

Chapter 7 The Hydrogen Atom in Quantum Mechanics

Central Potentials in Quantum Mechanics

In 3D Cartesian coordinates the SE for bound states is given by

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) \quad (1)$$

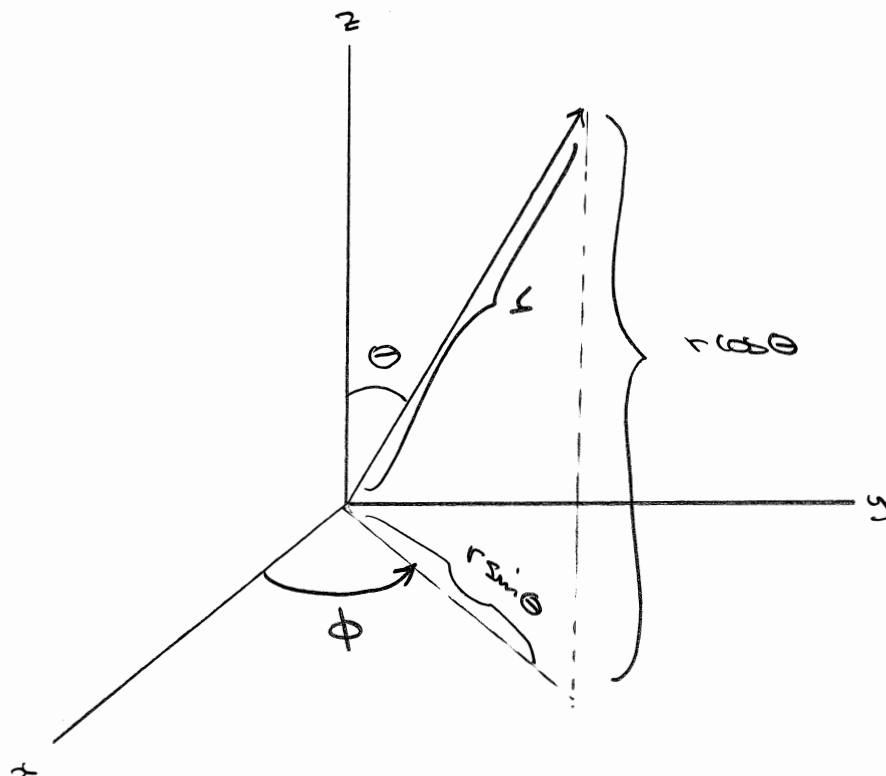
$$\text{where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (2)$$

The attractive force between the proton and the electron is "central"

$$V(\vec{r}) = V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (3)$$

↑ only depends
on the
distance
between the
 e^- and p

If this is the case, we use r, θ, ϕ instead of x, y, z



r is the distance from the center of the potential
 θ is the polar angle, declination from z -axis
 ϕ is the azimuthal angle

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

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

$$z = r \cos \theta$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\vec{r}) d\vec{r} \rightarrow \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \int_0^{\infty} r^2 dr f(r, \theta, \phi)$$

(4)

R radial operator ^{differential}

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

convention ∇^2 angular operator (please work this out on your own!)

Since $V(\vec{r}) = V(r)$ only, θ, ϕ separate out. In fact, since θ, ϕ are independent they separate out from each other.

$$\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

$$\nabla^2 Y_{lm}(\theta, \phi) = -l(l+1) Y_{lm}$$

(6)

$$l = 0, 1, 2, \dots \text{ (positive integers)} \\ -l \leq m \leq l \text{ (zero)}$$

l	m_l	$Y_{lm_l}(\theta, \phi)$
0	0	$(\frac{1}{4\pi})^{1/2}$
1	0	$(\frac{3}{4\pi})^{1/2} \cos\theta$
1	± 1	$\mp (\frac{3}{8\pi})^{1/2} \sin\theta e^{\pm i\phi}$
2	0	$(\frac{5}{16\pi})^{1/2} (3\cos^2\theta - 1)$
2	± 1	$\mp (\frac{15}{8\pi})^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$
2	± 2	$(\frac{15}{32\pi})^{1/2} \sin^2\theta e^{\pm 2i\phi}$
	$\vdots$	

$$(7) \quad Y_{lm_l}(\theta, \phi) = (-1)^{m_l} \left[\frac{2l+1}{2} \frac{(l-m_l)!}{(l+m_l)!} \right]^{1/2} P_l^{m_l}(\cos\theta) \times \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$$

note: for $m_l=0$
 $P_l^0(\cos\theta) = \text{regular}$
 Legendre's
 $P_l(\cos\theta)$

for $m_l \geq 0$

for $-ve$ m_l

These are
 called the
 "generalized
 Legendre
 Polynomials"

$$(8) \quad Y_{l-m_l}(\theta, \phi) = (-1)^{m_l} Y_{lm_l}^*(\theta, \phi)$$

Properties

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi Y_{lm_l}^* Y_{lm_l} = 1 \quad \text{normalized}$$

