Physics 472 Lecture 13

Applications of Perturbation Theory:

The Fine Structure of Hydrogen

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r}$$

- $$E_n^{(0)} = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}, \quad n = 1, 2, \ldots, \infty$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N} \qquad \mu = \frac{m_e}{1 + m_e/m_N}$$

Fine-structure constant

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137.036}$$

- $$E_n^{(0)} = -\alpha^2 \frac{\mu c^2}{2n^2}$$

These energy levels, originally found by Bohr, are not the whole story, however. We have already seen that there is an additional spin-orbit interaction, that was omitted from H_0. There is also a relativistic correction to the kinetic energy, which is comparable in size. Together, these two effects determine the <u>fine structure</u> of hydrogen. There are even higher-order effects due to quantum electrodynamics (Lamb shift) and due to the magnetic dipole interaction of the electron and proton (hyperfine structure).

Bohr energies	$\mathcal{O}(\alpha^2 m_e c^2)$
Fine structure	$\mathcal{O}(\alpha^4 m_e c^2)$
Lamb shift	$\mathcal{O}(\alpha^5 m_e c^2)$
Hyperfine structure	$\mathcal{O}\left(\frac{m_e}{m_p} \alpha^4 m_e c^2\right)$

First, the fine structure. The <u>spin-orbit interaction</u> is

$$H_{s.o.} = \left(\frac{g}{4 m_e^2 c^2} \frac{1}{r} \frac{dV}{dr}\right) \vec{L} \cdot \vec{S},$$

where $g = 2 + \frac{\alpha}{\pi} + \cdots \simeq 2.002$

and $V(r) = -\frac{e^2}{r}$ (see lecture 9).

$$H_{s.o.} \cong \frac{e^2}{2 m_e^2 c^2 r^3} \vec{L} \cdot \vec{S}$$

Degenerate perturbation theory:

$[\vec{L}^2, H_0] = 0$, $[\vec{L}^2, H_{s.o.}] = 0$,

so $H_{s.o.}$ does not couple states with different ℓ. Eigenvalues of H_0 are independent of $\vec{S}$ (degenerate).

Eigenstates of $H_{s.o.}$ are eigenstates of $\vec{J}^2$, with $j = \ell \pm 1/2$

$$\vec{L} \cdot \vec{S} \, | \ell s j m \rangle = \frac{1}{2} \left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right) | \ell s j m \rangle$$

$$E^{(1)}_{s.o.} = \frac{e^2}{2m_e^2c^2} \langle n\ell j m | \frac{\vec{L}\cdot\vec{S}}{r^3} | n\ell j m \rangle$$

$$= \frac{e^2\hbar^2\left(j(j+1) - \ell(\ell+1) - \frac{3}{4}\right)}{4m_e^2c^2} \langle n\ell | \frac{1}{r^3} | n\ell \rangle$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)\, n^3 a_0^3},$$

where $a_0 = \frac{\hbar^2}{m_e e^2}$ = Bohr radius

$$\boxed{E^{(1)}_{s.o.} = \frac{m_e c^2}{4}\left(\frac{e^2}{\hbar c}\right)^4 \frac{j(j+1) - \ell(\ell+1) - 3/4}{n^3 \ell(\ell+1/2)(\ell+1)}}$$

$E^{(1)}_{s.o.}$ is apparently undefined for $\ell=0$ ($j=1/2$) since both numerator and denominator are zero. In fact $E^{(1)}_{s.o.}=0$ for $\ell=0$, since in that case $\vec{L}\cdot\vec{S}=0$

Relativistic correction to the kinetic energy

According to Einstein, the kinetic energy of a particle of rest mass m_e is

$$T = \sqrt{\vec{p}^{\,2}c^2 + m_e^2c^4} - m_e c^2$$

$$= m_e c^2\left[\sqrt{1+\left(\frac{\vec{p}}{m_e c}\right)^2} - 1\right]$$

$$= \frac{\vec{p}^{\,2}}{2m_e} - \frac{\vec{p}^{\,4}}{8m_e^3c^2} + \mathcal{O}(\vec{p}^{\,6})$$

The lowest-order relativistic correction is

$$H^{(1)}_{rel} = -\frac{\vec{p}^{\,4}}{8m_e^3c^2} = -\frac{1}{2m_e c^2}\left(\frac{\vec{p}^{\,2}}{2m_e}\right)^2$$

$[H^{(1)}_{rel}, \vec{L}^2] = 0$, $[H^{(1)}_{rel}, L_z] = 0$,

so the eigenstates of H_0, $|n\ell m\rangle$ are the "good" states for deg. pert. thy.

$$E^{(1)}_{rel} = \langle n\ell m | H^{(1)}_{rel} | n\ell m\rangle$$

$$= -\frac{1}{2m_e c^2}\left\langle\left(\frac{\vec{p}^2}{2m_e}\right)^2\right\rangle$$

To estimate $\left\langle\left(\frac{\vec{p}^2}{2m_e}\right)^2\right\rangle$, note that $\left\langle\frac{\vec{p}^2}{2m_e}\right\rangle = \frac{m_e e^4}{2\hbar^2}\frac{1}{n^2}$.

