H-atom of course...

$$\hat{H}\psi_{r,\theta,\phi} = E\,\psi_{r\theta\phi}$$

$$\left(\frac{\hat{p}^2}{2m} + V(r,\theta,\phi)\right)\psi_{r\theta\phi} = E\,\psi_{r\theta\phi}$$

IF $V(r,\theta,\phi) = V(r)$ only

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

just went on
Angular momentum side track

why?

because
$\hat{L}^2$ in spherical coordinates is...

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

Fits Right into

$\hat{H}\psi = E\psi$

For H-atom!

& seperates out the "θ,ϕ" part of $\psi_{r,\theta,\phi}$

& Found — This is recap!

$[\hat{L}^2, L_z] = 0$ so

$$\hat{L}^2\psi_{\theta,\phi} = (\text{mag } L^2)\,\psi_{\theta,\phi} = \hbar^2(l(l+1))\,\psi_{\theta,\phi}$$

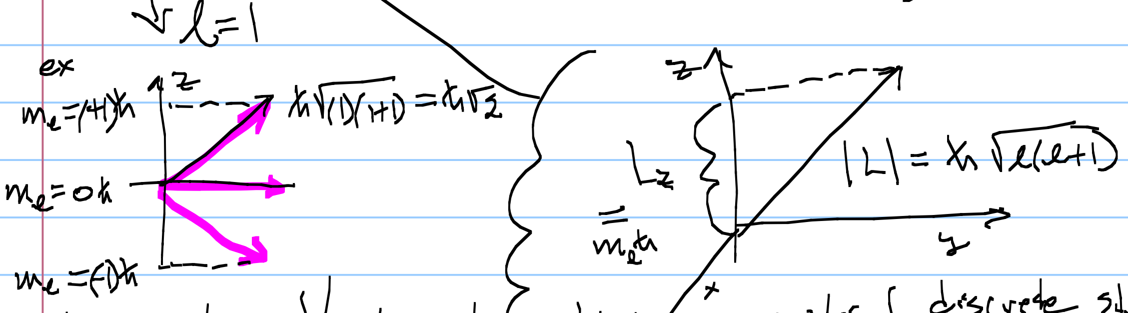
$$\hat{L}_z\psi_{\theta\phi} = \left(\begin{matrix}\text{proj of}\\ L \text{ on } z\end{matrix}\right)\psi_{\theta\phi} = \hbar m_l\,\psi_{\theta,\phi}$$

where $\psi_{\theta,\phi} = Y_l^m(\theta,\phi)$ = spherical Harmonics

& For give l = Integer

$+l \le m_l \le l$ are only possible values of m_l for give l

which we Recognize as



All Quantized! ie not continuous values / discrete steps in $\hbar$ units

So this is amazing

$$\hat{H}_{r,\theta,\phi}\,\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

$$\left[\frac{p^2}{2m} + \underbrace{V(r)}\right]\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

special case $V = S(r)$ only

(not so restrictive, H-atom $V \propto \frac{1}{r}$)

Then

side track

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

why not multiply by $R(r)$ ... variables all separated!

$$\hat{L}^2 R(r)\,Y_\ell^m(\theta,\phi) = \hbar^2(\ell(\ell+1))\,R(r)\,Y_\ell^m(\theta,\phi)$$

or

$$\left.\hat{L}^2\psi_{r,\theta,\phi} = \hbar^2(\ell(\ell+1))\,\psi_{r,\theta,\phi}\right\}$$ cool!! we've got our solns ψ

or

Follow 1-2-3

①

$$-\hbar^2\Bigl[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta)\frac{\partial}{\partial\theta}\Bigr] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Bigr]\psi_{r,\theta,\phi} = \hbar^2(\ell(\ell+1))\,\psi_{r,\theta,\phi}$$

③

recall now ② full problem $\hat{H}\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$

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

to get ⇘

$$\underset{\text{atom}}{\hat{H}_{r,\theta,\phi}}\,\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2(l(l+1))}{2mr^2}\right]\psi_{r,\theta,\phi} + V(r)\,\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

But that's Huge Cause
we've separated out θ & ϕ
in Y_l^m

$$\psi_{r,\theta,\phi} = R(r)\,Y_l^m(\theta,\phi)$$

& we know for given
l = integer
$0, 1, 2, 3 \ldots$
that
$+l \le m_l \le l$
by 1 (integer)
are only
solns.

Therefore is

$$\left[(r\ \text{stuff}) + \frac{\hbar(l(l+1)}{2mr^2} + V(r)\right]R(r)\,Y_l^m = E\,R(r)\,Y_l^m$$

& divide by Y_l^m $(=\psi(\theta)\psi(\phi))$
which we
know already

we get

$$\left[r\ \text{stuff} + \frac{\hbar(l(l+1))}{2mr^2} + V(r)\right]R(r) = E\,R(r)$$

Just on r - diffy - Q!

