

Hydrogen atom

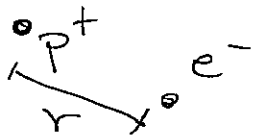
? how does this work in 3 dimensions

? how to apply to radial symmetry of atom

? real problem... no more "toy" potentials

- HW5 prob, redux
 - few HW6 probs
 - Midterms actually this week
 - grading (HW4, ex recd, etc) done by Wed
- PH253
S 2010
Start H atom
2 Mar

Prototype H atom



• electrical potential: $V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$

• from HW5, we know how to correct for proton mass, etc (can add later)

in 1D: $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi$

or $\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \left(\frac{e^2}{4\pi\epsilon_0 r} + E\right)\psi = 0$

3D?

we need to replace $\frac{\partial^2}{\partial x^2}$ with ~~$\frac{\partial^2}{\partial x^2}$~~

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \left(\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right)$$

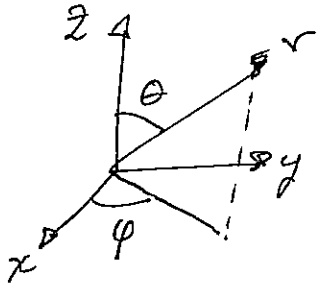
i.e., just take derivatives for each rectangular coordinate

$$\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0$$

problem: general solution is very tough.
analytic soln requires arcane math
So: well do it roughly.

Assume spher. symm solus for groundstate ⁽²⁾

- potential energy depends only on r (NOT θ or φ)



- if we worry only about spherically symmetric cases, where ψ depends on neither θ nor φ ... easier

- expect ground state is symm at least

- Now:
- 1) transform the problem \rightarrow radial coord. [like $(x,y) \rightarrow (r,\theta)$ in 2D]
 - 2) presume $\psi(r,\theta,\varphi) = f(\theta,\varphi) g(r) = (\text{const}) g(r)$

Note $\frac{\partial \psi}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial \psi}{\partial r}$

(and thus) $\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} \right)$

chain rule
madness

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} \left(\frac{\partial \psi}{\partial r} \right) \frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial r} \frac{\partial^2 r}{\partial x^2}$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi}{\partial r^2} \left(\frac{\partial r}{\partial x} \right)^2 + \frac{\partial \psi}{\partial r} \frac{\partial^2 r}{\partial x^2}}$$

- do the same for $y \hat{=} z$, and we have a word xform. (looks same)

$$\begin{aligned} \nabla^2 \psi &= \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \\ &= \frac{\partial^2 \psi}{\partial r^2} \left[\left(\frac{\partial r}{\partial x} \right)^2 + \left(\frac{\partial r}{\partial y} \right)^2 + \left(\frac{\partial r}{\partial z} \right)^2 \right] + \frac{\partial \psi}{\partial r} \left[\frac{\partial^2 r}{\partial x^2} + \frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial z^2} \right] \end{aligned}$$

Since $r = \sqrt{x^2 + y^2 + z^2}$, can eval:

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2 + y^2 + z^2}} \quad \text{and} \quad \frac{\partial^2 r}{\partial x^2} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} - \frac{x^2}{(x^2 + y^2 + z^2)^{3/2}}$$

$$\Rightarrow \nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} \left[\frac{x^2 + y^2 + z^2}{x^2 + y^2 + z^2} \right] + \frac{\partial \psi}{\partial r} \left[\frac{3}{\sqrt{x^2 + y^2 + z^2}} - \frac{x^2 + y^2 + z^2}{(x^2 + y^2 + z^2)^{3/2}} \right]$$

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} \quad \text{noting } r^2 = x^2 + y^2 + z^2$$

This gives us our Schrödinger eqn in radial coord

$$\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} \right) + \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0$$

Just a slightly diff 1D eqn!

$$\text{or, } \frac{d^2 y}{dx^2} + \frac{a}{x} \frac{dy}{dx} + by = 0$$

- The solution should be of the form e^{-cr}
need 1st, 2nd deriv ~ same

try it: $\psi = e^{-cr}$ (forget normalization for now)

$$\Rightarrow \frac{\partial \psi}{\partial r} = -c e^{-cr} = -c \psi$$

$$\frac{\partial^2 \psi}{\partial r^2} = c^2 e^{-cr} = c^2 \psi$$

$$\frac{\hbar^2}{2m} \left[c^2 e^{-cr} + \frac{2}{r} (-c e^{-cr}) \right] + \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] e^{-cr} = 0$$

to be valid for all r , $\frac{1}{r}$ and constant terms equate

$$\frac{1}{r} \text{ terms coeff: } \frac{e^2}{4\pi\epsilon_0} = \frac{\hbar c}{m} \quad \text{or} \quad \boxed{c = \frac{e^2 m}{4\pi\epsilon_0 \hbar^2}} = \frac{1}{a_0}$$

$$\text{const terms: } E = -\frac{\hbar^2 c^2}{2m} \Rightarrow \boxed{E = -\frac{m e^4}{2(4\pi\epsilon_0)^2 \hbar^2}}$$

So?

• bound state

• exactly ~~the~~ from Bohr model!

Same as $n=1$!

• even gives length scale a_0

Still, so what?

- probability of finding e^- at a distance r ?
- 1D: $|\psi|^2 dl$ per length

1) Normalize ψ : $|\psi|^2$ integrated over all volume = 1

$$1 = \int_{-\infty}^{\infty} |\psi|^2 dV$$

? radially symmetric (spherical)

\Rightarrow volume elements are shells

$$\psi = Ae^{-cr}$$

$$dV = 4\pi r^2 dr$$

$$1 = \int_0^{\infty} |\psi|^2 4\pi r^2 dr = 4\pi A^2 \int_0^{\infty} r^2 e^{-2cr} dr = 4\pi A^2 \int_0^{\infty} \frac{u^2}{4c^2} e^{-u} \frac{du}{2c}$$

(let $u = 2cr$
 $du = 2c dr$)

$$1 = \frac{\pi A^2}{2c^3} \int_0^{\infty} u^2 e^{-u} du$$

• by parts ... repeat

$$1 = \frac{\pi A^2}{2c^3} \left[\int_0^{\infty} u^2 e^{-u} du \right]$$

• $\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ (need this more)

~~probability about~~

~~scribbles~~

$$1 = \frac{\pi A^2}{2c^3} \cdot (2!) \Rightarrow A^2 = \frac{c^3}{\pi}$$

\Rightarrow

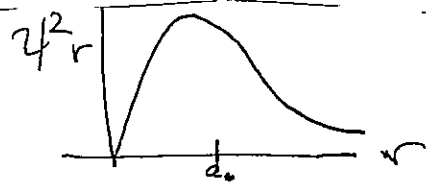
$$\psi = \sqrt{\frac{c^3}{\pi}} e^{-cr}$$

(2) with ψ normalized, $P(r)$ can be found in terms of Bohr radius

$$\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad \text{Hydrogen ground state ("1s")}$$

$$\Rightarrow \boxed{P(r) = |\psi|^2 4\pi r^2} \sim r^2 e^{-r} \quad (\text{turns out to be } \dots)$$

(3) How about e^- position?



(other sheet)

probability of finding e^- in $[r, r+dr]$ is

$$P(r) = |\psi|^2 dV = |\psi|^2 \cdot 4\pi r^2 = \frac{4r^2}{a_0^3} e^{-2r/a_0}$$

• most probable position is when $\frac{dP}{dr} = 0$

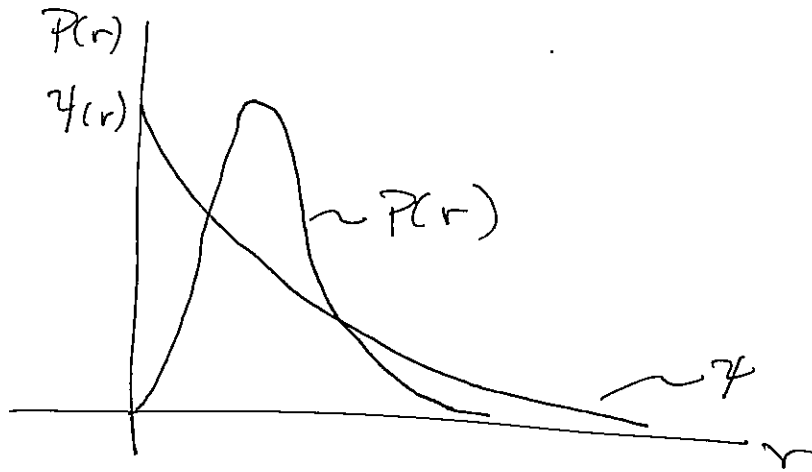
$$\text{i.e. } \frac{8r}{a_0^3} e^{-2r/a_0} - \frac{8r^2}{a_0^4} e^{-2r/a_0} = 0$$

$$\text{or } 1 - \frac{r}{a_0} = 0 \quad \text{i.e. } \boxed{r = a_0}$$

(note $P(r)$ is a "cloud" of probability, but we always measure just one electron!)

