Fine Structure of Hydrogen

Application of Perturbation Theory

A sort of "development parameter" in understanding details of the hydrogen atom is the...

FINE STRUCTURE CONSTANT

so named because of the perturbations we now explore...

$$\alpha \equiv \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c}}_{\text{compares electromagnetism to quantum mechanics + relativity.}} \simeq \frac{1}{137}$$

$\Rightarrow$ electromagnetism is "weak"

In Bohr atom, ground state,
(sophomore)

$$\frac{\text{electron velocity}}{c} = \frac{v_e}{c} \simeq \alpha$$

① |Binding Energy| ~ Kinetic Energy (Virial)

$$\sim m_e v^2 = \frac{p^2}{m_e} \text{ (order of magnitude)}$$

$$\sim \alpha^2 m_e c^2$$

② Relativistic Effects $O\Big(\underbrace{\frac{p^2}{m^2c^2}}_{\left(\frac{v_e}{c}\right)^2 \sim \alpha^2}\Big) \times \frac{p^2}{m_e}$

$$\sim \alpha^2 \times \alpha^2 m_e c^2$$

(3) Relativistic + proton "Hyperfine" $\sim \left(\frac{m_e}{m_p}\right) \alpha^4 m_e c^2$

(4) Relativistic Quantum Field Effect (Lamb Shift) $\sim \alpha \cdot \alpha^4 m_e c^2$

ONE POWER.

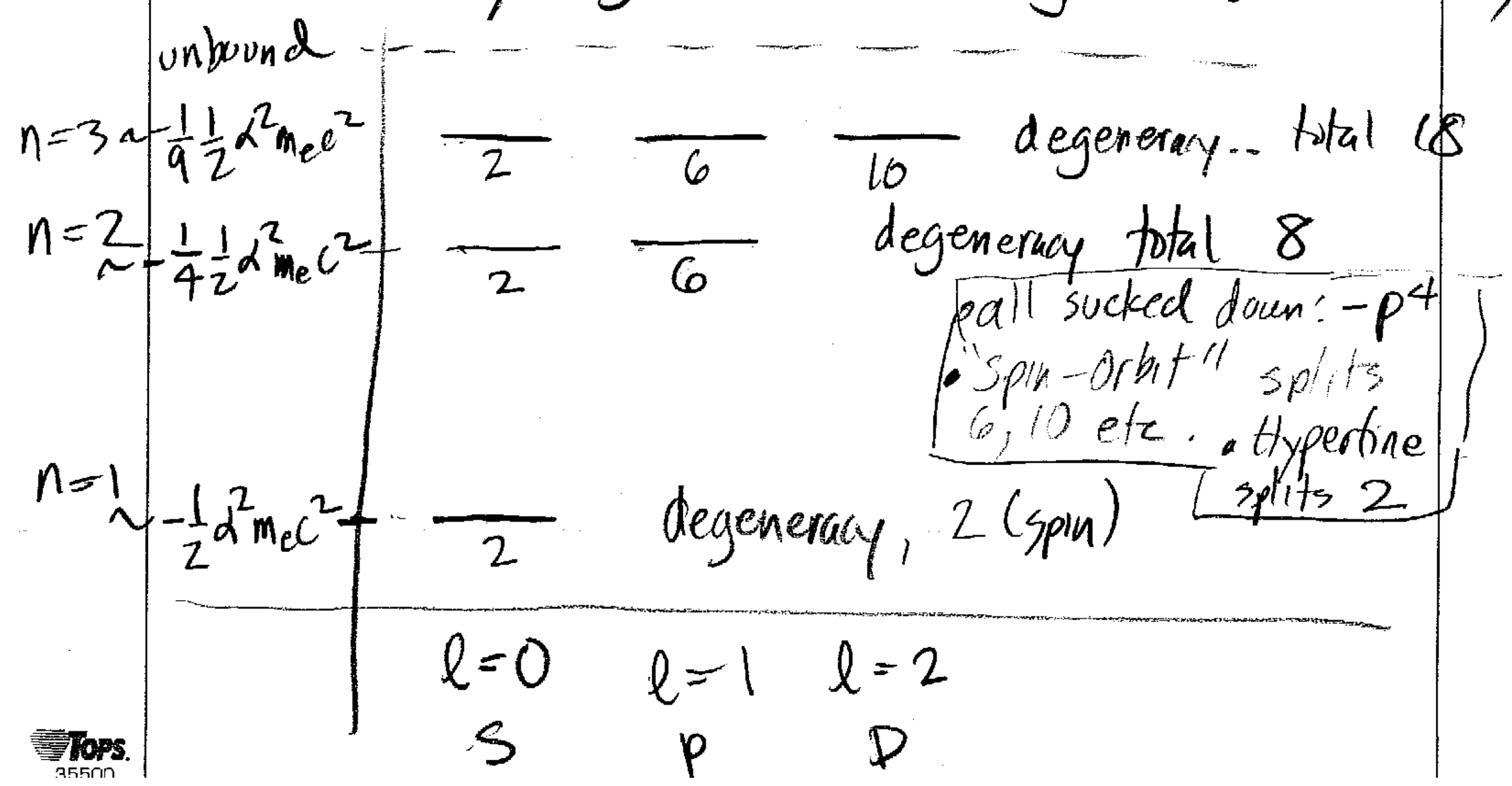
Comment: → Bound states of nucleons, aka, NUCLEI ... $\frac{v}{c} \sim 1/10$