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi Y_{l'm_l'}^* Y_{lm_l} = \delta_{ll'} \delta_{m_l m_l'}$$

$$\langle l' m' | l m \rangle = \delta_{l'l} \delta_{m'm} \quad (9)$$

Orthonormality

Parity $\vec{r} \rightarrow -\vec{r}$

$$\Rightarrow r \rightarrow r, \quad \theta \rightarrow \pi - \theta, \quad \phi \rightarrow \phi + \pi$$

$$\pi Y_{lm} = (-1)^l Y_{lm} \quad (10)$$

$$\pi |lm\rangle = (-1)^l |lm\rangle$$

A definite parity is expected since

$$V(\vec{r}) = V(|\vec{r}|) = V(|-\vec{r}|) = V(r)$$

$$\mathcal{L}^2 Y_{lm} = \underbrace{\hbar^2 l(l+1)}_{\text{total (angular momentum)}^2 \text{ operator}} Y_{lm}$$

l is symbol for angular momentum

$$\mathcal{L}_z Y_{lm} = m_l \hbar Y_{lm}$$

M_l "magnetic" quantum number

$\uparrow$
z-component of the angular momentum

$$\mathcal{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Remaining "radial" equation

$$\textcircled{11} \quad \underbrace{-\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right]}_{K_r \text{ radial kinetic energy term}} R_{nl}(r) + V(r) R_{nl}(r) + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}}_{\text{centrifugal repulsive force}} R_{nl}(r) = E_{nl} R_{nl}(r)$$

Completely general, only requires $V(\vec{r}) = V(r)$

The ^{radial} eigenfunctions only depend on n , the principle quantum number and (possibly) l , the angular momentum quantum number.

Given l there are $2l+1$ possible values of m_l , and these are all degenerate

Critically important result

Two non-relativistic particles m_1, m_2
attracted by a potential of the form
 $V(|\vec{r}_1 - \vec{r}_2|)$

$$(12) \quad \underbrace{-\frac{\hbar^2}{2m_1} \nabla_1^2}_{\text{KE of } m_1} U(\vec{r}_1, \vec{r}_2) - \underbrace{\frac{\hbar^2}{2m_2} \nabla_2^2}_{\text{KE of } m_2} U(\vec{r}_1, \vec{r}_2) + V(|\vec{r}_1 - \vec{r}_2|) U(\vec{r}_1, \vec{r}_2) = E_T U(\vec{r}_1, \vec{r}_2)$$

← total energy

(notes of Nov. 16)

$$(13) \quad -\frac{\hbar^2}{2\mu} \nabla_r^2 u(\vec{r}) + V(r) u(\vec{r}) = \underbrace{(E_T - E_{cm})}_{\equiv E} u(\vec{r})$$

(notes earlier in this lecture)

$$(14) \quad u(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad \leftarrow \text{with all its properties}$$

where

$R_{nl}(r)$ is a solution to the differential equation

$$(15) \quad -\frac{\hbar^2}{2\mu} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R_{nl}(r) + V(r) R_{nl}(r) + \frac{\hbar^2}{2\mu r^2} l(l+1) R_{nl}(r) = E_{nl} R_{nl}(r)$$

This is a completely general result for
any $V(r)$

e.g. $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$ Coulomb (about to do)

$V(r) = \frac{1}{2}kr^2$ Harmonic (already discussed)
as a separated sol'n in x, y, z

$V(r) = -V_0 \quad r \leq R$
 $= 0 \quad r > R$ } 1st approximation
to the nuclear
potential

(maybe 311, for sure 312)

Note: In general, E_{nl} depends on both $n \neq l$

In general $l = 0, 1, 2, \dots, \underbrace{l_{\max}(n)}$
can depend on
 n , may be ∞

all
cases }
all
potentials

$-l \leq m_l \leq l \quad m_l = -l, -l+1, \dots, -2, -1, 0, 1, 2, \dots, l$

The Hydrogen atom

(16)

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

By convention we use $m = \mu = \left(\frac{1}{m_e} + \frac{1}{m_p} \right)^{-1}$

Aside:

For Hydrogenic atoms
single e^- in "orbit"
about Z protons



Substitute

$$e^2 \rightarrow Ze^2$$

$$m = \mu = \left(\frac{1}{m_e} + \frac{1}{m_N} \right)^{-1}$$

↖ mass of the nucleus

① If $V(\vec{r}) = V(|\vec{r}|) \equiv V(r)$ i.e. "central" potential

② $U(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$

where

③ $Y_{lm}(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{\frac{1}{2}} P_l^m(\cos\theta) e^{im\phi}$ note

④ $Y_{l-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi)$ $l=0,1,2,\dots$
 $|m| \leq l$

$l \equiv$ orbital angular momentum #
 $m \equiv$ magnetic #

⑤ total angular momentum operator

$$\begin{aligned} \hat{L}^2 Y_{lm} &= \hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y_{lm}}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y_{lm}}{\partial\phi^2} \right\} \\ &= \hbar^2 l(l+1) Y_{lm} \end{aligned}$$

i.e. Angular momentum info carried by Y_{lm}

⑥ z-projection of $\vec{L}$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi} \quad ; \quad \hat{L}_z Y_{lm} = m\hbar Y_{lm}$$

⑦

$$\langle l'm' | l m \rangle$$

$$= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{l'm'}^* Y_{lm} = \delta_{ll'} \delta_{mm'}$$

orthonormality

⑧

Parity

$$\Pi Y_{lm} = (-1)^l Y_{lm}$$

- i.e. parity information also carried by Y_{lm}

⑨ Radial eq'n

$$-\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R_{nl}(r) + \frac{\hbar^2 l(l+1)}{2mr^2} R_{nl}(r) + V(r) R_{nl}(r) = E_{nl} R_{nl}(r)$$

KE associated with
vibrations along r

KE associated
with rotation
(centrifugal)

potential

E_{nl} can (does not have to)
depend on l, n

n is called the principle quantum #

$$n = [0, 1, 2, \dots]$$

orthonormality relation

(10)

$$\langle n'l | nl \rangle = \delta_{nn'}$$

$$\text{i.e.} \quad \int_0^{\infty} r^2 dr R_{n'l}^*(r) R_{nl}(r) = \delta_{nn'}$$

in general $\langle n'l' | nl \rangle \neq 0$ if $l' \neq l$ ^{correction}
 n, n' anything

The radial sol's depend on the form of the potential $V(r)$.