Bohr radius = most probable e^- position

$$P(r) = 4\pi r^2 \cdot \frac{1}{\pi a_0^3} e^{-r/a_0} = \frac{4r^2}{a_0^3} e^{-r/a_0}$$



is $P(r)_{\text{max}} = \langle r \rangle$?

NO! asym. dist!

mean \neq most likely (e.g. Max-Boltz)

mean = $\int x |\psi|^2 dx$ \sim average

most likely @ $\frac{\partial P}{\partial r} = 0$ \sim mode

Note: prob "cloud" tells us chance of

meas. e^- at R

Still measure $1e^-$ at def posn each time

Average (expectation) value of r ?

$$\langle r \rangle = \int_0^{\infty} \psi^* r \psi dV = \int_0^{\infty} 4\pi r^3 \cdot \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \int_0^{\infty} r^3 e^{-2r/a_0} dr \quad \left(\int_0^{\infty} e^{-ar} r^n dr = \frac{n!}{a^{n+1}} \text{ again} \right)$$

$$\langle r \rangle = \frac{4}{a_0^3} \cdot \frac{3!}{(2/a_0)^4} = \frac{3}{2} a_0 \quad (\neq \text{most probable...})$$

asymm. distr.

Similarly, $\langle r^2 \rangle = 3a_0^2$

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2} = \frac{\sqrt{3}}{2} a_0 \text{ uncertainty in radial posn}$$

or $r = \langle r \rangle \pm \Delta r = \frac{3}{2} a_0 \left(1 \pm \frac{1}{\sqrt{3}}\right)$

Probability e^- is within r_1 and r_2 ?

$$P(r_1 < r < r_2) = \int_{r_1}^{r_2} |\psi|^2 \cdot 4\pi r^2 dr \quad (\text{no analytic form})$$

... numerical

e.g. closer than Bohr radius?

$$P(r < a_0) = \int_0^{a_0} |\psi|^2 \cdot 4\pi r^2 dr \approx \frac{1}{3}$$

rotating classical system

$$E = \frac{1}{2}mv^2 + \frac{L^2}{2mr^2} + V(r)$$

}
 centrifugal
 repulsive force due to
 rotation

m_1
 \circ
 \circ

m_2
 \circ
 \circ
 \vec{p}

- general form for 2 particles

$$E = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(r_1, r_2)$$

presume potential $V(r_1, r_2)$ depends only on sep of particles
 (i.e. conservative)

$$V(r_1, r_2) = V(|r_1 - r_2|)$$

similarly, only rel. velocity matters

can generally transform this to an equiv single-body problem

$$E = \frac{P^2}{2\mu} + V(r)$$

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

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\vec{v} = \vec{v}_1 - \vec{v}_2$$

$$\vec{p} = m\vec{v}$$

transforming to radial coord, KE term changes

$$E = \frac{1}{2}\mu \left(\left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\theta}{dt}\right)^2 \right) + V(r) = \frac{1}{2}\mu \left[\underbrace{\left(\frac{dr}{dt}\right)^2}_{\text{linear}} + \underbrace{r^2 \omega^2}_{\text{angular}} \right] + V(r)$$

example: circular orbit. $\frac{dr}{dt} = 0$

$$E = \frac{1}{2} \mu [r^2 \omega^2] + V(r) = \frac{1}{2} I \omega^2 + V(r)$$

$$I = \mu r^2$$

example: along radial path: $\frac{d\theta}{dt} = 0$ (or spherically symm)

$$E = \frac{1}{2} \mu \left(\frac{dr}{dt}\right)^2 + V(r) = \frac{1}{2} \mu v^2 + V(r)$$

examine rotational term: $\frac{1}{2} \mu r^2 \omega^2 = \frac{1}{2} L \omega = \frac{1}{2} |(\vec{r} \times \vec{p})| \omega$

• due to angular momentum!

$$E = \frac{1}{2} \mu v_r^2 + \frac{1}{2} L \omega + V(r)$$

• can also write as

$$E = \frac{1}{2} \mu v_r^2 + \frac{L^2}{2 \mu r^2} + V(r)$$

just as in PH105: if there is rotation, we have

$$(Energy) = (translational) + (rotational) + (potential)$$

? quantum analogue? do not have it, °°
we assumed spherical symmetry

now back to our radial Schrödinger eqn:

③
revise

$$\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial r^2}}_A - \underbrace{\frac{\hbar^2}{mr} \frac{\partial \psi}{\partial r}}_? + \underbrace{V(r)\psi}_{\text{potential}} = \underbrace{E\psi}_{\text{total}}$$

$$p = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$p^2 = p^* p = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Kinetic (linear)

~~rotational kinetic~~
centrifugal term

• how to "translate" 2nd term?

• 1st is + 2nd Like using $p = \frac{\hbar}{i} \frac{\partial}{\partial r} \longleftrightarrow$ radial momentum

• if ~~like~~ L , $\frac{L^2}{2mr^2} \dots$ and $L = \vec{r} \times \vec{p}$

maybe our "translation" is done similarly

$$L = \vec{r} \times \vec{p} \longrightarrow (\vec{r} \times \vec{p}) \quad \left. \begin{array}{l} \text{turns out to} \\ \text{be correct.} \\ \text{(circle rot by } \theta \end{array} \right\}$$

(radial only)

but if $\psi = f(r)$

$$L\psi = \left(\vec{r} \times \frac{\hbar}{i} \frac{\partial}{\partial r} \hat{r} \right) = 0$$

since $\hat{r} \times \vec{r} = 0!$

• Sph Sym atom \neq sph sym state

• lowest sph sym state has no $L \dots$

~~at least~~ sph sym means rot invar
means $L=0$

• need to consider more compl shapes } e.g. excit of drum head

to construct a proper 3D Schrodinger, non-sph sym...

- need θ, ϕ dependence for excited states
- cannot have $\psi = f(r)$ only.

1st re-translate 3D eqn to spherical

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi$$

Cartesian: $\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$

Spherical: use coord xforms & grind through...

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

messy! apply to Schrodinger ... ~~convol~~

$$\frac{1}{r^2} \frac{\partial^2}{\partial r^2} (r^2 \psi) + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right\} = -\frac{2m}{\hbar^2} \left(E + \frac{ke^2}{r} \right) \psi$$

• Yuck. But, fully correct... no restr.

• can separate: $\psi(r, \theta, \phi) = f(r)g(\theta, \phi)$

• let's go back to spherically-symm solns 1st

i.e. ψ does not depend on θ or ϕ

in this case, $\psi = \psi(r)$ so $\frac{\partial \psi}{\partial \theta} = \frac{\partial \psi}{\partial \phi} = 0$

$$\Rightarrow \frac{1}{r} \frac{d^2}{dr^2}(r\psi) = -\frac{2m}{\hbar^2} \left(E + \frac{ke^2}{r} \right) \psi \quad \text{or} \quad \underline{\underline{\frac{d^2}{dr^2}(r\psi) = -\frac{2m}{\hbar} \left(E + \frac{ke^2}{r} \right) (r\psi)}}$$

$$(or) \frac{1}{r} \left[\frac{d}{dr} \left(r \frac{d\psi}{dr} + \psi \right) \right] = \frac{1}{r} \left[r \frac{d^2\psi}{dr^2} + \frac{d\psi}{dr} + \frac{d\psi}{dr} \right] = \frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr}$$

as we had previously, $\Rightarrow \psi_0 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$

let's look at more general solns now, but still sph. symm.