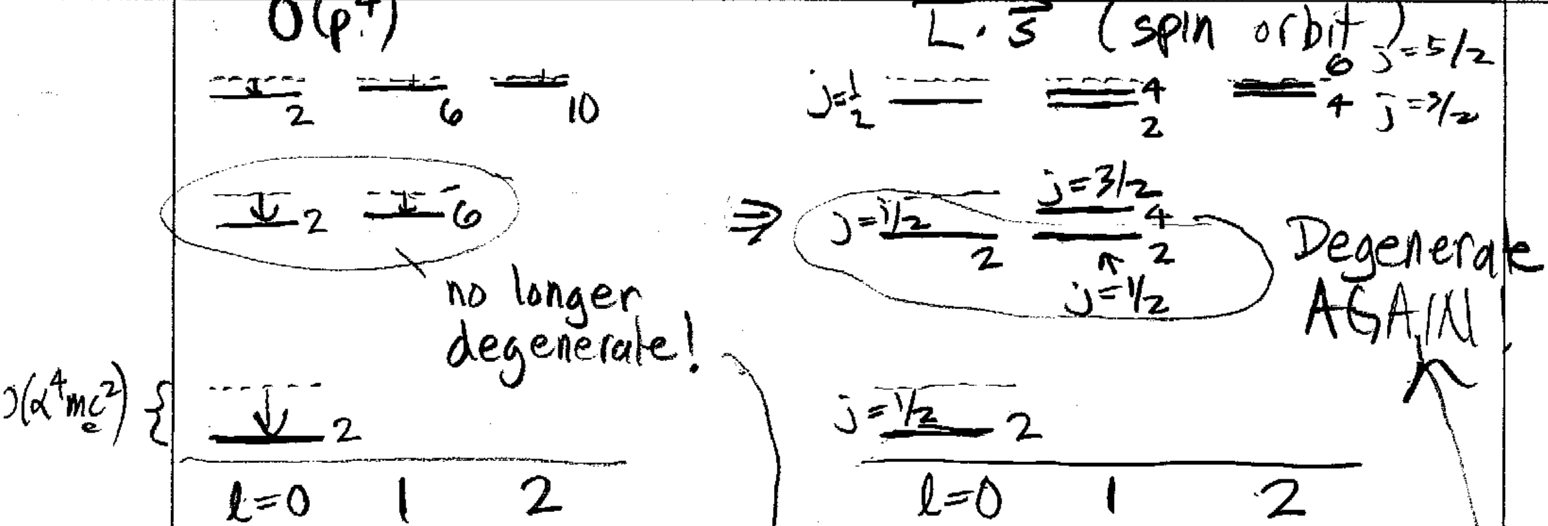
these effects bigger.

→ Bound states of quarks, aka, MESONS / BARYONS, $\frac{v}{c} \sim 1$

these effects HUGE

Recall: hydrogen term diagram (before fine structure)





$O(p^4)$ reduces kinetic energy
$O(\alpha^2)$ correction

$\vec{L}\cdot\vec{S}$ also of $O(\alpha^2)$!

SPLITS degeneracy of the 6, 10 into:

initially degenerate
$$\begin{cases} 6 \to \underbrace{l=1}, \text{ electron spin } \frac{1}{2} \\ 6 = 3 \times 2 \end{cases}$$

$\vec{L}\cdot\vec{S}$ ... this perturbation term is not diagonal in the 6-d degenerate subspace of "good" L quantum #.