So $\hat{H}_{\text{Hatom}}\psi_{r,\theta,\phi} = E\psi_{r,\theta,\phi}$

$$\psi = R(r)\,\psi(\theta)\,\psi(\phi) = R(r)\underbrace{Y_\ell^m(\theta,\phi)}_{\text{got it! all packaged in angular momentum story!}}$$

$\Big\}$ left with

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} + V(r)\right]R(r) = E\,R(r)$$

HUGE..... why?

1) **EVERY** Horrible $\hat{H}_{r,\theta,\phi}\psi_{r,\theta,\phi} = E\psi_{r,\phi,\theta}$

where $V(r,\theta,\phi) = V(r)$ only

AUTOMATICALLY Has the same Soln

$$\psi_{r,\theta,\phi} = R(r)\underbrace{Y_\ell^m(\theta,\phi)}_{\text{Spherical Harmonics}}$$

This is why they are so important!

ALL V(r) problem HAVE EXACTLY The Same angular dependence!

2.) The Energy doesn't Depend @ all on the angular dependence ($V(r)$, Y_ℓ^m)

3.) The entire energy part of problem is reduced to a

one dimensional problem in r = radial coordinate only!
where
we can always get a quick handle on what its going on if we recognize...

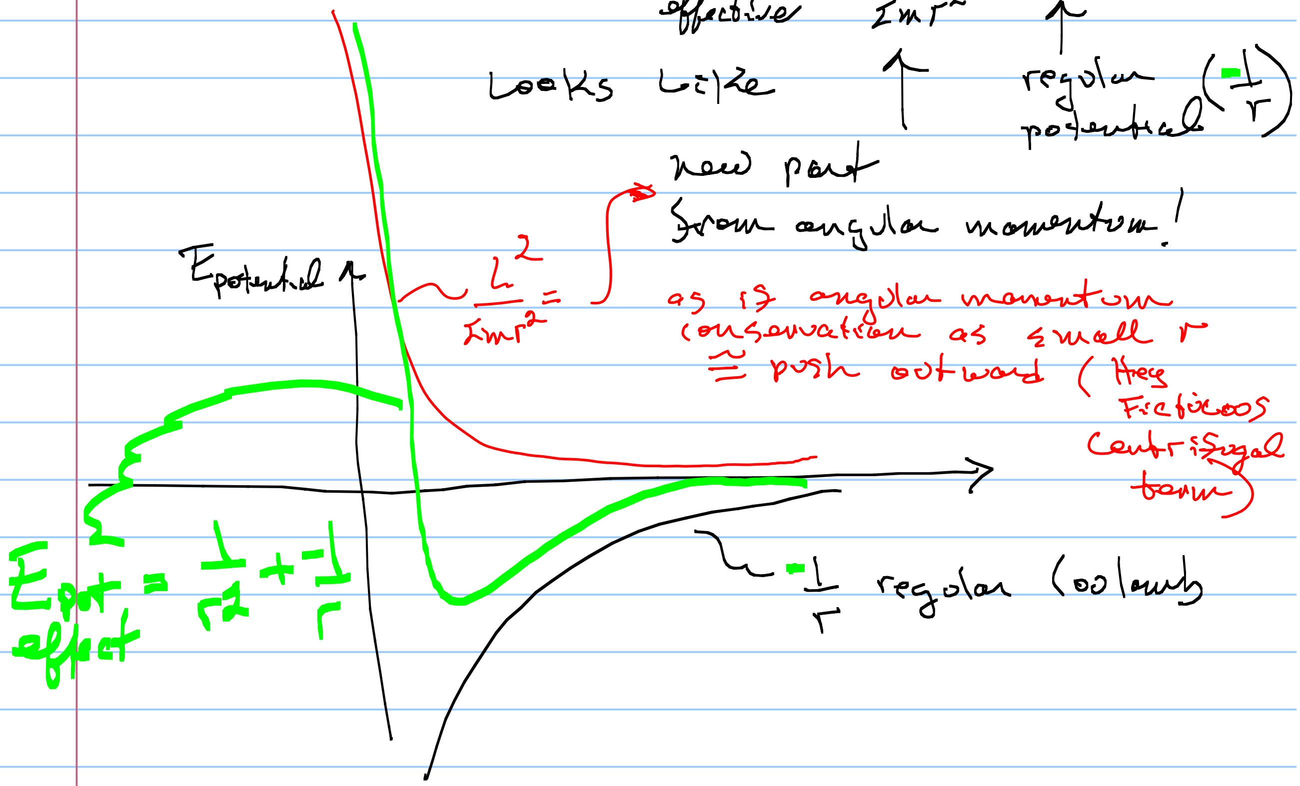
all V(r) problems ($\hat{H}\psi = E\psi$) reduce to new 1-D problem in R that looks like USING TRICK

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]}_{\text{This Looks Like}} R(r) = E\,R(r)$$