(1) get rid of constants. let

$$\boxed{r = \frac{\hbar^2}{kme^2} \rho = a_0 \rho} \quad \boxed{E = \left(\frac{me^4 k_e^2}{2\hbar^2} \right) \epsilon = \epsilon_0 \epsilon}$$

reduced dist reduced E

$$\Rightarrow \boxed{\frac{d^2(\rho\psi)}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho} \right) \rho\psi} \quad (\text{after multiplying all by } \rho)$$

basically : distance in units of $a_0 = 0.053 \text{ nm}$
energy in terms of $\epsilon_0 = -13.6 \text{ eV} = 1 \text{ Ry}$

we only see $\rho\psi$ here ... so let $f = \rho\psi$

$$\Rightarrow \frac{d^2 f}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho} \right) f$$

- again, $e^{-\rho} = e^{-r/a_0}$ will work for γ (or $f = \frac{a_0}{r} e^{-r/a_0} = \frac{e^{-\rho}}{\rho}$)
- more general soln? could still be something like

$$f(\rho) = e^{-\alpha\rho} g(\rho) \quad \boxed{\text{factor known soln out}}$$

i.e. $f = (\text{exponential})(\text{other fn of } \rho)$

if $g(\rho) = \frac{1}{\rho}$, back to an old soln. General $g(\rho)$?

$$\boxed{\text{plug this in}} \Rightarrow \boxed{\frac{d^2 g}{d\rho^2} - 2\alpha \frac{dg}{d\rho} + \left(\frac{2}{\rho} + \epsilon + \alpha^2\right)g = 0}$$

Since α is just a free constant, we can choose it (analogous to choosing your energy)

So pick $\alpha^2 = -\epsilon$ for convenience

$$\Rightarrow \boxed{\frac{d^2 g}{d\rho^2} - 2\alpha \frac{dg}{d\rho} + \frac{2}{\rho} g = 0}$$

So what? Can easily solve this with a power series

i.e. write $g(p) = \sum_{k=1}^{\infty} a_k p^k$ $a_k = \text{coeff of polynomial}$

"any function" can be written as an ∞ -degree poly...

thus $\frac{dg}{dp} = \sum_1^{\infty} a_k k p^{k-1}$

$\frac{d^2g}{dp^2} = \sum_1^{\infty} a_k k(k-1) p^{k-2}$

} plug in last eqn...

$$\sum_{k=1}^{\infty} k(k-1) a_k p^{k-2} - \sum_{k=1}^{\infty} 2\alpha k a_k p^{k-1} + \sum_{k=1}^{\infty} 2a_k p^{k-1} = 0$$

? keep going... it gets better. Combine sums

! in 1st term, sum could easily be shifted by $k \rightarrow k+1$
since series starts w/0

i.e. $\sum_{k=1}^{\infty} k(k-1) a_k p^{k-2} = \sum_{k=1}^{\infty} (k+1)k a_{k+1} p^{k-1}$ since 1st term is zero in original

$$\Rightarrow \sum_1^{\infty} [(k+1)k a_{k+1} - 2\alpha k a_k + 2a_k] p^{k-1} = 0$$

this can only work for all p if $[] = 0$!

$$\Rightarrow (k+1)k a_{k+1} - 2(\alpha k - 1) a_k = 0$$

$$\sigma, \quad a_{k+1} = \frac{2(\alpha k - 1)}{k(k+1)} a_k$$

◦ if we pick a_0 (choice! normalization fixes rest...) we get all other a_k and general soln!

$\psi_{\text{full}} = \sum_i \psi_k$ (sum of all solns) each term satisfies sep. linear eqn!

$$\psi_k = \frac{f_k(\rho)}{\rho} = \frac{e^{-\alpha \rho}}{\rho} g_k(\rho) \quad g_k(\rho) = \sum_i a_k \rho^k$$

◦ Still ... could be nicer. What is the meaning of k ?

◦ Let's insert some prior knowledge

recall $\epsilon = \frac{E}{E_0} = -\alpha^2$

but to agree w/ semi-classical Bohr result and expt, we need

$$\frac{E}{E_0} = \frac{-1}{n^2} \Rightarrow \alpha = \frac{1}{n} = -\alpha^2$$

or $\boxed{\alpha = \frac{1}{n}} \quad n \in \mathbb{N}_+ = \{1, 2, \dots\}$

thus $a_{k+1} = \frac{2(k/n - 1)}{k(k+1)} a_k$

Neat: $\boxed{a_{k>n} = 0} \Rightarrow$ finite poly

and n is again our energy level!
PLUS: POLY is finite!!

putting it all together: for any n we have a solution

$$\psi_n = \frac{f_n(\rho)}{\rho} = \frac{e^{-\rho/n}}{\rho} g_n(\rho)$$

$$g_n(\rho) = \sum_k a_k \rho^k \quad a_{k+1} = \frac{2(k/n - 1)}{k(k+1)} a_k$$

n = energy level ; k = sum of terms

Since we normalize anyway, we can pick a_1 !

so let $a_1 = 1$!

~~Then the 1st term of ψ is for $n=1$ (lowest state)~~

~~$$\psi = \frac{e^{-\rho}}{\rho} \sum_k \frac{2(k-1)}{k(k+1)} a_k \rho^k$$~~

then

$$\left\{ \begin{array}{l} a_1 = 1 \\ a_2 = \frac{1}{n} - 1 \\ a_3 = \frac{1}{3} \left(\frac{2}{n^2} - \frac{3}{n} + 1 \right) \\ \vdots \end{array} \right.$$

can readily show:

for a given n ,
all a_k for $k > n$

VANISH!

i.e., for $n=3$ only 3 terms!

so $g_n(\rho) = \rho + \rho^2 \left(\frac{1}{n} - 1 \right) + \frac{\rho^3}{3} \left(\frac{2}{n^2} - \frac{3}{n} + 1 \right) + \dots$

for the lowest state, $n=1 \Rightarrow a_2 = a_3 = 0 \Rightarrow g_1(\rho) = \rho$

$$\Rightarrow \psi_1 = e^{-\rho} = e^{-r/a_0}$$

✓

(10)

$$\text{for } n=2, \quad g_2(\rho) = \rho + \left(\frac{1}{2} - 1\right)\rho^2 = \rho - \frac{\rho^2}{2} = \rho\left(1 - \frac{\rho}{2}\right)$$

$$a_3 = a_4 = \phi$$

$$\Rightarrow \psi_2 = \frac{e^{-\rho/2}}{\rho} \cdot \rho\left(1 - \frac{\rho}{2}\right) = e^{-\rho/2} \left(1 - \frac{\rho}{2}\right)$$

$$\boxed{\psi_2 = e^{-r/2a_0} \left(1 - \frac{r}{2a_0}\right)}$$

~~$$\psi_3 = e^{-r/3a_0} \left[1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right]$$~~

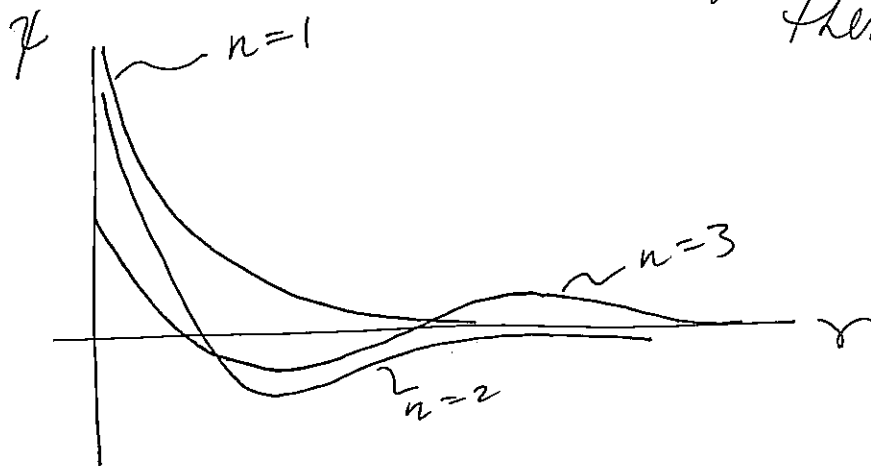
$$n=3, \quad g_3(\rho) = \rho + \rho^2\left(\frac{1}{3} - 1\right) + \frac{\rho^3}{3}\left(\frac{2}{9} - 1 + 1\right)$$

$$= \rho \left[1 - \frac{2\rho}{3} + \frac{2\rho^2}{27}\right]$$

$$\Rightarrow \boxed{\psi_3 = e^{-r/3a_0} \left[1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right]}$$

and so on!

general: $n-1$ oscillations
then rapidly to zero



What we've just done: derived all "s" states!

