ⇐ new kind intrinsic

& $\vec{J}$ = Total angular momentum in general

So

$[J_x, J_y] = i\hbar \vec{J}_z$

$[J_z, J_x] = i\hbar \vec{J}_y$

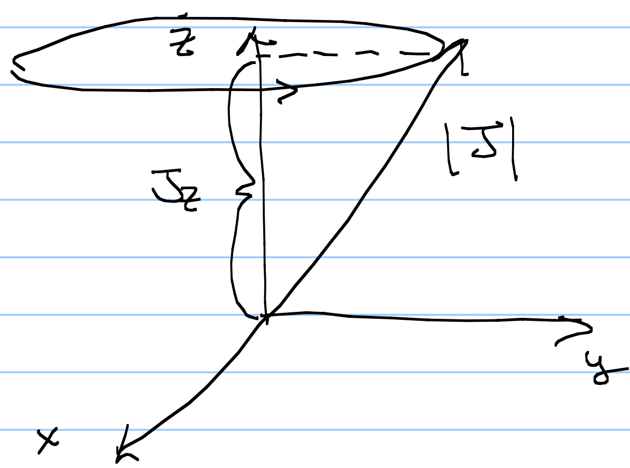
$[J_y, J_z] = i\hbar \vec{J}_x$

& $[\hat{J}^2, \vec{J}_x \; \vec{J}_y \; \vec{J}_z] = 0$

So.... Best you can hope to know ~~simultaneously~~ definitively about angular momentum in Q.M. w/ shared eigenfunct & soln to Schrö's ψ

is $J^2$ ∝ magnitude

$J_x, J_y, J_z$ = projection onto 1 of the axis




we usually by convention chose to look for max info ψ that is simultaneous ψ of $[J^2, J_z] = 0$

So, if we have angular momentum, the Best $\psi$ will

$$\hat{L}^2\psi = l_{TOT}^2\psi \quad \& \quad \hat{L}_z\psi = l_z\psi \quad \Big\} \text{ cause } [\hat{L}^2, \hat{L}_z] = 0$$

So the next ? is to find the simultaneous eigen function & eigen vectors of $\hat{L}^2$ & $\hat{L}_z$

To do that, you do it the same old way

1) Find $\hat{L}^2$ & $\hat{L}_z$

2) Then solve eigen value problems

OK: $\hat{L}_z = \underbrace{\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x}$ in cartesian coords

$= $ ex: 6.2 Scherrer

$= -i\hbar \dfrac{\partial}{\partial\phi}$ in spherical Coords!

So $\quad \hat{L}_z\psi = l_z\psi \quad$ since we know $l_z$ eigenvalue = project of angular momentum & angular momentum units = energy·sec... try

$$\hat{L}_z\psi = m_l\hbar\psi$$

$\psi = \psi(\phi)\psi(\theta)$ = separable eigenstate

or $\left(-i\hbar \frac{d\psi_\phi}{d\phi} = m_\ell \hbar \psi_\phi\right)\psi(\theta)$

or $\int \frac{d\psi_\phi}{\psi_0} = \int i\, m_\ell\, d\phi$

$$\psi(\phi) = e^{i m_\ell \phi} e^{\text{const}} = (\text{Norm}) e^{i m_\ell \phi}$$

Some See Later

$$\psi_\phi(\phi) = e^{i m_\ell \phi}$$

But... little complication

in spherical coordinate

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

So we need

$$e^{i m_\ell(\phi + 2\pi)} = e^{i m_\ell \phi}$$

or

$$\cancel{e^{i m_\ell \phi}}\, e^{i m_\ell 2\pi}\, \cancel{e^{-i m_\ell \phi}} = 1$$

$$e^{2\pi i m_\ell} = 1$$

$$\cos(2\pi m_\ell) + i \sin(2\pi m_\ell) = 1$$

So $m_\ell$ has to be $m_\ell = 0, \pm 1, \pm 2 \ldots$

So proj of $\vec{L}$ = Quantized!

$$\hat{L}^2_{r,\theta,\phi}\psi = \ell^2\psi$$

again, $L^2$ eigenvalue
so expect $\sim \hbar^2$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi = \hbar^2\underbrace{l(l+1)}_{\text{experience!}}\psi$$

recall also need

$$\hat{L}_z\psi = m_\ell\hbar\psi$$

Can show

$$\psi(\theta,\phi) = Y_\ell^m(\theta,\phi)$$

$$Y_\ell^m(\theta,\phi) = \varepsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\;\underbrace{e^{im\phi}}_{\text{already got!}}\;\underbrace{P_\ell^m(\cos\theta)}_{\text{associated Legendre Polynomials}}$$

$\varepsilon = (-1)^m$ for $m \geq 0$
$= 1$ for $m \leq 0$

restricts $m$'s

A.L.P $- \; P_\ell^m(x) = (1-x^2)^{\frac{|m|}{2}}\left(\frac{d}{dx}\right)^{|m|}\underbrace{P_\ell(x)}_{\text{Legendre Polynomials}}$

Legendre Polynomials

$P_0(x) = 1$

$P_1(x) = x$

$P_2(x) = \frac{1}{2}(3x^2-1)$

$P_3(x) = \frac{1}{2}(5x^3-3x)$

so

$P_0^0(\cos\theta) = 0$

$P_1^1(\cos\theta) = \sin\theta \quad P_1^0(\cos\theta) = \cos\theta$

$P_2^2 = 3\sin^2\theta, \; P_2^1 = 3\sin\theta\cos\theta$

$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$