Fine Structure & 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

\[ \alpha = \frac{1}{4\pi \varepsilon_0} \frac{e^2}{mc} \approx \frac{1}{137} \]

compares electromagnetism to quantum mechanics + relativity.

\Rightarrow \text{electromagnetism is "weak"}

In Bohr atom, ground state,

(sophomore)

\[ \frac{\text{electron velocity}}{c} = \frac{V_e}{c} \approx \alpha \]

1. Binding Energy \( \sim \) Kinetic Energy (Virial)

\[ \sim mc \cdot \frac{\varepsilon}{m_e} \sim \alpha^2 m_e c^2 \]

2. Relativistic Effects

\[ 0 \left( \frac{\varepsilon}{m_e c^2} \right) \times \frac{\varepsilon}{m_e} \]

\[ \left( \frac{V_e}{c} \right)^2 \sim \alpha^2 \times \alpha^2 m_e c^2 \]
3. Relativistic + proton \( \sim \left( \frac{m_e}{m_p} \right) \alpha^4 m_e c^2 \) "Hyperfine"

4. Relativistic Quantum Field Effect (Lamb Shift) \( \sim \alpha \cdot \alpha^4 m_e c^2 \) \( \Rightarrow \) ONE POWER.

Comment: \( \Rightarrow \) Bound states of nucleons, aka, NUCLEI \( \frac{v}{c} \sim \frac{1}{10} \)

these effects bigger.

\( \Rightarrow \) Bound states of quarks, aka, MESONS/BARYONS, \( \frac{v}{c} \sim 1 \)

these effects HUGE

Recall: hydrogen term diagram (before fine structure)

unbound

\[ n = 3 \Rightarrow \frac{11}{4} \alpha^2 m_e c^2 \]

\[ n = 2 \Rightarrow -\frac{11}{4} \alpha^2 m_e c^2 \]

\[ n = 1 \Rightarrow -\frac{1}{2} \alpha^2 m_e c^2 \]

\[ \sqrt{2} \quad \sqrt{6} \quad \sqrt{10} \quad \text{degeneracy} \quad \text{total 18} \]

\[ \sqrt{2} \quad \sqrt{6} \quad \text{degeneracy total 8} \]

Pauli Sucked down: \(-p^4\)

"Spin-orbit" splits (8, 10) etc., hyperfine splits 2

\( \ell = 0 \quad \ell = 1 \quad \ell = 2 \)

\[ s \quad p \quad d \]
\[ O(p^4) \]
\[ \frac{1}{2} \quad 0 \quad 1 \quad 2 \]

\( O(p^4) \) reduces to kinetic energy \( O(x^2) \) correction

\[ \text{no longer degenerate!} \]

\( L \cdot s \) (spin orbit) \( \frac{3}{2} \quad \frac{5}{2} \)
\( J = \frac{1}{2} \quad \frac{3}{2} \quad \frac{5}{2} \)

\( J = \frac{1}{2} \quad \frac{3}{2} \quad \frac{5}{2} \)
\( \Rightarrow J = \frac{1}{2}, \quad J = \frac{3}{2}, \quad J = \frac{5}{2} \)

Degenerate AGAIN

\( l = 0 \quad 1 \quad 2 \)

\( L \cdot s \) is also of \( O(x^2) \)!

\[ \text{Splits degeneracy of the } (6,10) \text{ in } \mathfrak{su}(6) \]

\[ l = 0 \quad 1 \quad 2 \]

Initially degenerate

\[ \begin{align*}
6 & \rightarrow l = 1, \text{ electron spin } \frac{1}{2} \\
6 & = 3 \times 2
\end{align*} \]

\( L \cdot s \) this perturbation term is not diagonal in the \( 6-l \) degenerate subspace of "good" \( L \) quantum number.

\[ \text{Is diagonal in subspace of eigenvectors of } \]
\[ J = L + \frac{3}{2} \]

\[ \text{Eigenvalues of } J^2 \]
\[ \text{are } J(J+1)\hbar^2 \]
\( J \text{ ranges from } |l-s|, |l-s|+1, \ldots, l+s \)

\( s = \frac{1}{2} \ldots \) it is just...
\( l = 0, \quad J = \frac{1}{2} \)
\( l > 1, \quad J = l - \frac{1}{2}, \ldots, l + \frac{1}{2} \)

\( l = 1; \quad J = \frac{3}{2} (4 \text{ states}) \); \( l = \frac{1}{2} (2 \text{ states}) \) are degenerate with \( l = 0, \) \( \frac{1}{2} \).
There is even more!