$\boxed{\text{Is}}$ diagonal in subspace of eigenvectors of ..

$$\vec{J} = \vec{L} + \vec{S}$$

↪ eigenvalues of $\underline{J}^2$ are $j(j+1)\hbar^2$

j ranges from $|l-s|, |l-s|+1, \ldots\ l+s$

$s=\frac{1}{2}$ ... it is just... $l=0,\ j=1/2$

$l \geq 1,\ j = l-\frac{1}{2},\ l+\frac{1}{2}$

$l=1$: $j=3/2$ (4 states) ; $j=\frac{1}{2}$ (2 states) $\Rightarrow$ degenerate with $l=0, n=2$

There is even more!

- The degeneracy to $O(\alpha^4 mc^2)$ between the $n=2$, $l=0$, $j=\frac{1}{2}$ state + the $n=2$, $l=1$, $j=\frac{1}{2}$ is split at order $\alpha^5 mc^2$ by... Relativistic Quantum Field Theory effects that on first blush, look infinite! Called the LAMB SHIFT, crucial to history of post WWII physics.
- All states further split by "spin-spin" or hyperfine splitting induced by the proton magnetic moment...

$$\vec{I} = \vec{J} + \vec{S}_n \Big\} \; O\left(\frac{m_e}{m_p}\alpha^4 m_e c^2\right)$$

Most important: $l=0$, $n=1$ split into $I=0$, $I=1$, with $\Delta E \Rightarrow$ transition gives photon of $\lambda = 21$ cm, in microwave regime (like cell phone) so it is penetrating ... used to map the spiral arms of the Milky Way galaxy (ours).

Mathematics of this Story:

① Best studied with the Dirac Equation, relativistic generalization of the Schrödinger Equation (S.E.)

② S.E. + perturbation theory... illuminating but WARTY

Warts: at least 5 warts

- non-Hermitian operator ($\hat{p}^4$)
- $\frac{0}{0}$ ($\frac{\text{zero}}{\text{zero}} \rightarrow$ nice limit)
- electron magnetic moment 2 times classical expectation
- "Thomas Precession" = weird relativistic effect of circular $\boxed{\text{acceleration}}$ ← challenging in Special Relativity.
- "Darwin Term"

→ lots of hand waving to get through. "Real Physics" however.

$\boxed{\hat{p}^4}$:

$T = \sqrt{(mc^2)^2 + (cp)^2} - mc^2$ kinetic energy

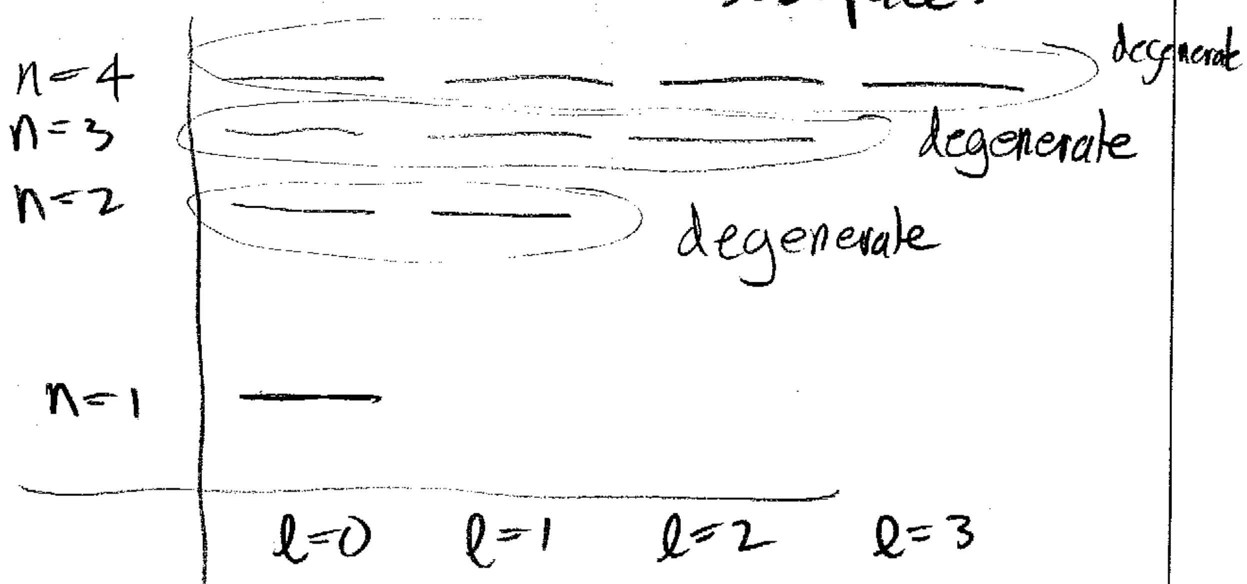
$= (mc^2)\left[1 + \frac{1}{2}\frac{(cp)^2}{(mc^2)^2} + \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\frac{(cp)^4}{(mc^2)^4}\right] - mc^2$