Applications

The Hydrogenic atom

(11) $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$ (one electron in orbit)
around a nucleus
with Z protons

It can be shown for the Hydrogenic atom

(12) $R_{nl}(r) = -2 \left(\frac{Z}{na_0}\right)^{3/2} \left[\frac{(n-l-1)!}{n[(n+l)!]} \right]^{1/2} \left(\frac{2Zr}{na_0}\right)^l$ — note:

a_0 = Bohr radius

$$\times \exp\left[-\frac{Zr}{na_0}\right] \left[\sum_{k=0}^{2l+1} \left(\frac{2Zr}{na_0}\right)^k \right]$$

$n = 1, 2, \dots, \infty$

$l = 0, 1, 2, \dots, n-1$
↑ stops

(13) $E_{nl} = E_n = -\frac{E_0}{n^2}$; $E_0 = \left(\frac{Ze^2}{4\pi\epsilon_0\hbar c}\right)^2 \frac{mc^2}{2}$
↑
does not
depend on l

$$= \frac{Z^2 \alpha^2 mc^2}{2} \quad (\text{Bohr's result})$$

$$= Z^2 (13.6 \text{ eV})$$

recall $\alpha \approx \frac{1}{137}$

fine structure
constant

The $E_n = -\frac{E_0}{n^2}$ was just about the only thing Bohr got right.

Some examples of radial wave functions

(14)

$$R_{10} = \left(\frac{Z}{a_0}\right)^{3/2} 2 \exp\left(-\frac{Zr}{a_0}\right)$$

$$R_{20} = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$$

$$R_{21} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}} \left(\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$$

$$\left. \begin{matrix} R_{30} \\ R_{31} \\ R_{32} \end{matrix} \right\} = \left(\frac{Z}{3a_0}\right)^{3/2} \left\{ \begin{matrix} 2\left[1 - \frac{2}{3}\frac{Zr}{a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right] \\ 4\frac{\sqrt{2}}{3}\frac{Zr}{a_0}\left(1 - \frac{1}{6}\frac{Zr}{a_0}\right) \\ \frac{2}{27}\sqrt{\frac{2}{5}}\left(\frac{Zr}{a_0}\right)^2 \end{matrix} \right\} \exp\left(-\frac{Zr}{3a_0}\right)$$

and so on

As n increases, wave function gets more spread out.

$$(15) \quad \langle r \rangle = \frac{a_0 n^2}{Z} \left[1 + \frac{1}{2} \left\{ 1 - \frac{2(l+1)}{n^2} \right\} \right]$$

$$(16) \quad \langle r^2 \rangle = \frac{a_0^2 n^4}{Z^2} \left[1 + \frac{3}{2} \left\{ 1 - \frac{(2(l+1) - \frac{1}{2})}{n^2} \right\} \right]$$

Recall Bohr model

$$r_n = \frac{a_0 n^2}{Z}$$

↑
fixed
orbit

$$a_0 \approx 0.0529 \text{ nm}$$

Radial probability densities

$$(17) P_{nl}(r) = r^2 |R_{nl}(r)|^2$$

↑
important

$$\int_0^{\infty} dr P_{nl}(r) = 1 \quad \text{by normalization}$$

Energy level degeneracy in the Hydrogenic atom

$$D(n) = \sum_{l=0}^{n-1} \sum_{m=-l}^l (1)$$

$\underbrace{\quad}_{\substack{\text{degeneracy} \\ \text{for energy} \\ \text{level } n}}$
 $\underbrace{\quad}_{\substack{\text{\# of} \\ l\text{'s}}}$
 $\underbrace{\quad}_{\substack{\text{\# of} \\ m\text{'s per } l}}$

$$= \sum_{l=0}^{n-1} (2l+1)$$

$$= \sum_{l=1}^n (2l-1) \quad l \rightarrow l+1$$

$$= 2 \sum_{l=1}^n l - \sum_{l=1}^n 1$$

$$= 2 \left(\frac{n(n+1)}{2} \right) - n$$

Gaussian
sum

$$= n^2 + n - n = n^2$$

$$(18) \boxed{D(n) = n^2}$$

Hydrogenic
atoms
only

The special case of $l=0$

These are called the s state solutions

No angular momentum.