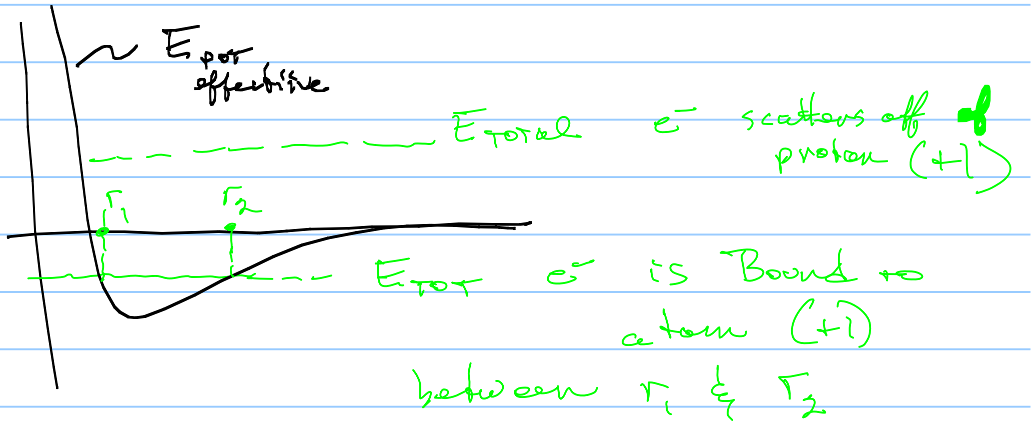
$$\left[E_K\left(\frac{p^2}{2m}\right) + E_{\substack{\text{potential}\\ \text{Effective}}}\right] R(r) = E\,R(r)$$

so $E_{\substack{\text{pot}\\ \text{effective}}} = \frac{|L|^2}{2mr^2} + V(r)$

Looks Like $\uparrow$ new part from angular momentum! $\uparrow$ regular potential $\left(-\frac{1}{r}\right)$



where can get an idea of what R(r) looks like



So BACK to Full Soln!

$$\hat{H}_{atom}\,\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

is $V = V(r)$ only

Then $\psi_{r,\theta,\phi} = R(r)\,Y_\ell^m(\theta,\phi)$

$$\Psi_{tot} = e^{-\frac{iEt}{\hbar}}\,R(r)\,Y_\ell^m(\theta,\phi)$$

where $\hat{L}^2\,\Psi = \hbar^2\,\ell(\ell+1)\,\Psi$

& $L_z\,\Psi = \hbar m_\ell\,\Psi$

Because all solns are from sep of variables

recognizing ℓ & m_ℓ fixed by

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

& proj on z-axis $= m_\ell\hbar$

$\ell \le m_\ell \le -\ell$

& all that is left to do is solve the one 1-D radial part

$$\left[-\frac{\hbar^2}{2m}\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}} + \frac{\hbar^2\,\ell(\ell+1)}{2mr^2} + V(r)\right]R(r) = E\,R(r)$$

Still pretty messy, so try some tricks

Not obvious trick!

$$\boxed{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)} = \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial r^2} = \boxed{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r}}$$

So

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2(rR(r))}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}R(r) + V(r)R(r)\right] = E\,R(r)$$

Now another NOT obvious step.
multiply everything by r

$$-\frac{\hbar^2}{2m}\frac{\partial^2\boxed{(rR(r))}}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\boxed{(rR(r))} + V(r)\boxed{(rR(r))} = E\boxed{(rR(r))}$$

which suggest substitution

$$\boxed{u(r) = rR(r)}$$

So ultimately solve $u(r)$ then remember that $R(r) =$ what we want $= \frac{u(r)}{r}$

* So keep in mind B.C.'s since $\psi(r\to\infty)=0$
$u \to 0$ as $r\to\infty$
& since $\psi \propto \frac{u}{r}$
$u(r=0)$ must $=0$ to keep ψ finite $\Rightarrow$ @ $r=0$

BIG

So you have

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}u + V(r)u = Eu$$

Reminder.... our $\hat{H}_{r\theta\phi}\psi_{r\theta\phi} = E\psi$

has reduced down to

$$\psi_{r,\theta,\phi} = R(r)Y_\ell^m(\theta,\phi) = \frac{u(r)}{r}Y_\ell^m(\theta,\phi)$$

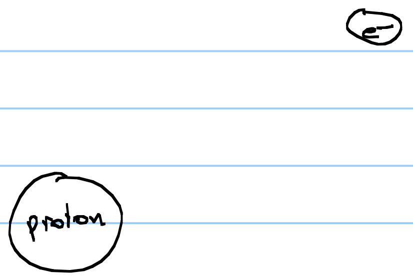
So must now solve $u(r)$ BUT...

we have one more COMPLICATION!