Spherically-symmetric solns for H atom

①

radial eqn #3
 $L, \psi(\theta, \phi)$
9 Mar 10
PH253

$$\frac{\partial^2}{\partial r^2}(r\psi) = -\frac{2m}{\hbar^2} \left(E + \frac{ke^2}{r} \right) (r\psi)$$

$$\text{let } \rho = \frac{r}{a_0} \quad \epsilon = \frac{E}{E_0}$$

$$\Rightarrow \frac{d^2(\rho\psi)}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho} \right) (\rho\psi)$$

$$\psi_n = \frac{a_0}{r} e^{-r/na_0} \sum_k a_k \left(\frac{r}{a_0} \right)^k \quad a_{k+1} = \frac{2(k/n - 1)}{k(k+1)} a_k$$

$$\psi_1 = e^{-r/a_0}$$

$$\psi_2 = e^{-r/2a_0} \left(1 - \frac{r}{2a_0} \right)$$

$$\psi_3 = e^{-r/3a_0} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right)$$

} unnormalized

$$P_n(r) = 4\pi r^2 |\psi_n|^2 \quad \text{prob. to find } e^- \text{ in } [r, r+dr]$$

• these spherically-symmetric states are those with zero angular momentum, i.e. "s" states

• what about the rest?

recall full scany form:

(2)

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

• There are no "cross terms" - the equation is sep.

$$\psi \rightarrow R(r) P(\theta) F(\phi)$$

\Rightarrow 3 "Schrod-like" eqns

• three quantum numbers appear as constants of separation

- if we can isolate variables, we can in principle integrate both sides ... making them = up to a const

- or, we can set both sides equal to a constant to be determined (x 3)

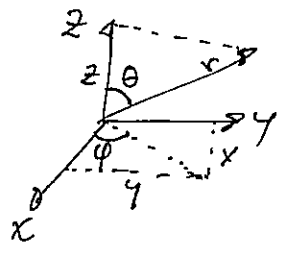
• Basically: separate Schrod. for r and 2 angles

(1) let $\psi = R(r) Y(\theta, \phi)$

$\frac{d^2}{dr^2} (rR) + \frac{2m}{\hbar^2} \left(E + \frac{ke^2}{r} \right) (rR) = (\text{const}) R$	$-\frac{\hbar^2}{Y} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial\phi^2} \right] = -C$ <p style="text-align: center;">sep, factor $\frac{1}{r^2}$</p>
--	--

$$\Psi(r, \theta, \varphi) = R(r)P(\theta)F(\varphi)$$

$$Y(\theta, \varphi) = P(\theta)F(\varphi)$$



$\varphi =$ in $x-y$ plane

$\theta =$ inclination from z

hard to solve still ... intuition!

- binding of $p^+ \text{ ; } e^-$ is a central force

$\Rightarrow E$ conserved	\rightarrow 1 quantum # (E)
$\Rightarrow L$ conserved	\rightarrow 2 quantum # ($ L , L_z$)

- energy already found from radial eqn \Rightarrow [quantum number n]

- Sep. of variables gives same radial eqn!

$E_n = -\frac{\alpha^2 mc^2}{2n^2} = \frac{-13.6 \text{ eV}}{n^2}$ } angular momentum doesn't change E (w/o relativity)

- other 2 variables (θ, φ) give 2 new quantum numbers!

By the way:

n	Spectroscopy ("shell")
1	K
2	L
3	M
4	N

Separation

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} (rR) + \frac{2m}{\hbar^2} \left(E + \frac{ke^2}{r} \right) R = \frac{K}{r^2} R$$
$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -KY$$

} $K = \text{const}$
} same for both!

Further separate: $Y = F(\theta)P(\phi)$ θ and ϕ part

$$\Rightarrow \frac{1}{F} \frac{\partial^2 F}{\partial \phi^2} = \text{const} \Rightarrow F(\phi) = Ae^{i m \phi}$$

we require $F(\phi) = F(\phi + 2\pi)$ same after 2π rot!

$$\Rightarrow F(\phi) = Ae^{i m \phi}$$

$m = \text{integer} - 2^{\text{nd}}$ quantum #

$$Y = Ae^{i m \phi} P(\phi)$$

note $\frac{\partial F}{\partial \phi} = i m F$...

- plugging this into Y eqn gives $K = l(l+1)$ } $l = \text{integer}$
 - for soln to exist ... constraint } $l > |m|$

$l = 3^{\text{rd}}$ quantum #!

- any state has 3 quantum #'s to describe $\{n, l, m\}$
like 3D box (body) - n_x, n_y, n_z

using this in radial equation:

$$\frac{1}{r^2} \frac{\partial^2}{\partial r^2} (rR) = -\frac{2m}{\hbar^2} \left\{ E + \frac{ke^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2} \right\} R$$

? new term in energy recall $\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} E_{tot} \psi$

implies $E_{tot} = \frac{1}{2}mv^2 + \frac{ke^2}{r} - \underbrace{\frac{l(l+1)\hbar^2}{2mr^2}}_?$

Classical orbiting system?

Analogy tells us what it is ...

~~total~~ $V(r) + \frac{1}{2}mv^2 = \text{const}$

• V can have radial \equiv angular part

$$v^2 = v_r^2 + r\omega^2 \quad \omega = \frac{d\theta}{dt}$$

• note $L = mr^2\omega$ or $r\omega = \frac{L}{mr}$ just from coord x form

$$\Rightarrow \frac{1}{2}mv_r^2 + V(r) + \frac{L^2}{2mr^2} = \text{const}$$

! new term is due to angular momentum! "Centrifugal"

- rotational KE, neglected before by assuming
- = spherically-symm solutions

Apparently, Quantum angular momentum is quantized by

$$L^2 = l(l+1)\hbar^2$$

(NOT $l^2\hbar^2$ as one might expect)

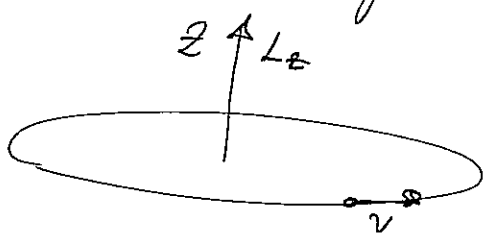
$l = \text{integer}, l < n$

Orbital quantum #

Why $l(l+1)$? uncertainty for one

- if we knew L perfectly, that fixes an axis

e.g. L_z known fixes z axis of rot



classical orbit

- in this case, orbit is in xy plane, so $\Delta z = 0$!

then $\Delta p_z \Delta z = 0$! NO

• uncertainty requires $\Delta p_z \Delta z \geq \hbar/2$

• we can't know ~~ALL~~ ^{ALL} components of L precisely

• we can know $L^2 = L_x^2 + L_y^2 + L_z^2$ precisely

$$L^2 = l(l+1)\hbar^2$$

meaning of l ? m ?

- L^2 is a precisely-knowable quantity
- L_x, L_y, L_z are not

$$L^2 = l(l+1)\hbar^2 \quad l = 0, 1, 2, \dots, (n-1)$$

for state n , there are n sub-states of different angular num.

n	$l=0$	1	2	3	states $\{n, l\}$
1	1s	-	-	-	1
2	2s	2p	-	-	2 states (1)
3	3s	3p	3d	-	3 for n=3
4	4s	4p	4d	4f	4

↑
new
bohn

"Shells"

- w/o relativity, n fixes energy
all states of same n have same E ("degenerate")
- angular momentum changes (l) w/in n -level
total energy does not for same n
- what about m ? \Rightarrow further multiplicity

one more quantum number m (from φ eqn)

$$F(\varphi) = A e^{im\varphi} \quad m = \text{integer}$$
$$|m| \leq l$$

- we can know L^2 precisely - magn of L
- we can also know one component w/o breaking uncertainty
 - arbitrarily choose z ... knowing L_z but NOT L_x or L_y
Maintains uncertainty in orientation of L
 - $\Delta L_z \Delta \varphi \approx \hbar$ $\Delta \varphi = \text{angle in } X-\varphi \text{ plane}$
can know L_z precisely, at expense of L_x, L_y

$$\Rightarrow \boxed{L_z = m \hbar} \quad \frac{m = -l, -l+1, \dots, l-1, l}{\text{from comb. } \theta, \varphi \text{ solns}}$$

2 observables for angular momentum

L^2 — magn — from l
 L_z — one component — from m

L_x, L_y uncertain

m = magnetic quantum number

- given $l \leq n-1$ there are $2l+1$ sub-states for a given value of l

$n \longrightarrow l$ substates $\longrightarrow m$ substates

	l	m		
"s"	0	0	\longrightarrow	one e^- (no spin)
"p"	1	-1, 0, +1	\longrightarrow	3 e^-
"d"	2	-2, -1, 0, +1, +2	\longrightarrow	5 e^-
"f"	3	-3, -2, -1, 0, +1, +2, +3	\longrightarrow	7 e^- / x 2 for spin...