$$(19) \quad -\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R_{n0}(r) + V(r) R_{n0}(r) = E_{n0} R_{n0}(r)$$

$$\text{Or, } \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R_{n0}(r) + \frac{2m(E_{n0} - V(r))}{\hbar^2} R_{n0}(r) = 0$$

$$\text{Set } R_{n0}(r) = \frac{u_n(r)}{r}$$

$$(20) \quad R' = \frac{u'}{r} - \frac{u}{r^2}$$

$$R'' = \frac{u''}{r} - \frac{u'}{r^2} - \frac{u'}{r^2} + \frac{2u}{r^3}$$

$$(21) \quad R'' = \frac{u''}{r} - \frac{2u'}{r^2} + \frac{2u}{r^3}$$

$$(20) \text{ and } (21) \Rightarrow (19)$$

 R''
 $\frac{2}{r} R'$

$$(22) \quad \left(\frac{u''}{r} - \frac{2u'}{r^2} + \frac{2u}{r^3} \right) + \left(\frac{2u'}{r^2} - \frac{2u}{r^3} \right) + \frac{2m(E_{n0} - V(r))}{\hbar^2} \frac{u}{r} = 0$$

(22) $\times r \Rightarrow$

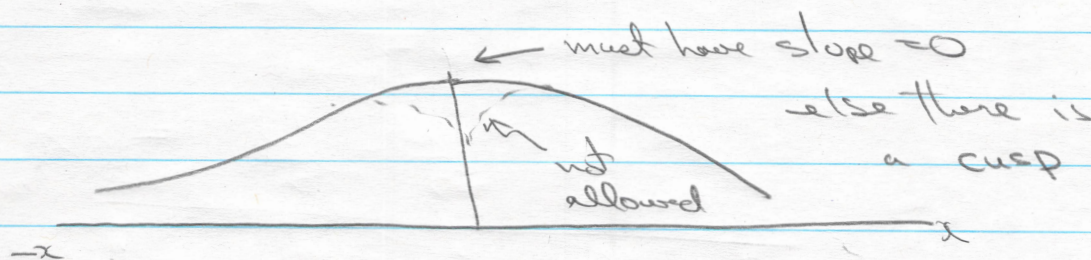
$$(23) \quad u_n'' + \frac{2m}{\hbar^2} (E_n - V(r)) u_n = 0$$

This "looks" exactly like a 1D sol'n.