- The degeneracy to \( O(\alpha^4 m c^2) \) between the \( n=2, l=0, j=\frac{1}{2} \) state and the \( n=2, l=1, j=\frac{1}{2} \) is split at order \( \alpha^5 m c^2 \) 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...

\[
\hat{I} = \hat{J} + \hat{S}_n \quad \Rightarrow \quad O\left(\frac{m_e}{m_p} \alpha^4 m c^2\right)
\]

Most important: \( l=0, n=1 \) split into \( I=0, I=1 \), with

\( \Delta E \) 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).
\[ v = \sqrt{\left( mc^2 \right)^2 + \left( \frac{1}{2} \frac{1}{c^2} \right)^2} - mc^2 \]

Lots of hand waving to get through. "Real physics" however, challenging in Special Relativity. "Relativistic effect of circular motion" weird.

Darwin Term non-Hermitian operator \( \sigma^4 \).

Wants electron magnetic moment 2 times classical expectation. WANTS illuminating, but "WARPY..."

\( \theta \) S.E. + perturbation theory... Schrödinger Equation (S.E.) relativistic generalization of the Dirac Equation.
\[ T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \] (non-relativistic term)

\[ \text{perturbation m: technically} = \frac{m_e m_p}{m_e + m_p} \]

For a given \( n = \text{principal quantum \#} \), \( \frac{p^4}{8m^3c^2} \) is diagonal in the degenerate subspace.

\[ \begin{align*}
  n &= 4 \\
  n &= 3 \\
  n &= 2 \\
  n &= 1 \\
  l &= 0 \\
  l &= 1 \\
  l &= 2 \\
  l &= 3
\end{align*} \]

all terms like \( \langle \psi_{n'l'm'} | \hat{P}^4 | \psi_{n'l'm} \rangle = 0 \) \( \forall l' \neq l \) \( m' \neq m \)

Why? \( \hat{P}^4 \) is "spherically symmetric," or, a "scalar operator".

Consequence: \( E_n^1 \equiv \bar{E}_r = -\frac{1}{8m^3c^2} \langle \psi_{n'l'm'} | \hat{P}^4 | \psi_{n'l'm} \rangle \uparrow \)

\[ \langle \hat{P}^2 \cdot \hat{P}^2 \rangle \]

Good trick! \[ \hat{P}^4 \] sometimes ill-conditioned \( (l = 0) \) Ignore
Another good trick:

\[
\left( \frac{\hat{p}^2}{2m} + V(\vec{r}) \right) \psi_{nle} = E_{ne} \psi_{nle}
\]

\[
\hat{p}^2 \psi_{nle} = 2m \left( E_{ne}^0 - V(\vec{r}) \right) \psi_{nle}
\]

\[
\langle \hat{p}^2 \psi_{nle} | \hat{p}^2 \psi_{nle} \rangle = 4m^2 \langle \psi_{nle} | (E_{ne}^0 - V(\vec{r}))^2 | \psi_{nle} \rangle
\]

\[
E_{r}^1 = -\frac{1}{2m} \left[ E_{ne}^{02} - 2E_{ne}^0 \langle \psi_{nle} | V(\vec{r}) | \psi_{nle} \rangle + \langle \psi_{nle} | V(\vec{r})^2 | \psi_{nle} \rangle \right]
\]

**Note:**
- Dimensions OK.
- Have not yet specified
  
  \[ V(\vec{r}) = -\frac{e^2}{4\pi \varepsilon_0 r} \quad \text{(proton - electron)} \]
- Could use for other problems
  
  For \( \frac{1}{r} \), \( E_{ne} \) independent of \( e \).

**Now,** \( V(\vec{r}) = \frac{-e^2}{4\pi \varepsilon_0 r} \quad \text{Virial Theorem} \)

\[
-\frac{e^2}{4\pi \varepsilon_0} \langle \psi_{nle} | \frac{1}{r} | \psi_{nle} \rangle = -\frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{n^2} \right) \quad \text{a = Bohr Radius} \]

\[
\left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \langle \psi_{nle} | \frac{1}{r^2} | \psi_{nle} \rangle = \left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \left( \frac{1}{(l+\frac{1}{2})n^3} \right) \quad \text{hard to get.} \]

\[
\left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \left( \frac{1}{(l+\frac{1}{2})n^3} \right) \quad \text{mathematical} \]

**Important:** all terms in brackets positive
With some algebra (p. 149, 4.70)

\[ E_n^0 = -\frac{1}{2} \frac{mc^2}{h^2} \alpha^2 \]

\[ E_r^1 = -\frac{1}{8} \alpha^4 \frac{mc^2}{n^4} \left[ \frac{4n}{l+\frac{3}{2}} - 3 \right] \quad \text{eq. 6.57} \]

\[ n^4 \text{ arises always positive.} \]

\[ \text{from slowing down of electron in higher orbits} \]