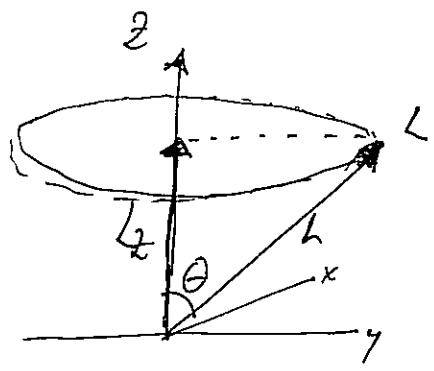
l and m specify angular momentum

\vec{L} "precesses" around \hat{z} at angle θ

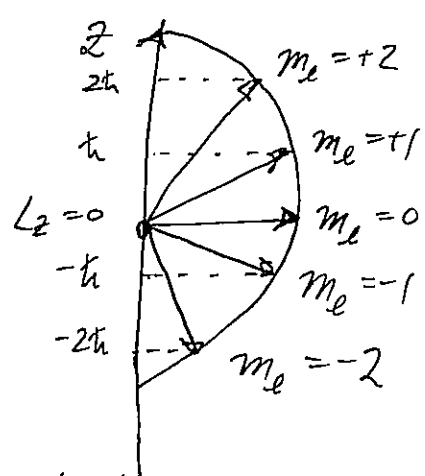
$$\cos\theta = \frac{L_z}{L} = \frac{L_z}{\sqrt{L^2}} = \frac{m}{\sqrt{l(l+1)}}$$

$\Rightarrow \theta$ has discrete values, as do L_z, L^2

(no actual precession/orbit: average value of measmt)



total $L \hat{=} L_z$
 $\Rightarrow L_x^2 + L_y^2$ fixed
 L_x, L_y are NOT



$|L| = \text{length} = \text{const}$

values $\hat{=} \text{quant of } L$
 for ~~orbital~~
 $l=2$

$\Rightarrow L = \sqrt{6} h$ total
 $L_z = m h$

Summary

- sep of variables $\rightarrow n, l, m$

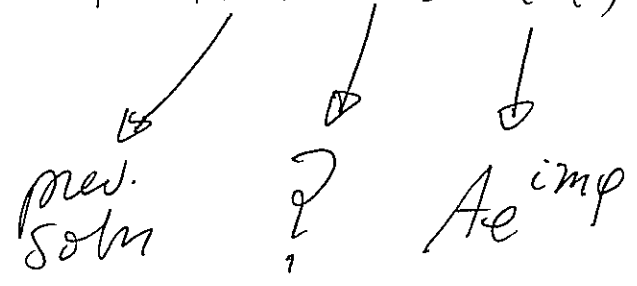
$n =$ principle quant # ["level"]

$l =$ orbital quantum # [int angular momentum], spdf

$m =$ magnetic quantum # [z component of L]

So, what do the orbits look like?

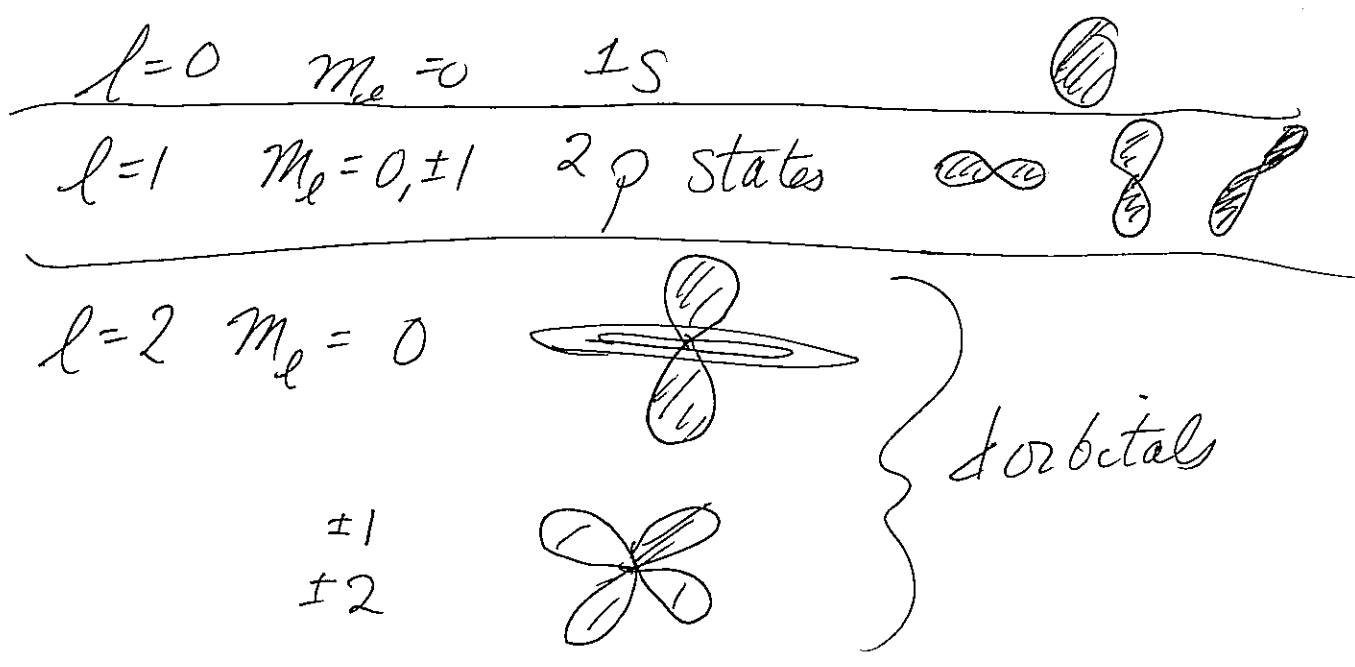
$\psi = R(r) P(\theta) F(\phi)$



$$Y_{lm}(\theta, \varphi) = P_{lm}(\theta) F_m(\varphi) \quad F_m(\varphi) = e^{im\varphi}$$

ignoring normalization:

n	l	m	F	P	R	
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	1s
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}} a_0^{3/2} (2 - \frac{r}{a_0}) e^{-r/2a_0}$	2s
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}} a_0^{3/2} \cdot \frac{r}{a_0} e^{-r/2a_0}$	2p _z
2	1	± 1	$\frac{e^{\pm i\varphi}}{\sqrt{2\pi}}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}} a_0^{3/2} \cdot \frac{r}{a_0} e^{-r/2a_0}$	2p _{x,y}



What do the radial parts give? same as before

(12)
opt

$$\Psi = R(r) Y(\theta, \varphi)$$

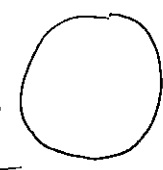
$$Y_{l,m}(\theta, \varphi) = P(\theta) F(\varphi) = P_{m_l}^l(\cos\theta) e^{im_l\varphi}$$

\uparrow
 (Series of polynomials)

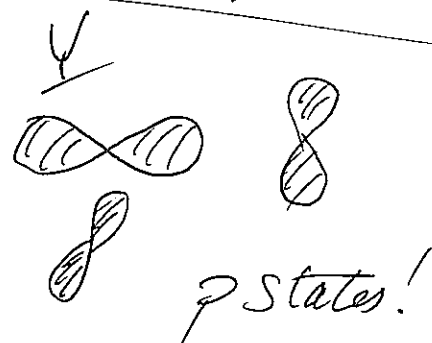
$l = \text{pos int}$
 $|m_l| < l$
 \uparrow
 int

$$l=0 \Rightarrow m_l = 0$$

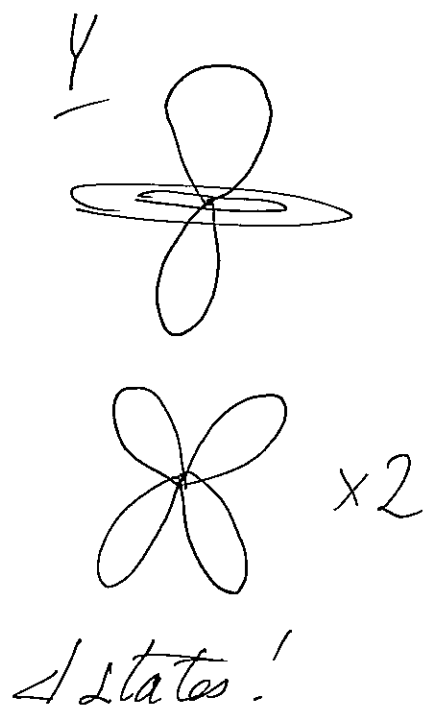
$$Y(\theta, \varphi) = \sqrt{\frac{1}{4\pi}}$$

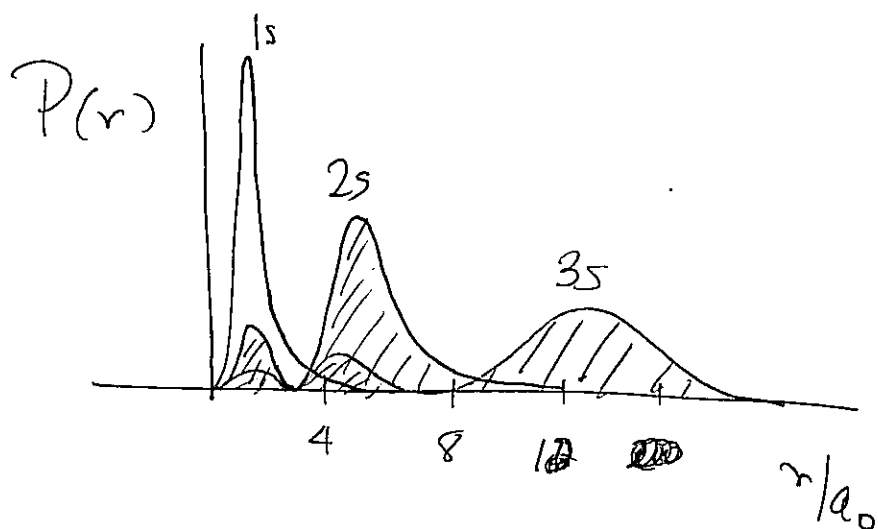
just "s" state again 

$$l=1, m_l = 0, 1 \begin{cases} \sqrt{\frac{3}{4\pi}} \cos\theta \\ \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\varphi} \end{cases}$$



$$l=2, m_l = \begin{cases} 0 \\ 1 \\ 2 \end{cases} \begin{cases} \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) \\ \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{i\varphi} \\ \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\varphi} \end{cases}$$