However, there is one important difference

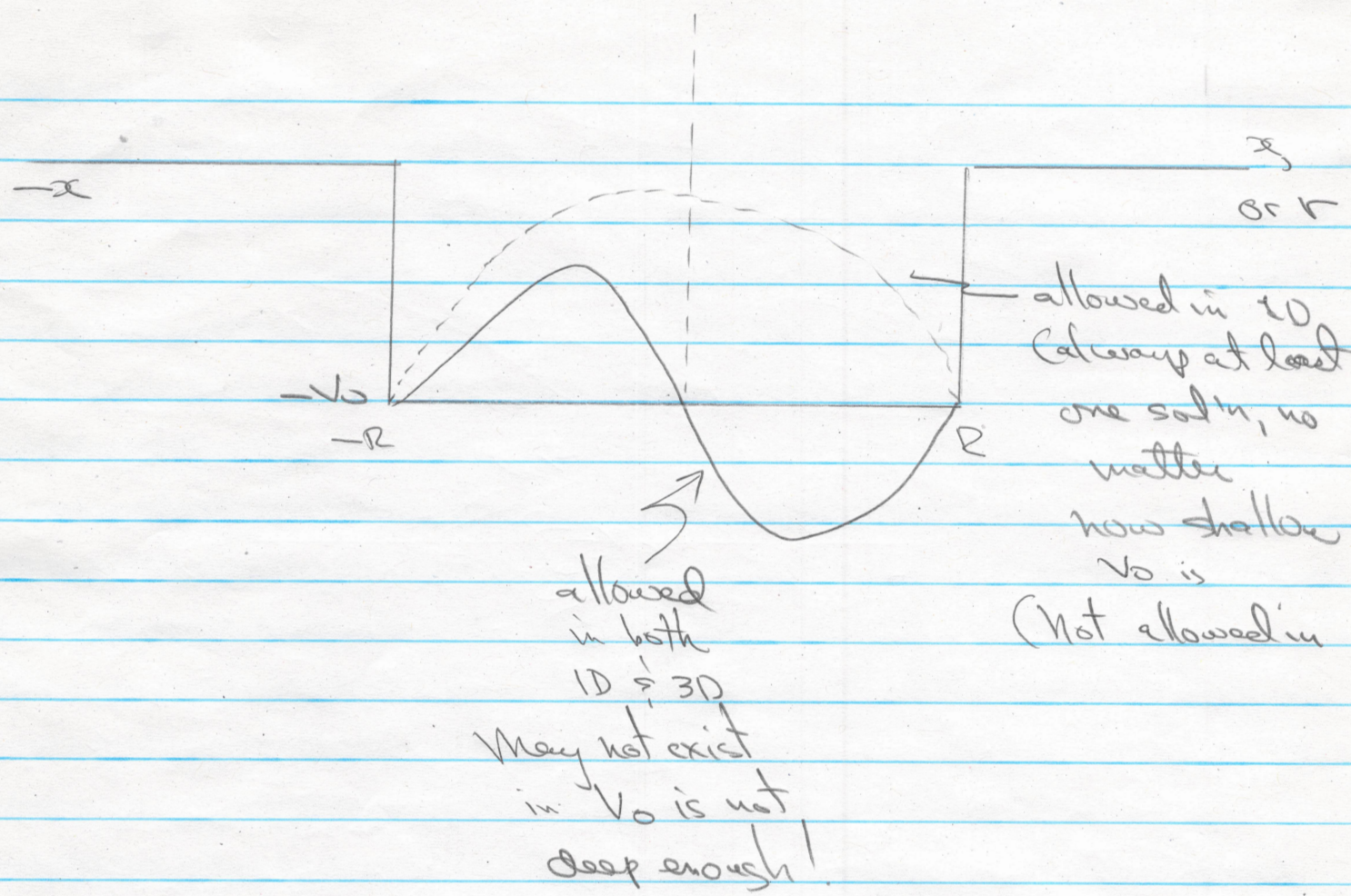
$$R_{n0}(r) = \frac{u_n(r)}{r}$$

$R_{n0}(r)$ must be continuous at the origin
 $\Rightarrow u(0) = 0$



Application to nuclear physics

$$\begin{aligned} V &= -V_0 & \text{inside nucleus} \\ V &= 0 & \text{outside} \end{aligned}$$



The potential is "just" bound

7.4 Angular momentum

With respect to angular momentum, there are two constants of the motion: $\left\{ \begin{array}{l} \textcircled{1} \text{ total } \langle \mathbf{p}^2 \rangle = \hbar^2 l(l+1) \textcircled{1} \\ \textcircled{2} \hat{z}\text{-comp } \langle p_z \rangle = \hbar m_l \textcircled{2} \end{array} \right.$

From $\textcircled{1} \div \textcircled{2}$

$$\textcircled{3} \quad \langle \mathbf{p}^2 - p_z^2 \rangle = \langle p_x^2 + p_y^2 \rangle = \hbar^2 [l(l+1) - m_l^2]$$

$$\text{So, } \textcircled{4} \quad \hbar^2 l \leq \langle p_x^2 + p_y^2 \rangle \leq \hbar^2 l(l+1)$$

$m_l = \pm l$ $m_l = 0$

We can also show that

$$\langle p_x \rangle = \langle p_y \rangle = 0$$

since $\Delta p_x, \Delta p_y \neq 0$

$$\textcircled{5} \quad \Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$$

$\neq 0$ from $\textcircled{4}$

This is really a consequence of the Heisenberg Uncertainty relationship

$$\Delta L_z \Delta \phi \geq \frac{\hbar}{2}$$

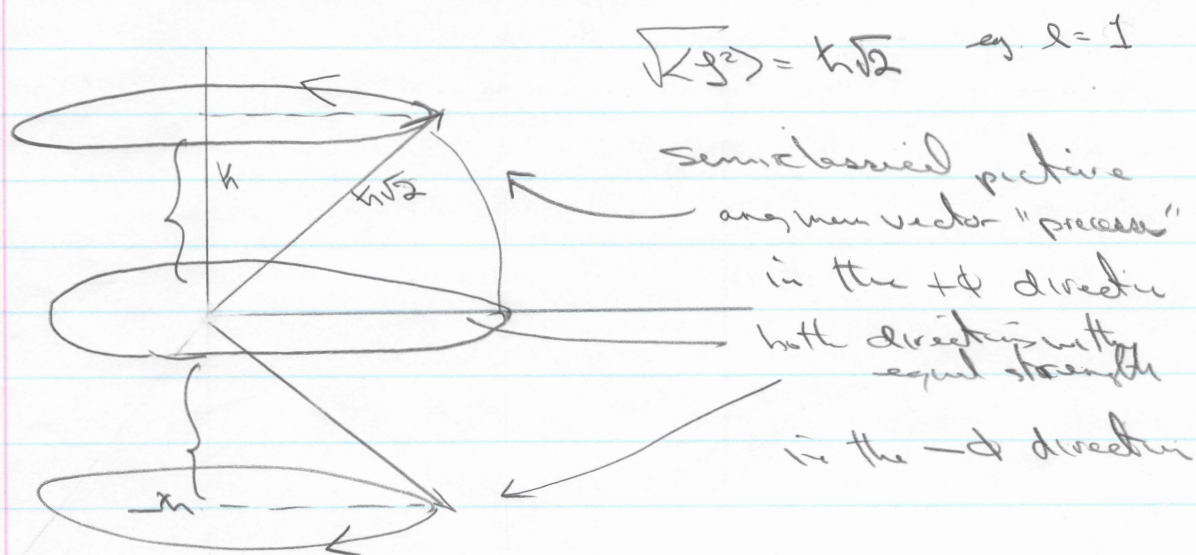
↑
azimuthal
angle

Since $\Delta L_z = 0$ $\Delta \phi$ must be infinite

(very much like $\Delta E \Delta t \geq \frac{\hbar}{2} \Rightarrow \Delta t = \infty$ for stable bound states)

So, the azimuthal angle can not be specified, hence L_x, L_y can not be specified