$T \cong \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{perturbation term}}$ (non-relativistic OVERESTIMATES T)

m: technically $= \frac{m_e m_p}{m_e + m_p} \sim m_e$

For a given n = principal quantum #,

$-\frac{p^4}{8m^3c^2}$ is __diagonal__ in the degenerate subspace.



all terms like $\langle \psi_{nl'm'} | \hat{p}^4 | \psi_{nlm} \rangle = 0$

$l' \neq l \quad m' \neq m$

__Why?__ $\hat{p}^4$ is "spherically symmetric," or, a "scalar operator".

__Consequence__: $E_n^1 \equiv E_r^1 = -\frac{1}{8m^3c^2} \langle \psi_{nlm} | \hat{p}^4 | \psi_{nlm} \rangle$

$\leftarrow \hat{p}^2 \cdot \hat{p}^2 \rightarrow$

$E_r^1 = -\frac{1}{8m^3c^2} \langle \hat{p}^2 \psi | \hat{p}^2 \psi \rangle$

Good trick! $\hat{p}^4$ sometimes ill-conditioned ($l=0$) IGNORE

WART

Another good trick:

$$\left[\frac{\hat{p}^2}{2m} + V(\vec{r})\right]\psi_{n\ell m} = E^0_{n\ell}\psi_{n\ell m}$$

$$\hat{p}^2\psi_{n\ell m} = 2m\left(E^0_{n\ell} - V(\vec{r})\right)\psi_{n\ell m}$$

$$\langle \hat{p}^2\psi_{n\ell m}|\hat{p}^2\psi_{n\ell m}\rangle = 4m^2\langle\psi_{n\ell m}|(E^0_{n\ell}-V(\vec{r}))^2|\psi_{n\ell m}\rangle$$

$$\boxed{E^1_r = -\frac{1}{2mc^2}\left[E^{0\,2}_{n\ell} - 2E^0_{n\ell}\langle\psi_{n\ell m}|V(\vec{r})|\psi_{n\ell m}\rangle + \langle\psi_{n\ell m}|V^2(\vec{r})|\psi_{n\ell m}\rangle\right]}$$

Note:
- Dimensions OK.
- Have not yet specified $V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0 r}$ (proton - electron)
  - ⇒ could use for other problems
- for $1/r$, $E^0_{n\ell}$ independent of ℓ.

Now, $V(\vec{r}) = \frac{-e^2}{4\pi\varepsilon_0 r}$

Virial Theorem

$$\left.\begin{aligned}\frac{-e^2}{4\pi\varepsilon_0}\langle\psi_{n\ell m}|\frac{1}{r}|\psi_{n\ell m}\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{n^2 a}\right)\end{aligned}\right\}$$

a = Bohr Radius p.150 4,72

$$\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\langle\psi_{n\ell m}|\frac{1}{r^2}|\psi_{n\ell m}\rangle = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{\underbrace{(\ell+\frac{1}{2})n^3a^2}}$$

- hard to get.
- mathematical

Important: all terms in <u>brackets</u> <u>positive</u>

With some algebra (p.149, 4.70)

$$E_n^0 = -\frac{1}{2}\frac{mc^2\alpha^2}{n^2}$$

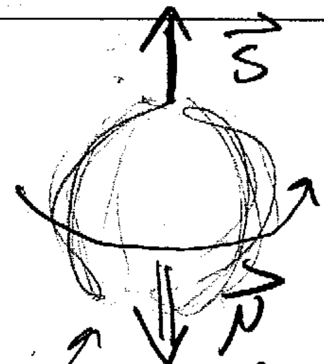
$$\boxed{E_r^1 = -\frac{1}{8}\frac{\alpha^4 mc^2}{n^4}\underbrace{\left[\frac{4n}{l+\frac{1}{2}} - 3\right]}_{\text{always positive.}}}$$ eq 6.57 p.270

n^4 arises from slowing down of electron in higher orbits

Spin-Orbit ($\vec{L}\cdot\vec{S}$) Coupling

- This breaks degeneracy of the $2\cdot(2l+1)$ states
  spin
- LOAD of PHYSICS
  - ⇒ $-\vec{\mu}\cdot\vec{B}$ ... $\vec{\mu}$ of electron, unexpectedly twice as big as expected.
  - ⇒ $\times\frac{1}{2}$, accelerating frame issure ("Thomas Precession")
  - ⇒ Darwin Term