$\langle r \rangle$ increases w/n
 so does most prob. r

notation $\psi_{n,l,m}$ e.g. $\psi_{100} = 1s$
 $\psi_{210} = 2p_z$

next time: more on orbitals, Spin

spectra \updownarrow
 superposn of orbitals (e.g. p_x, p_y, p_z)

\updownarrow
 periodic table

\updownarrow
 Solids ; devices

- So far: have enumerated states of H atom (STATIONARY STATES)
- categorized by 3 "quantum numbers"

n - principle - overall size of dist.

l - (angular orbital) - elongation or "lumpiness"
total angular momentum

m - magnetic - z component of angular momentum.

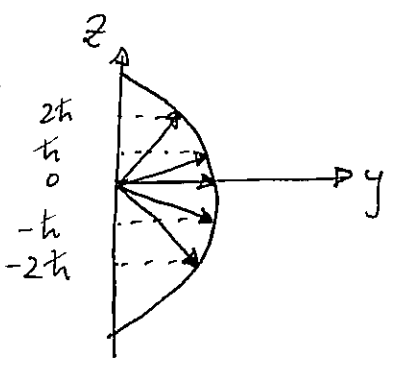
• l - quantizes $|\vec{L}|$ $|\vec{L}| = \sqrt{l(l+1)} \hbar$

$$l < n \Rightarrow l = \{0, 1, 2, \dots, n-1\}$$

e.g. $n=3 \Rightarrow l = \{0, 1, 2\} \Rightarrow |\vec{L}| = \begin{cases} 0 \\ \sqrt{2} \hbar \\ \sqrt{6} \hbar \end{cases}$

• m - quantizes z component of \vec{L}
(can know ONE component $\hat{=}$ obey uncert.)

$$L_z = m \hbar \quad |m| \leq l \Rightarrow m = \{-l, -l+1, \dots, l\}$$



- L_z can range from $+l\hbar$ to $-l\hbar$
- $L_z < |\vec{L}|$ always, so overall \vec{L} always points away from \hat{z}

$l=2$
 $m = -2, -1, 0, +1, +2$

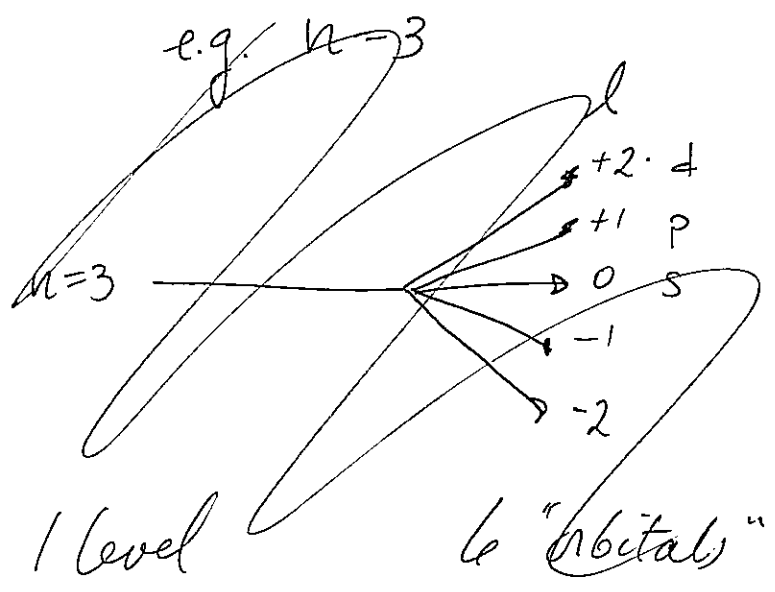
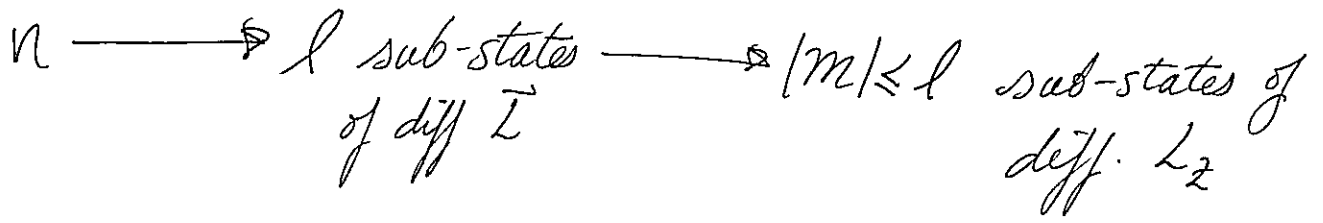
$$\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m}{\sqrt{l(l+1)}} < 1$$

• L_x, L_y uncertain!

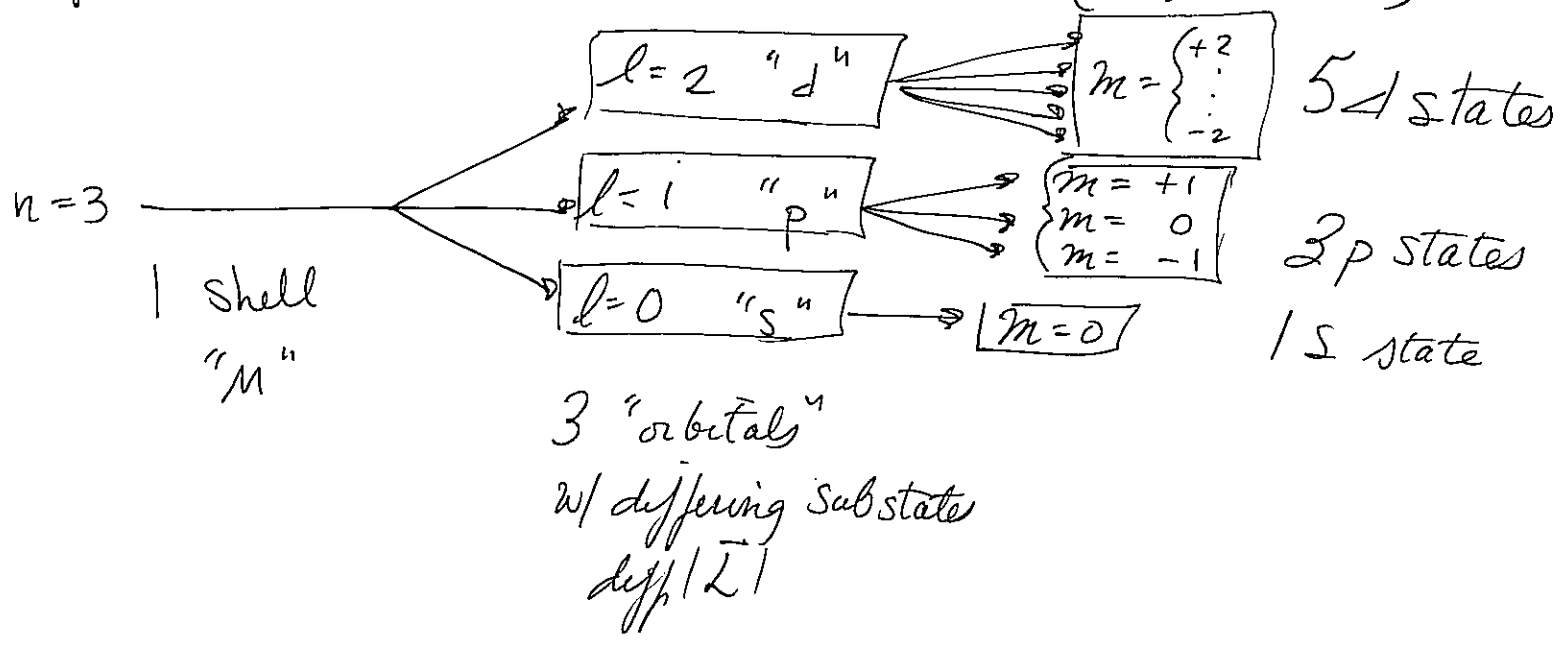
We have missed 1 quantum number yet...