In classical mechanics we learn 2 masses attracting each other (gravity or E&M)

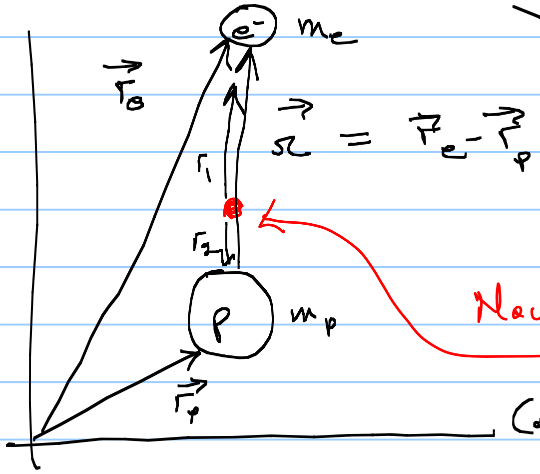
the two mass really orbit their center of mass!

So



now we are really only interested in solving the Electronic Problem (ie what the e⁻'s are doing About the proton!)

So need to look a bit closer.....



$\vec{\Omega} = \vec{r}_e - \vec{r}_p$

Now let chose origin = C of M

so can write

$$E_{TOT} = \frac{1}{2}m\left(\frac{d\vec{r}_1}{dt}\right)^2 + \frac{1}{2}m_2\left(\frac{d\vec{r}_2}{dt}\right)^2 + V(r)$$

C of M is defined as

$$m_1 r_1 + m_2 r_2 = 0$$

using $\vec{\Omega} = \vec{r}_1 - \vec{r}_2$

get

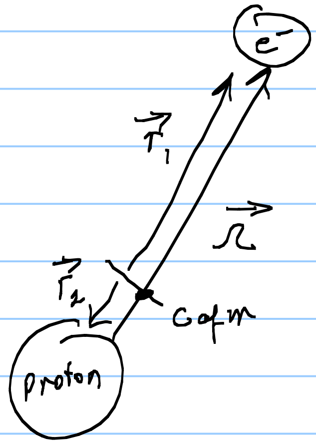
$$\vec{r}_1 = \frac{m_2}{m_1+m_2}\vec{\Omega}$$

$$\vec{r}_2 = \frac{-m_1}{m_1+m_2}\vec{\Omega}$$

plug these into E_{TOT} & get

$$E_{TOT} = \frac{1}{2}\mu\left(\frac{d\vec{\Omega}}{dt}\right)^2 + V(r)$$

were $\mu = \frac{m_1 m_2}{m_1+m_2}$ = Reduced Mass!



$$\vec{r}_e = \vec{r}_1 = \frac{m_2}{m_1+m_2}\vec{\mathcal{R}} = \frac{m_{proton}}{m_e+m_p}\mathcal{R} \cong \frac{m_p}{m_p}\mathcal{R} \cong \mathcal{R}$$

&

$$\vec{r}_p = \vec{r}_2 = -\frac{m_1}{m_1+m_2}\vec{\mathcal{R}} = -\frac{m_e}{m_p+m_e}\vec{\mathcal{R}} \cong \frac{m_e}{m_p}\vec{\mathcal{R}} \cong 0$$

where $m_p \cong 1836\, m_e$

So, all of this to say that

C of M of Ⓟ + Ⓔ is $\cong$ ON the heavier proton (no kidding)

& $E_T = \frac{1}{2}\mu\left(\frac{d\vec{\mathcal{R}}}{dt}\right)^2 + V(\vec{r})$

So Idea is $\hat{H}$ instead of $\frac{p^2}{2m} + V(r)$

should be

$$\frac{p^2}{2\mu} + V(r)$$

reduced mass $= \frac{m_e m_p}{m_e + m_p} = \frac{(m_e)(1836\, m_e)}{(m_e + 1836\, m_e)}$

$$\boxed{\mu = \frac{1836}{1+1836} m_e = 0.9995\, m_e}$$

So use reduced mass instead of m.

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 u}{\partial r^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}u + V(r)\,u = E\,u$$

Reminder.... our $\hat{H}_{r\theta\phi}\psi_{r\theta\phi} = E\psi$

has reduced down to

$$\psi_{r,\theta,\phi} = R(r)\,Y_\ell^m(\theta,\phi) = \frac{u(r)}{r}\,Y_\ell^m(\theta,\phi)$$

So must now solve $u(r)$

Finally

Now not easy...

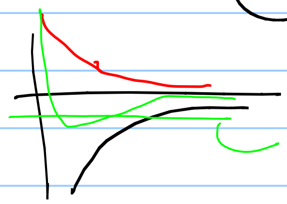
$$V(r) = \text{Coulomb} = \ominus\frac{1}{4\pi\varepsilon_0}\frac{|q_1||q_2|}{r} = \frac{-e^2}{4\pi\varepsilon_0 r}$$

attractive

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \frac{\hbar^2\ell(\ell+1)u}{2\mu r^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}u = Eu$$

$$\frac{d^2u}{dr^2} + \frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}\frac{u}{r} - \frac{\ell(\ell+1)}{r^2} = \frac{-2\mu}{\hbar}E\,u$$

now since $\boxed{E_\psi}$ is always $(-)$



only way to have bound states

is to have $E_{TOT} = \ominus$

so

so

$$\frac{d^2u}{dr^2} + \frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}\frac{u}{r} - \frac{\ell(\ell+1)}{r^2} = \frac{2\mu}{\hbar^2}\varepsilon u$$

where $\varepsilon = +$

& $E_T = -\varepsilon$

OK... Finally... solve this

Tough.... try guesses & try

<u>building</u> good soln.