**Spin-Orbit (L \cdot S) Coupling**

- This breaks degeneracy of the 2 \cdot (2l+1) states

\[ \text{spin} \]

- LOAD of PHYSICS

\[ \Rightarrow - \vec{p} \cdot \vec{B} \quad \text{\( \vec{p} \) of electron, unexpectedly twice as big as expected.} \]

\[ \Rightarrow x \frac{1}{2} 1 \text{ accelerating frame issue ("Thomas Precession"))} \]

\[ \Rightarrow \text{Darwin Term} \]

\[ \text{Wars \& all.} \]
if an electron was a spinning ball of charge, "internal angular momentum" \( \vec{J} \), its magnetic moment \( \vec{\mu} \) would be (from E+M):

\[
\vec{\mu} = \frac{1}{2} \left( -e \right) \frac{\vec{J}}{m}
\]

**SURPRISE SURPRISE**

**EXPERIMENTALLY**

\[
\mu_e = g_e \left( -\frac{1}{2} \frac{e}{m} \frac{\vec{J}}{m} \right)
\]

*truly great experiments*

\[
ge_e = 2.0023193043615 \pm 0.0000000000006
\]

\[0.3 \text{ parts per trillion}
\]

**Dirac Equation**

"helicity conservation"

**LOOK AT SITUATION OF \( L \neq 0 \) FROM ELECTRON'S POINT OF VIEW:**

\[ \vec{B}_p \rightarrow \text{proton's motion} + \vec{L} \]

causes a \( \vec{B} \) field at electron (in an accelerating frame)

\[
\vec{B}_p = \frac{1}{4\pi\varepsilon_0} \frac{e}{mc^2 r^3} \vec{L}
\]
Energy this would seem to induce would be \(-\vec{\nu}_e \cdot \vec{B}_p\). Naught effect from accelerating frame, though

\[
H'_{\text{so}} = -(g e^{-1}) \left(-\frac{1}{2} \frac{e^2}{m^2} \frac{\vec{s} \cdot \vec{L}}{s} \right) \cdot \frac{1}{4\pi \varepsilon_0} \frac{e}{mc^2 r^3} \vec{L}
\]

\[\text{Wart!} \quad g e^{-1} \approx 1\]

Thomas hmm. looks classical

\[H'_{\text{so}} \approx + \left(\frac{e^2}{8\pi \varepsilon_0}\right) \frac{1}{m^2 c^2} \frac{\vec{s} \cdot \vec{L}}{s} \]

\(\vec{s} \cdot \vec{L}\) is not diagonal in the original "product basis" of \(s, \vec{L}\).

\(\vec{J} = \vec{L} + \vec{s}\)

\(\Rightarrow e.v. \text{ of } \vec{J}^2 \text{ are } \hbar^2 \vec{J}(\vec{J}+1)\)

\(J = l - \frac{1}{2} \text{ or } l + \frac{1}{2}\)
**Cool Trick:**

\[ J^2 = (L + \frac{3}{2})^2 = L^2 + \frac{9}{4} + 2L\cdot\frac{3}{2} \]

\[ L\cdot\frac{3}{2} = \frac{1}{2}(J^2 - L^2 - \frac{3}{4}) \]

In eigenbasis of \( J^2, L^2, S^2, M_J \), not \( M_L, M_S \)

\[ \langle L\cdot S \rangle = \frac{1}{2} \hbar^2 (j(j+1) - l(l+1) - s(s+1)) \]

Only missing piece...

\[ \langle \Psi_{nem} | \frac{1}{r^3} | \Psi_{nem} \rangle = \frac{1}{e(l+\frac{1}{2})(l+1)n^3a^3} \]

Warn: Blows up for \( l=0 \)

(Saved by: \( \langle L\cdot S \rangle = 0 \) for \( l=0 \)

+ Darwin term gives 0)

From above, can get

\[ E_{so}^{1} = \langle \Psi_{nem} | H_{so}^{1} | \Psi_{nem} \rangle \]

Amazing or pedestrian (magnetic effects also relativistic!)

Also of order \( \alpha^4 mc^2 \)
"TRULY AMAZING!" Look back at $E_r^1$.

All the $\ell,s$ term does is change $\ell$ to $j$.

\[
E_r^1 + E_{so}^1 = E_{fs} = \frac{-1}{2} \frac{\alpha^2 mc^2}{n^2} \cdot \frac{\alpha^2}{n^2} \cdot \left[ \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right]
\]

\[
E_n^0 \quad \text{relativity}
\]

- There is new degeneracy, since only $j$ and not "parentage" of $\ell + s$ matter.

- This degeneracy is split by the \textsc{LAMB SHIFT} $O(\alpha^5 mc^2)$.