So far:

level



e.g. $n=3 \Rightarrow l = \{0, 1, 2\} \Rightarrow m = \{-2, -1, \dots, 2\}$



each $l=2$ "d" state/orbital has 5 sub-levels
 $l=1$ "p" has 3
 $l=0$ "s" has 1

so 9 states in the $n=3$ level

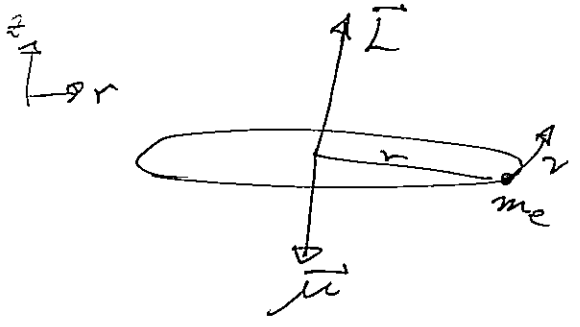
What did we miss? the electron also has its own angular momentum!

"Spin" quantum number $m_s = \pm \frac{1}{2}$

basically: 2 types of electrons, can put each in our states above $\Rightarrow 2 \times$ multiplicity

What is spin? first, connection between \vec{L} and magnetism

Consider classical orbiting e^-



- the e^- also makes a current loop!
 - this means there is a magnetic field, $\hat{=}$ magnetic moment!

$\vec{\mu} = I A \hat{z}$ current loop $I = \frac{-e}{\Delta t} = \frac{-ev}{2\pi r}$ since $2\pi r = v \Delta t$

$\mu = \frac{-evA}{2\pi r}$ but $\vec{L} = \vec{r} \times m_e \vec{v} = m_e v r \hat{z}$
 and $A = \pi r^2$

$\Rightarrow \vec{\mu} = \frac{-e}{2m_e} \vec{L} \equiv \gamma \vec{L}$
 NEGATIVE

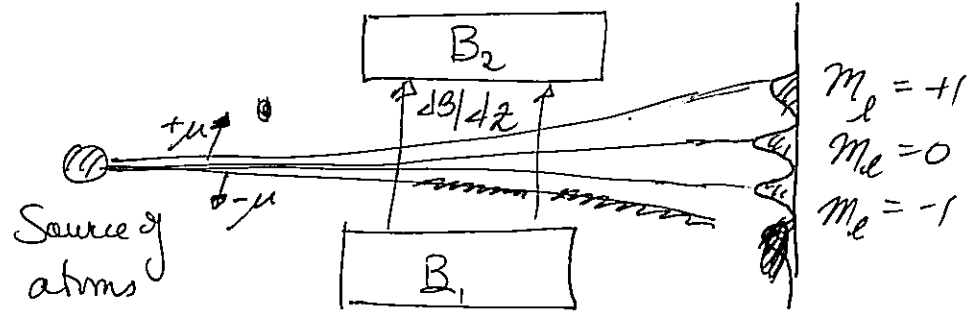
$\gamma = 1461 \text{ Hz/T} = -8.8 \times 10^{-10} \text{ C/kg}$
 recall $\Delta U = -\vec{\mu} \cdot \vec{B}$

- H atoms should possess a magnetic moment based on their \vec{L}

- it is also then quantized, different for each l, m

$\Rightarrow |\vec{\mu}| = \frac{eh}{2m_e} \sqrt{l(l+1)} = \mu_B \sqrt{l(l+1)}$ $\mu_z = -\frac{eh}{2m_e} m = -\mu_B m$
 $\mu_B = \text{Bohr magneton} = \text{fund}$ \uparrow quantized

So what? We can test this. moment in a field!



- Send atoms through a B gradient!
- experience a force based on their moment, i.e. m value
 - o if moment is along or against $\frac{\partial B}{\partial z}$, force
 - o if moment is orthog., nothing ... $L_x \hat{y} L_y$ (μ_x, μ_y) will be
 - o separate by μ_z (thus L_z) values

$$F = -\nabla U = -\vec{\mu}_z \cdot \frac{\partial \vec{B}}{\partial z} \quad \text{since } U = \vec{\mu} \cdot \vec{B}$$

- o doing this, one can sort out the L_x, L_z states of atoms
- o So what? too many lines were seen!

• For only "orbital" moment (\vec{L}) expect each ~~state~~ m gives a different result, but no more

$L_z = m \hbar$, $\mu_z = m \mu_B$ given total $|L| = \sqrt{l(l+1)} \hbar$
 $|m| \leq l$

→ So if $l=3$ state is studied, 7 lines
 $l=2$ 5 lines expected for $m = \{-2 \dots 2\}$

- Experiment: some lines were doubled! more states of \vec{L}

Conclusion: electrons have their own intrinsic angular momentum, or magnetic moment!
Analogy: spinning ball of charge!

- Takes only 2 values: either $\pm \frac{1}{2} \hbar$ ("up" & "down")
i.e. half of angular L_z quanta
- purely relativistic & quantum

Math: multiply our wave function by a 2-component function

$$\Psi = \chi(s) R(r) Y(\theta, \phi)$$

↑
spin

• This intrinsic angular momentum is called SPIN

- has only 2 values, char. by 1 new quantum #

$$m_s = \pm \frac{1}{2} \quad \text{or "up" and "down"}$$

• electron ang mom. $L_{s,z} = S_z = m_s \hbar$ $m_s = \pm \frac{1}{2}$

- leads to doubling of states

- just like angular momentum of atom it has:

2X larger than expt from L

Magnitude $|\mu_s| = 2\mu_B \sqrt{m_s(m_s+1)} = \sqrt{3}\mu_B$

Z Component $\mu_{s,z} = -2\mu_B m_s = \mp \mu_B$ (2X larger!)

~~FACTOR 2 of orbital L since $m_s = \pm \frac{1}{2}$~~

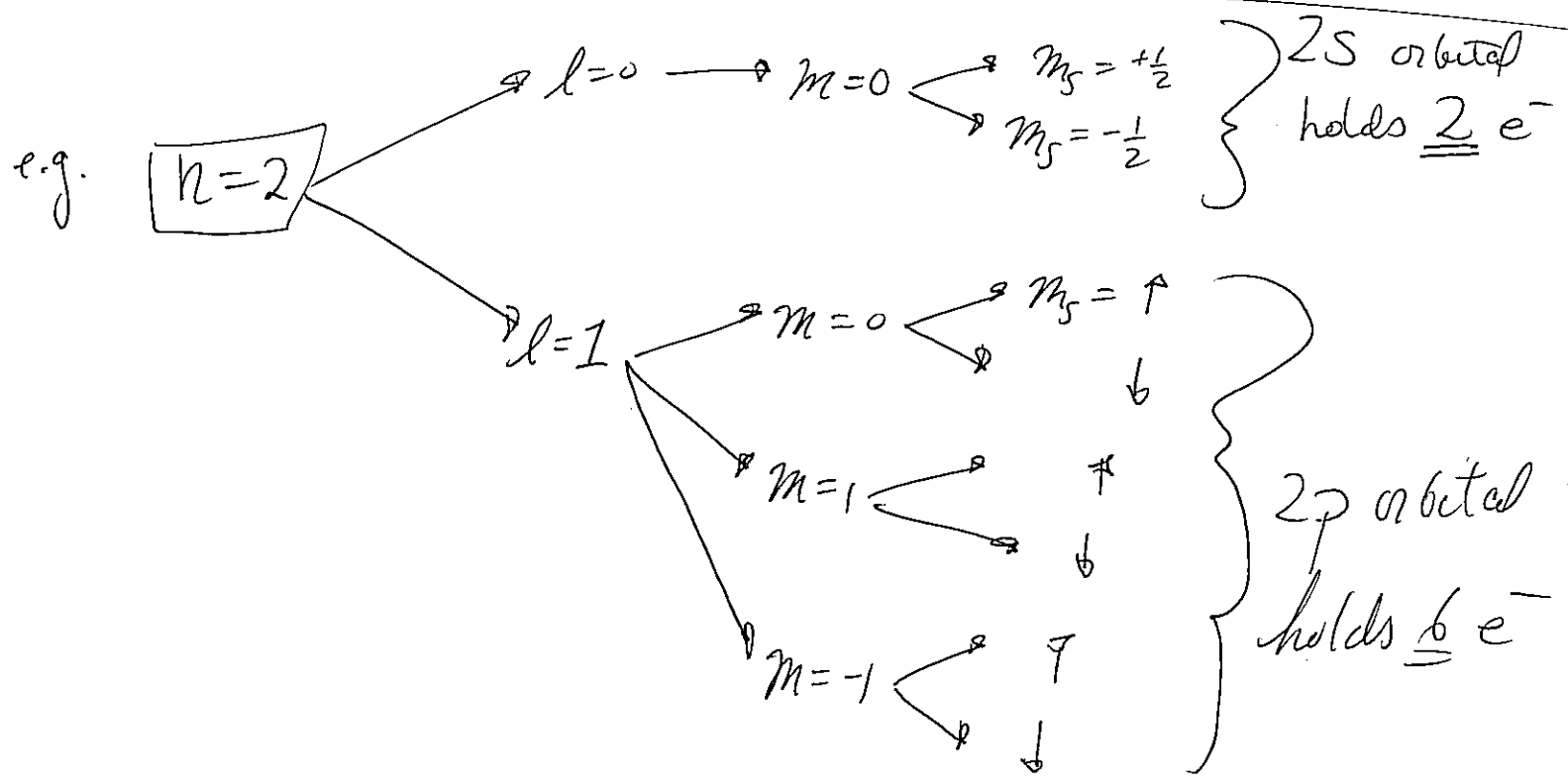
⊕ we observe for a single e^- μ_z projection onto \bar{z} axis
So either \uparrow or \downarrow moment.