Start at asymptotic Limit.

as $r \to \infty$

$$\frac{d^2u}{dr^2} + \sim 0 + \sim 0 = \frac{2\mu}{\hbar^2}\varepsilon u$$

$$\underbrace{\frac{d^2u}{dr^2} = \frac{2\mu}{\hbar^2}\varepsilon u}$$

NO problem!

$$\underbrace{u(r) = e^{-\left(\frac{\sqrt{2\mu\varepsilon}}{\hbar}\right)r}}$$

of course only part of soln.

But it is suggestive

so <u>guess</u>

$$u(r) = \underbrace{v(r)}\, e^{-\left(\frac{\sqrt{2\mu\varepsilon}}{\hbar}\right)r} = \text{Full soln}$$

Find

this by subbing into

oK ... after a while you get

$$\frac{d^2v}{dr^2} - \frac{2\sqrt{2\mu\varepsilon}}{\hbar}\frac{dv}{dr} + \frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}\frac{v}{r} - \frac{l(l+1)v}{r^2} = 0$$

not much easier But try again

why not try

$$v(r) = \sum_{p=0}^{\infty} A_p r^p$$

recall $u(r) = v(r)e^{-(\;)r}$

& $\psi = \frac{u(r)}{r}$

need $u(r=0)$

so $\psi = \frac{u(r=0)}{r=0}$ = finite

so

$A_{p=0}$ must be $= 0$

otherwise $u(r) = \underset{\substack{\uparrow \\ \text{non } 0}}{A_0} + \cdots$

So

$$V(r) = \sum_{p=1}^{\infty} A_p r^p$$

take this & sub into

See Scherrer

But - - -

For this soln to work,
you can show several conditions
must be true:

1.) $p \geq l+1$

2.) in order for the series $\sum_{p=1}^{\infty} A_p r^p$
to TERMINATE @
$p=n$

$$\frac{2n\sqrt{2\mu\mathcal{E}}}{\hbar} - \frac{2\mu e^2}{\hbar^2 4\pi\varepsilon_0} = 0$$

or $$E = -\mathcal{E} = \frac{-\mu e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2}$$

$$\boxed{E = \frac{-13.6eV}{n^2}}$$

Wow!

E_{TOT} only $f(n)$

Not l or m of Y_l^m

But for each n; $E_n = \frac{-13.6eV}{n^2}$

can only have
$n \geq l+1$
or $n-1 \geq l$

so very n has
$n-1 \leq l \leq 0$
& for each l
$l \leq m \leq -l$

So what? We've solved Schrö equation for H-atom!

$$\underset{\text{H-atom}}{\hat{H}_{r,\theta,\phi}} \; \underset{\text{H-atom}}{\psi_{r,\theta,\phi}} = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2}u + V(r)u = Eu$$

Reminder.... our $\hat{H}_{r\theta\phi}\psi_{r\theta\phi} = E\psi$

was reduced down to

$$\psi_{r,\theta,\phi} = R(r)Y_l^m(\theta,\phi) = \frac{u(r)}{r}Y_l^m(\theta,\phi)$$

So must now solve $\boxed{u(r)}$

Where the polynomial soln to

$$\boxed{u(r)} = V(r)e^{(\ )r} = \left(\sum_{p=1}^{\infty} A_p r^p\right)e^{-\frac{\sqrt{2\mu E}}{\hbar}r}$$

You Get... The entire deal ..

$$\Psi_{r,\theta,\varphi} = R(r)\, Y_\ell^m(\theta,\varphi) = \frac{u(r)}{r}\, Y_\ell^m(\theta,\varphi) = \left(\sum_{p=1}^{\infty} A_p r^p e^{-\frac{\sqrt{2\mu E}}{\hbar} r}\right) Y_\ell^n(\theta,\varphi)$$

Becomes ----

$$\Psi_{r,\theta,\varphi} = \Psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-1-\ell)!}{2n[(n+\ell)!]^3}}\; e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na}\right) Y_\ell^m(\theta,\varphi)$$

* where $a \equiv \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.529\times 10^{-10}$ m = Bohr radius

& $L^p_{q-p}(x) = (-1)^p\left(\frac{d}{dx}\right)^p L_q(x)$ & $L_q(x) = e^x\left(\frac{d}{dx}\right)^q\left(e^{-x}x^q\right)$

associated Laguerre Poly & Laguerre Poly

Actually, this is Normalized too!