Thus, one would expect

$$\left\langle\left(\frac{\vec{p}^2}{2m_e}\right)^2\right\rangle \sim \left(\frac{m_e e^4}{2\hbar^2 n^2}\right)^2 = \left(E^{(0)}_n\right)^2$$

In fact,

- $$\left\langle \left(\frac{\vec{p}}{2m_e}\right)^2 \right\rangle = \left[\frac{4n}{\ell + 1/2} - 3\right] \left(E_n^{(0)}\right)^2$$

(same dependence on m_e, e, and $\hbar$; different dep. on n + ℓ.)

Finally,

- $$\boxed{E_{rel}^{(1)} = -\frac{m_e c^2}{8} \left(\frac{e^2}{\hbar c}\right)^4 \frac{1}{n^4} \left[\frac{4n}{\ell + 1/2} - 3\right]}$$

As promised, both $E_{s.o.}^{(1)}$ and $E_{rel}^{(1)}$ are $\mathcal{O}(m_e c^2 \alpha^4)$. Combining them gives

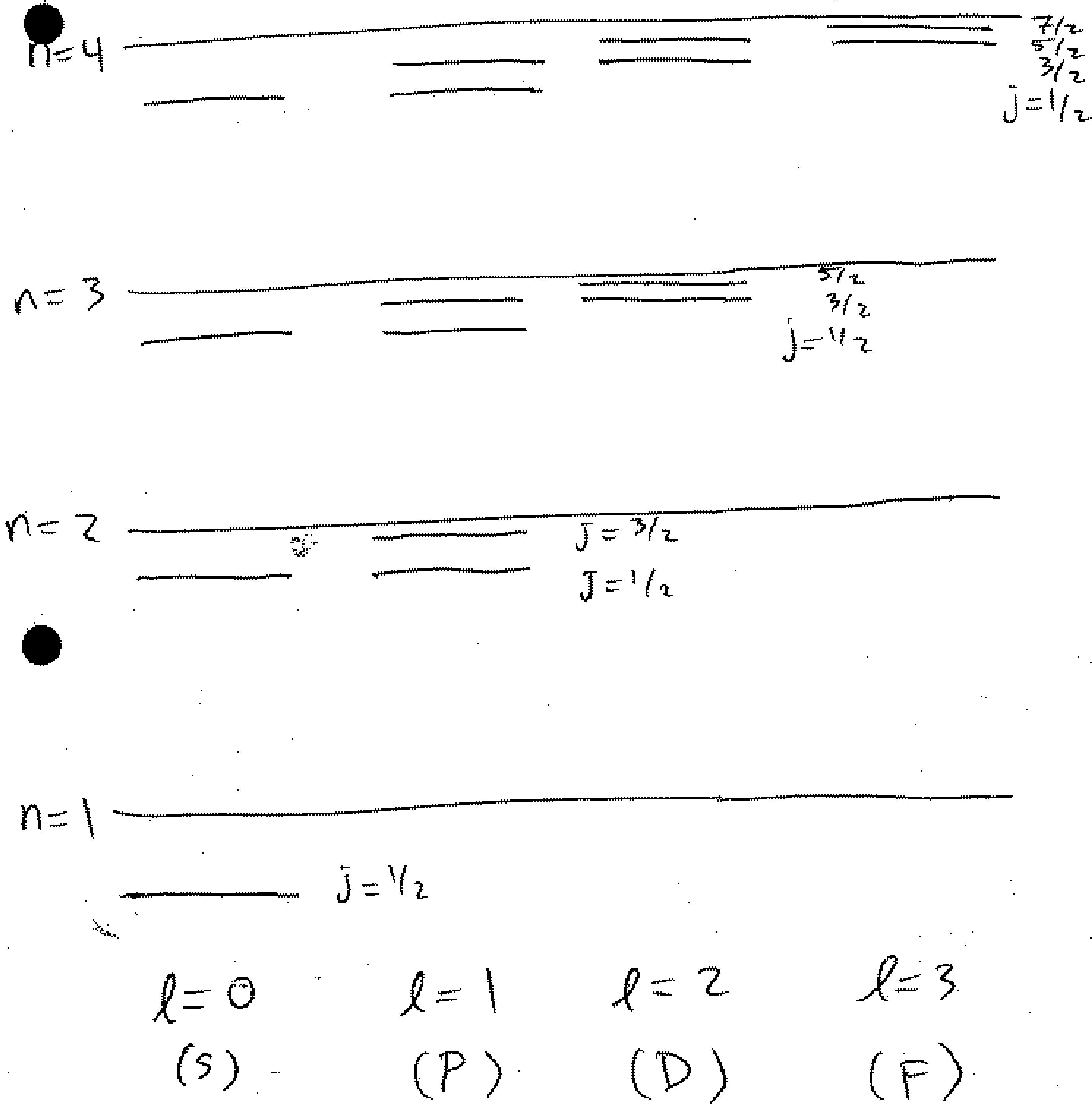
- $$E_{f.s.}^{(1)} = \frac{\left(E_n^{(0)}\right)^2}{2 m_e c^2} \left(3 - \frac{4n}{j + 1/2}\right)$$