⊕ Single e^- : measurement forces \uparrow or \downarrow

So: 4 quantum # to describe any state of a H atom

n, l, m, m_s

#	values	observable
principle n	1, 2, 3 ...	energy
orbital l	0, 1, ... n-1	magn of \vec{L} $ \vec{L} = \sqrt{l(l+1)} \hbar$
magnetic m	-l, -l+1, ... l-1, l	Z component of \vec{L} $L_z = m \hbar$
Spin m_s	$+\frac{1}{2}, -\frac{1}{2}$	Z component of spin $S_z = \pm \frac{1}{2} \hbar$



n	l		
1	"s"	$1s^2$	$2e^-$ in lowest state "K" shell
2	"s"	$2s^2$	$2e^-$ } $8e^-$ in "L" shell
	"p"	$2p^6$	
3	"s"	$3s^2$	} $18e^-$ in "M" shell
	"p"	$3p^6$	
	"d"	$3d^{10}$	

- how we are on our way to explaining the periodic table!
- Spin explains magnetism! e^- moments line up
- many consequences of L, S on emission/abs. spectra (next...)

Some details: ONLY one e^- can have a given set of 4 quant # $|n, l, m, m_s\rangle$

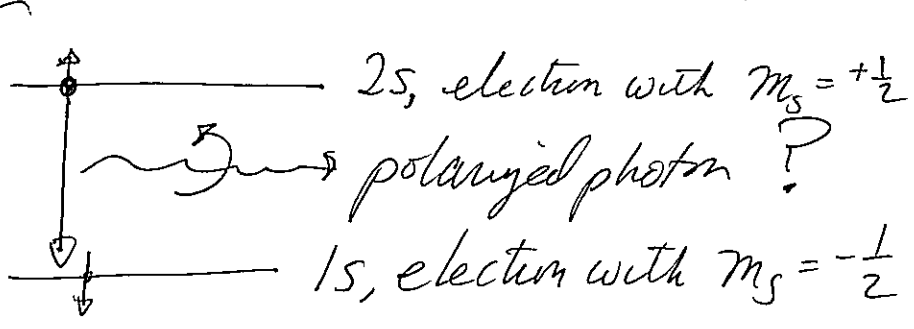
"Pauli exclusion"

more details

for e^- to change states, \vec{L} and \vec{S} must be conserved (conservation of energy/mom)

e.g., if we do a level change, PHOTON has \vec{L} too! ($\pm \hbar$)

- cannot happen...
- l is same
- m_s can't change

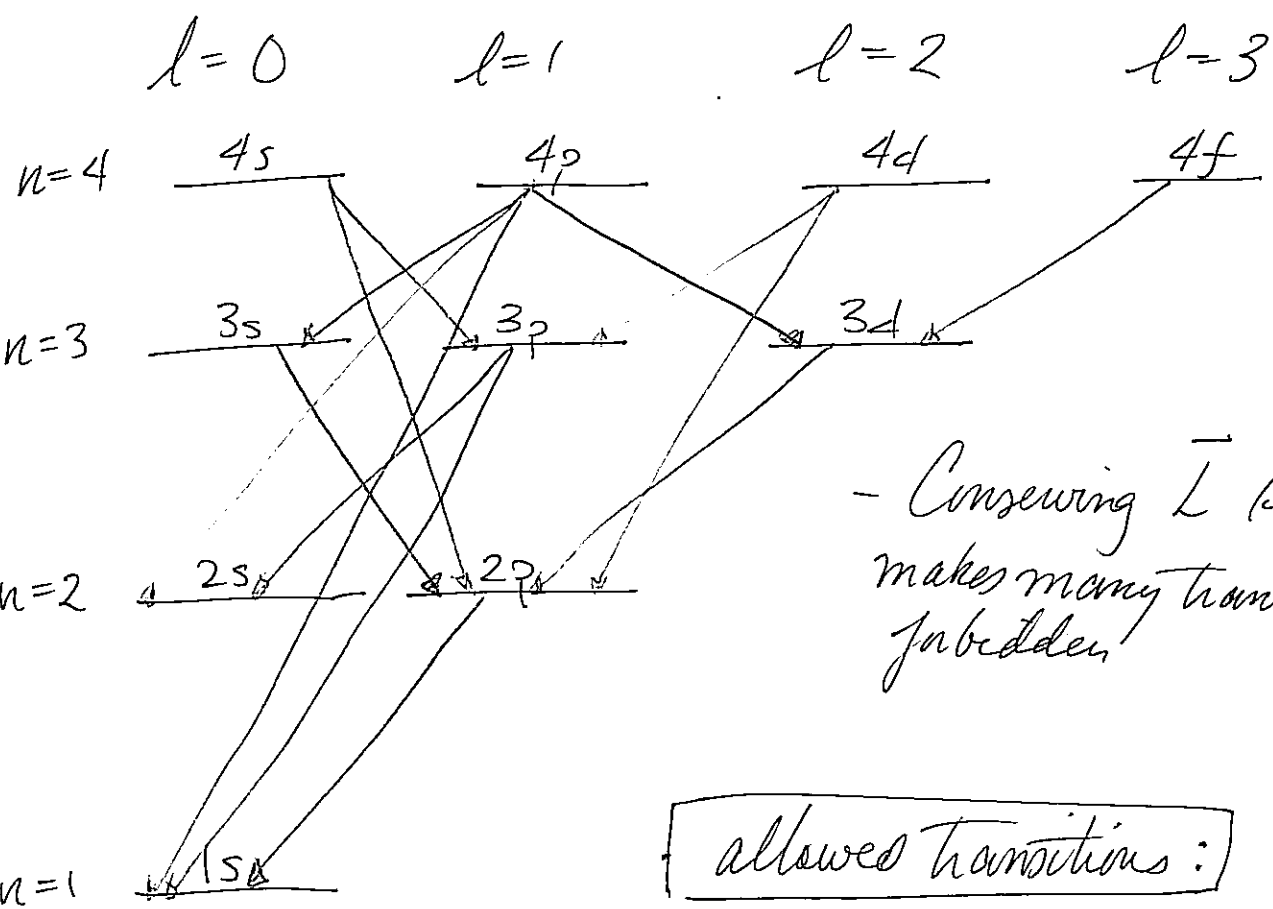


- photon emitted ~~must have~~ ^{needs} circ polarization to balance \vec{L} once we count spin!
- many transitions forbidden! ~~that are only allowed if spin flips~~

Further: electron's atom magnetic moments interact!
"spin-orbit coupling"

- \Rightarrow \uparrow and \downarrow electrons have diff energies, even if n, l, m are same!
- \Rightarrow fine structure in spectra

Transitions in Hydrogen (ignoring spin)



- Conserving \vec{L} (even w/o \vec{S}) makes many transitions forbidden

allowed transitions:

- L conserved counting photon
- photons can have only $\pm \hbar$ angular momentum
- ~~Can change spin keep it same~~
- ~~otherwise~~ to account for photon need $\Delta l = \pm 1$ (fewer possible than expected)

So $2s$ state has no mechanism to relax w/o spin flip!
 \Downarrow
 long lifetime
~~long~~

- o CANNOT go from $3s \rightarrow 2s$!
- o CANNOT have $\Delta l = 0$ e.g.

Next

- more on transitions $\hat{=}$ selection rules
- more on periodic table / multi-electron atoms
- Spin-orbit coupling $\hat{=}$ fine structure of spectra
- Fermions $\hat{=}$ statistics
- total spin, magnetism

Once this is done (\sim 2 lectures)

ON TO APPLICATIONS

- bonding
- theory of metals
- Semiconductors $\hat{=}$ devices
- Lasers