But we make it all look nicer: $\Psi_{r,\theta,\varphi} = \Psi_{n\ell m} = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$

where: from conditions on polynomial

got $E_n = \frac{-13.6\,eV}{n^2}$; Principle Quantum # = Shell

& $n-1 \geq \ell$

so a give n has

Energy $= \frac{-13.6\,eV}{n^2}$ w/ degenerate ℓ's from $n-1 \leq \ell \leq 0$ } Angular momenta states for given n

Projections of angular momentum { w/ m_ℓ's for each ℓ

$+\ell \leq m_\ell \leq \ell$

We are essentially done!

$$\underset{\text{H-atom}}{H_{r,\theta,\phi}}\,\psi_{r,\theta,\phi} = E\,\psi_{r,\theta,\phi}$$

$$\psi_{r,\theta,\phi} = \psi_{nlm} = \underbrace{|nlm\rangle}_{\text{abstract Ket...}} = \underbrace{R_{nl}(r)}_{\Uparrow} Y_l^m(\theta,\phi)$$

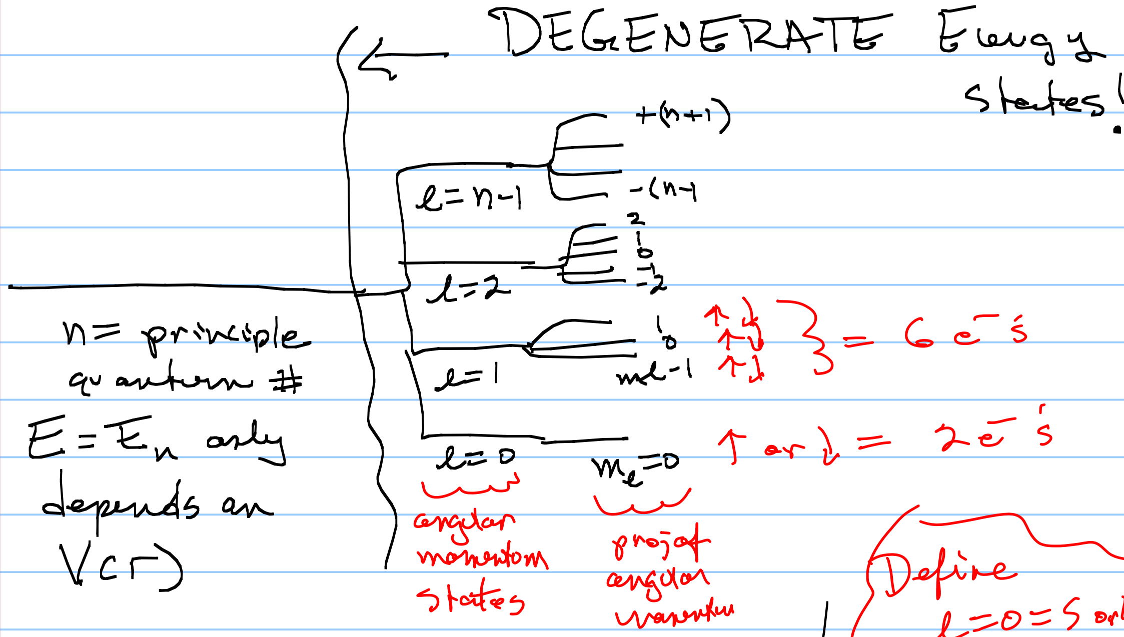
abstract Ket... Note carries all the info we need

completely depends on V(r)

same for any V=S(r) only

$$\text{where } E = E_{\textcircled{n}} = \frac{-13.6\text{eV}}{n^2}$$

only



n= principle quantum #

E=E_n only depends on V(r)

We've built the periodic Table!

Define
l=0=S orbital
l=1 = p orbital
l=2= D orbital
l=3= F orbital

lets see....

n=1 :
Shell

$$\underset{\underset{n}{\uparrow}}{1}\,\underset{\underset{l=0}{\uparrow}}{s}\;\overset{1e^-}{①}$$

n=1 , fixes l's: $(n-1)$ to 0 or $l=0$

fixes m_l's $\quad +l \le m_l \le -l$

$0 \le m_l \le 0 \quad m_l = 0$

So $\psi_{nlm} = R_{n=1,l=0}(r)\, Y_{l=0}^{m=0}$ is only state

& is $\psi_{TOT} = (R_{10} Y_0^0)\begin{pmatrix}|\uparrow\rangle \\ \text{or} \\ |\downarrow\rangle\end{pmatrix}$ = fit $2e^-$'s

n=1 fit 2 e^-'s

n=2: n=2, l's = $\underset{s}{0}$, $\underset{p}{1}$:

$$m_l \quad \underset{(2e's)}{0}\;,\;\underbrace{-1,0,-1}_{6\,e^-s} \Big\}\text{ all with } \begin{matrix}|\uparrow\rangle \\ \text{or} \\ |\downarrow\rangle\end{matrix}$$

n=2 shell $\quad 2s^2\, 2p^6$

In general:

	n=1	n=2		n=3		
	$l=0$	$l=0$	$l=1$	$l=0$	$l=1$	$l=2$
	$m_l=0$	0	-1 0 -1	0	-1 0 -1	-2 -1 0 1 2

$$1 + (1+3) + (1+3+5) + \cdots = n^2$$

So For $E_n = \frac{-13.6\ eV}{n^2}$

There are $1 + (1+3) + (1+3+5) + \cdots = n^2$

n^2

degenerate states!

each Sits $2\ e^-$'s

So $n=1$ shell holds $(n^2)(2) = 2e^-$

$n=2$ shell holds $(2^2)(2) = 8e^-$'s

$n=3$ " " $(9)(2) = 16e^-$'s

& so on!