Warts + all.



distributed ball of charge, total charge $-e$

if an electron was a spinning ball of charge, "internal angular momentum" $\vec{S}$, its magnetic moment $\vec{\mu}$ would be (from E+M).

$$\vec{\mu} = \frac{1}{2}\frac{(-e)}{m}\vec{S}$$

SURPRISE SURPRISE

$\underbrace{\text{EXPERIMENTALLY}}_{\text{truly great experiments}}$

$$\vec{\mu}_e = g_e \times \left(-\frac{1}{2}\frac{e}{m}\vec{S}\right)$$

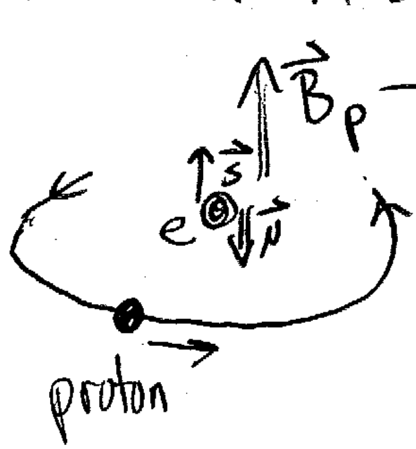
$g_e \simeq 2$] measured to incredible precision!

$g_e = 2.0023193043615$
$\pm .0000000000006$
experiment!
0.3 parts per trillion error

2? WHY?

- Dirac Equation
- "helicity conservation

LOOK AT SITUATION OF $\vec{L} \neq 0$ FROM ELECTRON'S POINT OF VIEW:



$\vec{B}_p \longrightarrow$ proton's motion + $\vec{L}$ causes a $\vec{B}$ field at electron (* an accelerating frame)

$$\vec{B}_p = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\vec{L}$$

Energy this would seem to induce would be $-\vec{\mu}_e \cdot \vec{B}_p$. Naughty effect from accelerating frame, though

Wait! $H'_{so} = \underbrace{-(g_e - 1)\left(-\frac{1}{2}\frac{e}{m}\vec{S}\right)}_{\text{instead of } \vec{\mu}_e\text{!}} \cdot \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2 r^3}\vec{L}$

Thomas Precession

hmm.. looks classical in the end!.

$g_e - 1 \simeq 1$

$$\boxed{H'_{so} \cong +\left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}}$$

$\vec{S}\cdot\vec{L}$ IS NOT DIAGONAL IN THE ORIGINAL "PRODUCT BASIS" of s, ℓ

IS DIAGONAL IN THE BASIS OF EIGENSTATES OF

$\vec{J} = \vec{L} + \vec{S}$

↳ e.v. of $\vec{J}^2$ are

$\hbar^2 J(J+1)$

$$\underbrace{J = \ell - \tfrac{1}{2} \text{ or } \ell + \tfrac{1}{2}}_{s}$$

COOL TRICK:

$$\vec{J}^2 = (\vec{L}+\vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S}$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

IN EIGENBASIS OF J^2, L^2, S^2, M_J, not M_L, M_S

$$\langle \vec{L}\cdot\vec{S}\rangle = \frac{1}{2}\hbar^2\left(j(j+1) - l(l+1) - s(s+1)\right)$$

Only missing piece..

$$\langle \psi_{nlm}|\frac{1}{r^3}|\psi_{nlm}\rangle = \frac{1}{l(l+\frac{1}{2})(l+1)n^3a^3}$$

Wart: BLOWS UP FOR $l=0$

Saved by: $\langle \vec{L}\cdot\vec{S}\rangle = 0$ for $l=0$
+ Darwin term gives $\underline{\underline{0}}$

From above, can get

$$E^1_{so} = \langle \psi_{nlm}|H'_{so}|\psi_{nlm}\rangle$$

AMAZING or PEDESTRIAN (magnetic effects also relativistic!).

Also of order $\alpha^4 mc^2$

$\boxed{\text{TRULY AMAZING}}$ Look back at E_r^1.

All the $\vec{L}\cdot\vec{S}$ term does is....

CHANGE l to j

$$E_r^1 + E_{so}^1 \equiv E_{fs}^1 = \underbrace{-\frac{1}{2}\frac{\alpha^2 mc^2}{n^2}}_{E_n^0} \cdot \underbrace{\frac{\alpha^2}{n^2}}_{\text{relativity}} \cdot \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]$$

- There is <u>new</u> degeneracy, since only j and not "parentage" of l + s matter
- This degeneracy is split by the LAMB SHIFT, $O(\alpha^5 mc^2)$