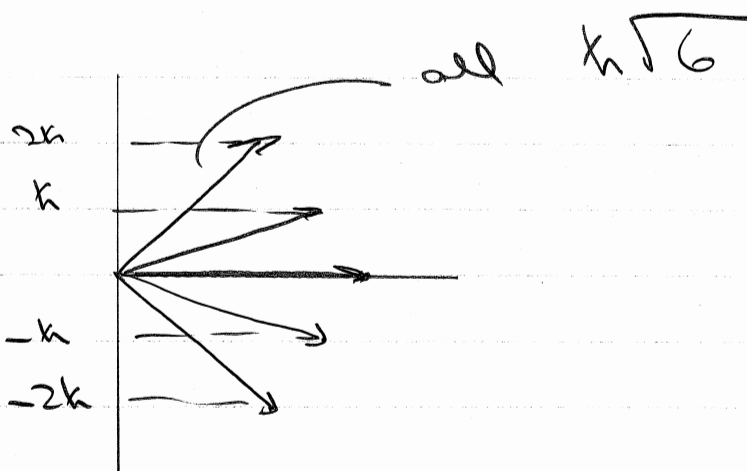
The vector model of angular momentum



This vector model, just use it as a tool for visualization

$$l=2$$

231



Show picture

$$|Y_0^0(\theta, \phi)|^2$$



$$|Y_1^0(\theta, \phi)|^2$$



$$|Y_1^1(\theta, \phi)|^2$$



$$|Y_2^0(\theta, \phi)|^2$$



$$|Y_2^1(\theta, \phi)|^2$$



$$|Y_2^2(\theta, \phi)|^2$$



$$|Y_3^0(\theta, \phi)|^2$$



$$|Y_3^1(\theta, \phi)|^2$$



$$|Y_3^2(\theta, \phi)|^2$$



$$|Y_3^3(\theta, \phi)|^2$$



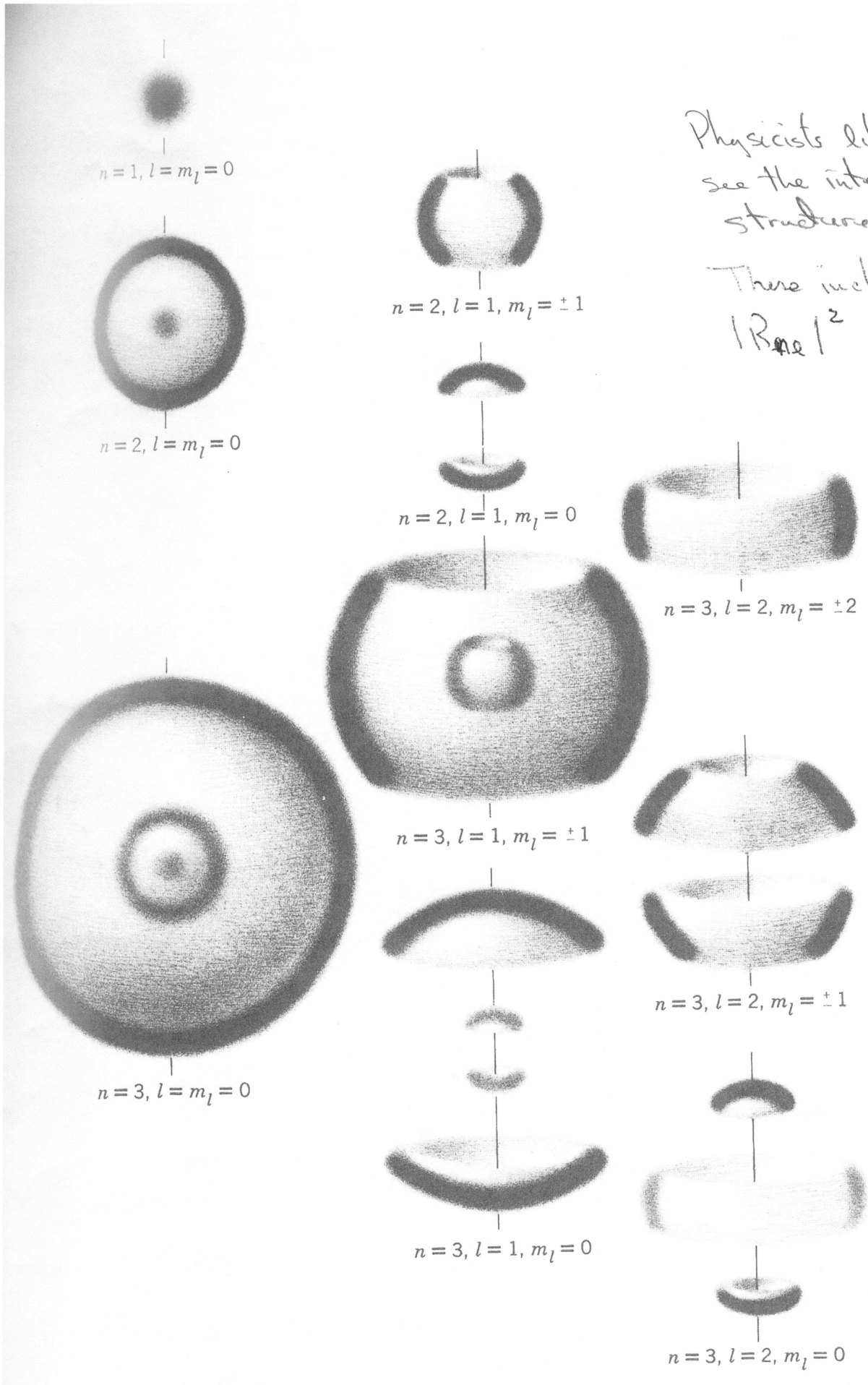
from
Mathematica
Website

google

"Spherical Harmonics"

Chemists use the Y_ℓ^m 's of the
valence "outermost" orbital
electrons to determine

how molecules
are pieced together
by atoms



Physicists like to see the internal structure

These include $|R_{nl}|^2$

7.5 Intrinsic Spin

When the H-atom gm wfs were discovered, it occurred to experimentalists that this phenomenon must be observed. The ability to observe this is known to classical physics, because we know that a magnet can exert a force on a current loop. [This is how electric motors work!]