Note ultimately

$$\psi_{n\ell m} = \psi_{r,\theta,\phi} \Longrightarrow \Psi(t,r,\theta,\phi)$$

$\{$ if include spin $|\uparrow\rangle$ or $|\downarrow\rangle$ $\}$ = linearly indep of t, r, θ, ϕ

so can multiply "separated soln"

Then

$$\boxed{\Psi_{\substack{TOT \\ w/spin}} = e^{-i\frac{E_n t}{\hbar}} R_{n\ell}(r)\, Y_\ell^m(\theta,\phi) \begin{pmatrix} |\uparrow\rangle \\ \text{or} \\ |\downarrow\rangle \end{pmatrix}}$$

↳ recall, this is a stationary state!

$$\hat{H}\psi_{n\ell m} = E\psi_{n\ell m}$$

$$\hat{H}|n\ell m\rangle = E_n|n\ell m\rangle$$

$$E_n = \frac{-13.6\,eV}{n^2}$$

$$\hat{L}_2|n\ell m\rangle = \hbar^2 \ell(\ell+1)|n\ell m\rangle$$

$$\hat{L}_z|n\ell m\rangle = m\hbar|n\ell m\rangle$$

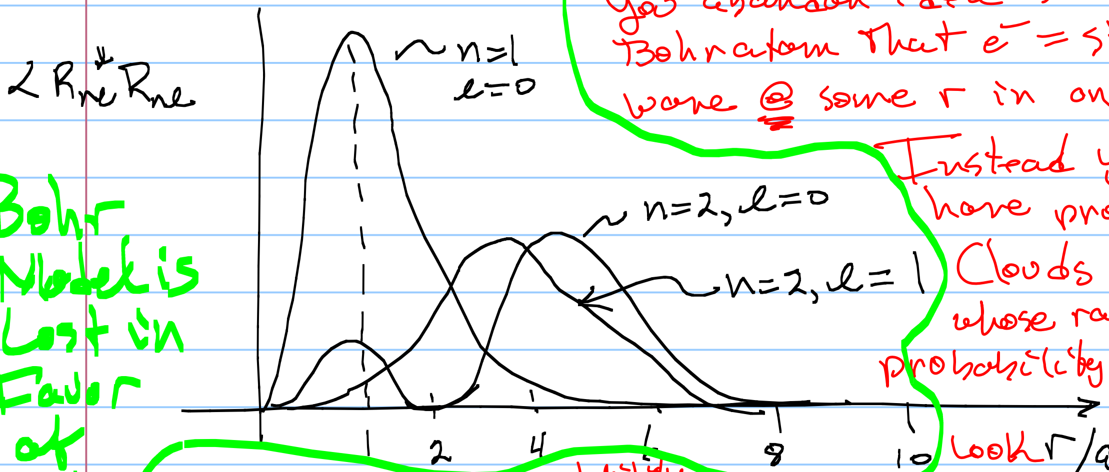
So what do these look like?

$$\Psi_{nlm} = |nlm\rangle = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

Now $\Psi^*_{nlm}\Psi_{nlm} = R^*_{nl}R_{nl}\, Y_l^{m*}\, Y_l^m = \dfrac{\text{prob}}{\text{volume}}$

$$\Psi^*_{nlm}\Psi_{nlm}\, d\text{Vol} = R^*_{nl}R_{nl}\, Y_l^{m*}\, Y_l^m\, r^2\, dr\, \sin\theta\, d\theta$$

If we look @ the prob density of different parts



BUT This is HUGE!
you abandon idea from Bohr atom that $e^- =$ standing wave @ some r in an orbit.

Instead you have probability Clouds whose radial probability density look like

Bohr Model is Lost in Favor of Full Q.M. Model.

So

$R_{10} =$  = probability Cloud max about r_0 that is nonzero for $r \cong$ nucleus so e^- spends time in the nucleus!