The energy levels of hydrogen, including the fine structure, are

$$E_{nj} = -\frac{\mu e^4}{2\hbar^2 n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]$$

The energy shift due to fine structure is always negative.

The good quantum numbers are n, ℓ, s, j, and m_j (not m_s or m_ℓ). For a given n, the degeneracy for $\ell = 0, 1, \ldots, n-1$ is lifted.



Energy levels of hydrogen, including the fine structure (not to scale).

Hyperfine Splitting

- The proton also has a magnetic dipole moment

$$\vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p, \quad \left(\vec{\mu}_e = -\frac{e}{m_e} \vec{S}_e \right)$$

with $g_p = 5.59$.

- According to classical electrodynamics, a dipole $\vec{\mu}$ sets up a magnetic field

$$\vec{B} = \frac{3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}}{r^3} + \frac{8\pi}{3}\vec{\mu}\,\delta(\vec{r}).$$

- The hyperfine Hamiltonian, describing

the magnetic dipole-dipole interaction of the electron and proton, is thus

$$H^{(1)}_{h.f.} = \frac{g_p e^2}{2m_p m_e} \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3}$$

$$+ \frac{4\pi g_p e^2}{3m_p m_e} \vec{S}_p \cdot \vec{S}_e \, \delta(\vec{r})$$

$$E^{(1)}_{h.f.} = \frac{g_p e^2}{2m_p m_e} \left\langle \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \right\rangle$$

$$+ \frac{4\pi g_p e^2}{3m_p m_e} \langle \vec{S}_p \cdot \vec{S}_e \rangle |\psi(0)|^2 .$$

In the ground state (or any other state with $l=0$), the wave function is spherically symmetric, so the first expectation value vanishes.

On the other hand

- $|\psi_{100}(0)|^2 = \dfrac{1}{\pi a_0^3}$, so

$$E^{(1)}_{h.f.} = \frac{4 g_p e^2}{3 m_p m_e a_0^3} \langle \vec{S}_p \cdot \vec{S}_e \rangle$$

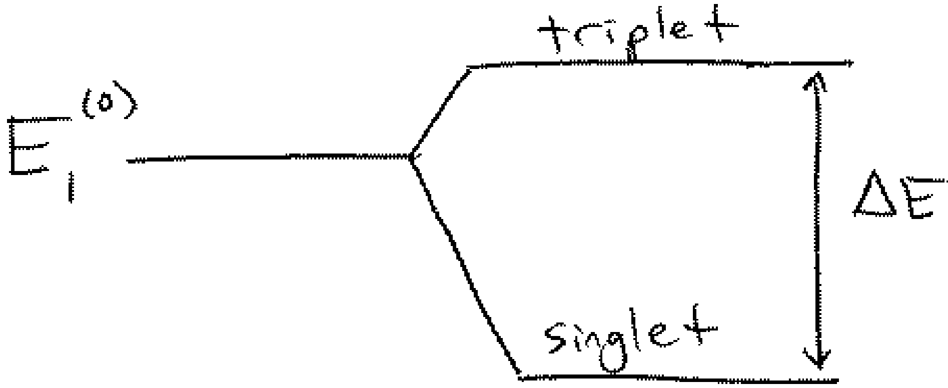
in the ground state.

- Recall $\quad \vec{S}_p \cdot \vec{S}_e = \begin{cases} \hbar^2/4 & \text{(triplet)} \\ -3\hbar^2/4 & \text{(singlet)} \end{cases}$

$$\Delta E_{h.f.} = \frac{4 g_p e^2 \hbar^2}{3 m_p m_e a_0^3} = 5.88 \times 10^{-6}\, eV$$

- $$= \frac{4}{3} g_p \frac{m_e}{m_p} (m_e c^2) \left(\frac{e^2}{\hbar c}\right)^4$$

Hyperfine splitting:



$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz}$$

$$\lambda = \frac{c}{\nu} = 21 \text{ cm}$$

This characteristic microwave radiation from hydrogen permeates the universe.