The potential for this is

$$\textcircled{1} \quad V = -\vec{\mu}_L \cdot \vec{B}$$

(Zeeman effect
7.7 in Krane)

$\uparrow$ magnetic field
 $\uparrow$ magnetic moment associated with the current loop

For the electron in an orbit, its magnetic moment is

$$\textcircled{2} \quad \vec{\mu}_L = -\frac{e}{2m_e} \vec{L}$$

assume $\vec{B} = B\hat{z}$

$$\textcircled{2} \Rightarrow \textcircled{1} \Rightarrow V = \frac{e\hbar}{2m_e} m_L B \quad (3)$$

This is why m_L is called the "magnetic" quantum number

$$\text{So, } V \doteq \mu_B m_L B$$

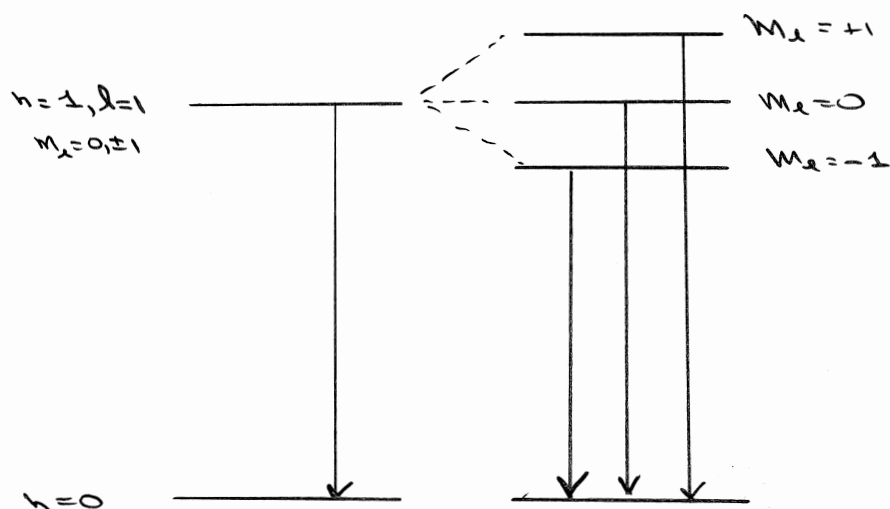
$\mu_B = \frac{e\hbar}{2m_e}$
 named e^- ,
 not μ
 hence

μ_B is called the Bohr magneton,
only depends on e, h, m_e

$$\mu_B = \frac{e\hbar}{2m_e}$$

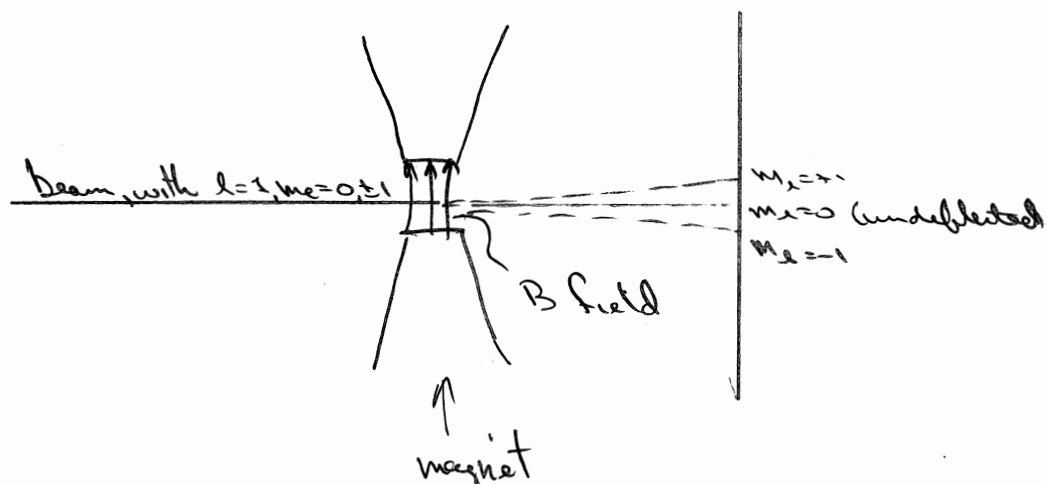
↖ this factor ($\frac{1}{2}$) is
the result of the e^- being
a "point-like" charge

The effect of the magnetic field



So, spectroscopy should be able
to see these lines

In stead of a spectroscopic expt, Stern & Gerlach did the following simpler thing