& ask, for example what is $\langle r\rangle$ for ground state H-atom

$$H\,(1s^1) \Rightarrow \Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\& \quad \langle r\rangle = \int_0^\infty \underset{\theta}{\int_0^\pi} \underset{\phi}{\int_0^{2\pi}} \Psi^*_{100}\, r\, \Psi_{100}\, r^2\, dr\, \sin\theta\, d\theta\, d\phi$$

$$= \int_0^\infty \left(r^3 dr \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0}\right) \underbrace{\int_0^\pi \sin\theta\, d\theta\, d\phi}_{4\pi}$$

$=$

$$\langle r \rangle = \frac{4}{a_0^3} \int_{r=0}^{\infty} e^{-\frac{2r}{a_0}} r^3 \, dr$$

$$= \frac{4}{a_0^3} \frac{6}{\left(\frac{2}{a_0}\right)^4} = \frac{24 a_0^4}{16 a_0^3} = \frac{3}{2} a_0$$

$\langle r \rangle \hat{=} 8 \times 10^{-11}$ m or about 10^{-10} m we can just consider the angular probability density

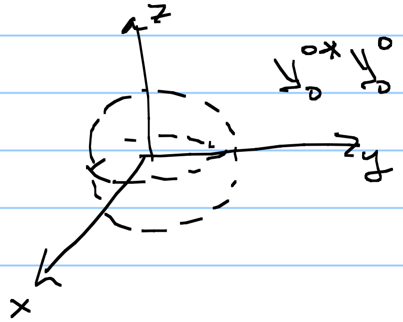
$Y_\ell^{m*}(\theta,\phi)\, Y_\ell^{m}(\theta,\phi)$

$*$ recall = SAME for all
$\hat{H}\psi = E\psi$
where $V = V(r)$ only!

$\psi_{n\ell m}$

$\psi_{100} \Rightarrow$

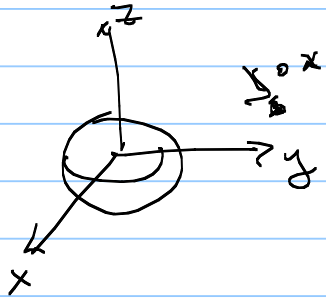
$E = \frac{-13.6eV}{1^2}$



$Y_0^{0*}\, Y_0^{0}$ = spherical symmetric
$n=1$ shell
$\ell=0$, s orbital
m_ℓ = proj of ℓ on z
= 0 for spherically symmetric

$\psi_{200} \Rightarrow$

$E = \frac{-13.6eV}{2^2}$



$Y_0^{0*}\, Y_0^{0}$

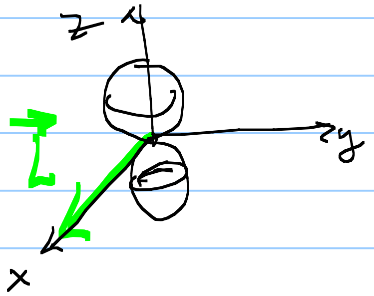
$n=2$
$\ell=0$
$m_\ell=0$

shape of orbital

projection of orbital angular momentum on z-axis!

ψ_{210}

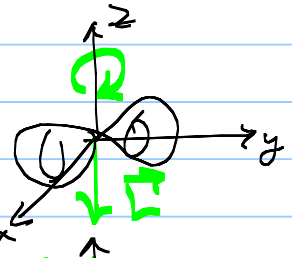
$E = \frac{-13.6eV}{2^2}$



$n=2, \ell=1, m_\ell=0$

ψ_{21-1}

$E = \frac{-13.6eV}{2^2}$

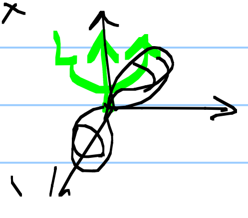


$n=2, \ell=1, m_\ell=-1$

$\hat{H}\psi_{n\ell m} = E\psi_{n\ell m}$
$E_n = -13.6eV/n^2$
$L^2\psi_{n\ell m} = \hbar^2\ell(\ell+1)Y$
$L_z\psi_{n\ell m} = m\hbar\, Y_\ell^m$

$n=2, \ell=1, m_\ell=+1$

ψ_{211} $E = \frac{-13.6eV}{2^2}$



$*$ Note: each orbital can contain $2e^-$'s $|\uparrow\rangle$ & $|\downarrow\rangle$

So in real sense.....

we've <u>derived</u> The periodic table

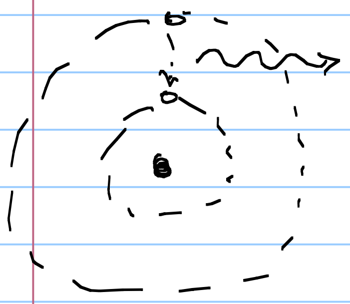
& Can PREDICT Out comes of

CHEMISTRY!

NoT Too Shabby!

Recall $\Psi = e^{-\frac{iE_n t}{\hbar}} |nlm\rangle |spin\rangle$ = stationary

To get



need $H_0 \psi = E \psi$

ψ = stationary, nothing changes

well this does get all of spectroscopy ΔE's right.... But not the rates

need $\hat{H}_{TOT} = \hat{H}_0 + \hat{H}'_{interaction}$

& Treat using Perturbation Theory

& get $\frac{\text{prob transitions}}{\text{time}} \propto |\langle n_f l_f m_f | H'_{in} | n_i l_i m_i \rangle|^2$

& Leads to correct Rates & LifeTimes!

Nothing Else CAN!