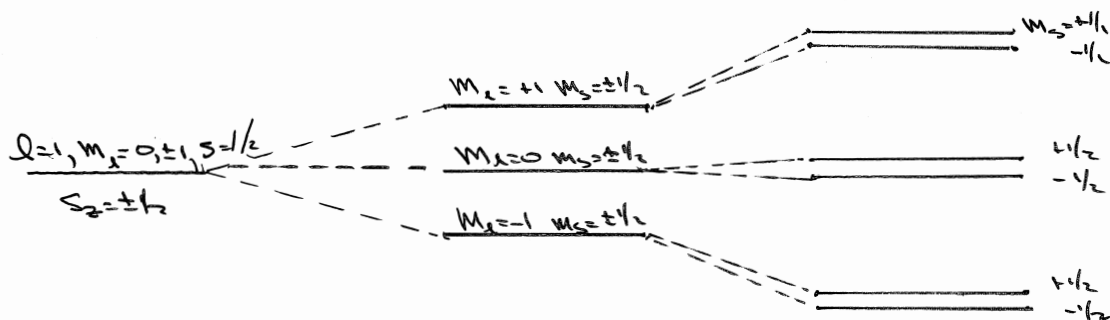


Great idea

no B field

modest B field

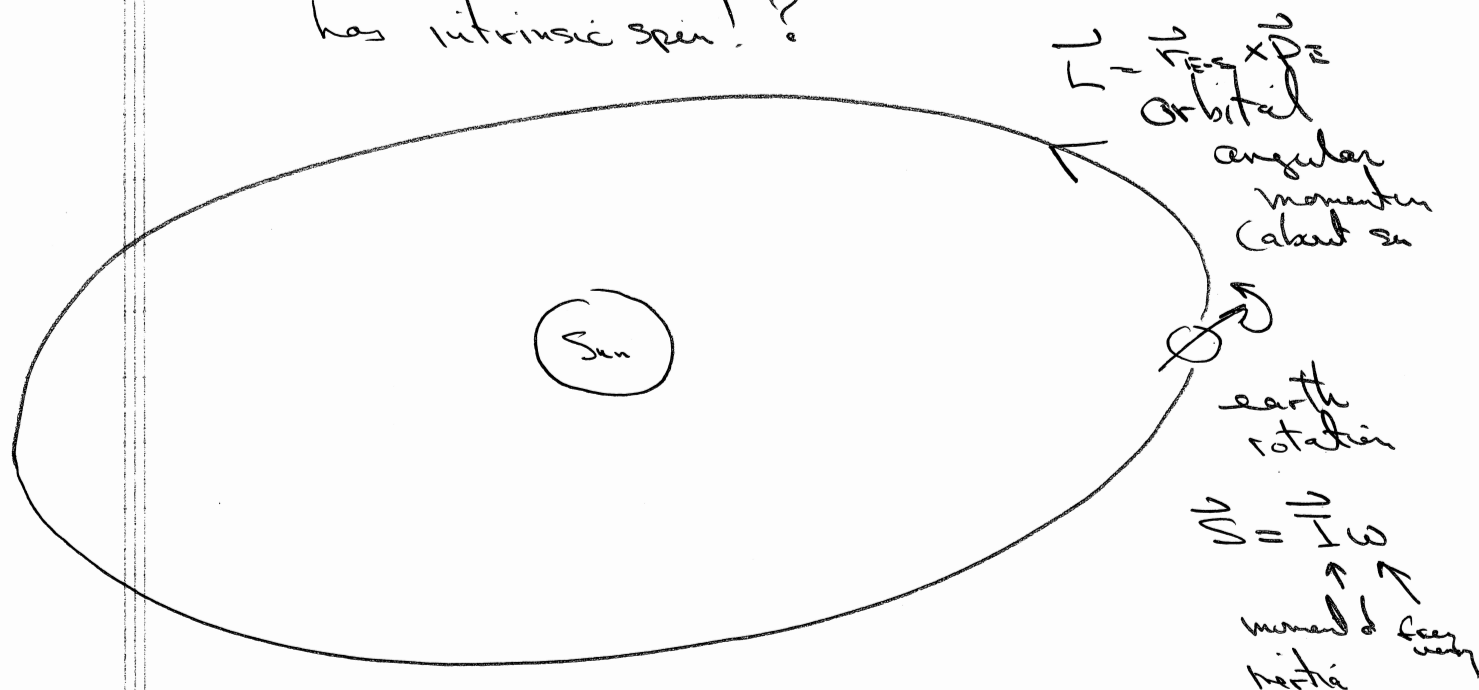
strong B field



!
 ↗
 invite a Theorist to
 lunch

With the experimental apparatus OK, and analysis OK,
the only conclusion is, that there is extra
angular momentum somewhere.

Goudsmit and Uhlenbeck (1925) that the electron
has intrinsic spin! ?



total ang momentum $\vec{J} = \vec{L} + \vec{S}$

The total angular momentum of the electron

$\langle S^2 \rangle = \hbar^2 s(s+1) = \hbar^2 \frac{3}{4}$ $s = \frac{1}{2}$ electrons

$\langle S_z \rangle = m_s \hbar = \pm \frac{1}{2} \hbar$ $m_s = \pm \frac{1}{2}$

note $-s \leq m_s \leq s$
integral jumps

$\hbar$ -component

Intrinsic magnetic moment is

$\mu_s = \frac{e\hbar}{m_e}$ ← factor of 2 higher

Spectroscopic notation

l	0	1	2	3	4	5	6
name	s	p	d	f	g	h	i
	sharp	principle	differ	fundamental			

properties observed in alkali metals

alphabetical order except i

7.8 Fine structure

$$\Delta E = (mc^2) \alpha^4 \frac{1}{n^5}$$

Spin-orbit term

Hyperfine structure

$$\Delta E \propto \frac{m_e}{m_p} \alpha^4 \frac{(mc^2)}{n^5}$$

spin spin interaction

about 2000 x less