CHAPTER 6: AN APPLICATION OF PERTURBATION THEORY
THE FINE AND HYPERFINE STRUCTURE OF THE HYDROGEN ATOM

(From Cohen-Tannoudji, Chapter XII)

We will now incorporate a weak relativistic effects as perturbation of the non-relativistic Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{H}_0 + W \\ &= \underbrace{m_e c^2 + \frac{\hat{\vec{P}}^2}{2m_e} + V(R)}_{\hat{H}_0} \underbrace{-\frac{\hat{\vec{P}}^4}{8m_e^3 c^2}}_{\hat{W}_{mv}} \underbrace{+\frac{1}{2m_e^2 c^2}\frac{1}{R}\frac{\mathrm{d}V(R)}{\mathrm{d}R}\hat{\vec{L}}\cdot\hat{\vec{S}}}_{\hat{W}_{SO}} \underbrace{+\frac{\hbar^2}{8m_e^2 c^2}\Delta V(R)}_{\hat{W}_D} + \ldots \end{aligned} \quad (6.1)$$

$\hat{W}_{mv}$ - variation of mass with velocity

$\hat{W}_{SO}$ - spin-orbit coupling

$\hat{W}_D$ - Darwin term

The energies relevant to the relativistic effects are weak compared to the energy associated with $\hat{H}_0$

$$\frac{\hat{W}_{mv}}{\hat{H}_0} \simeq \frac{\hat{W}_{SO}}{\hat{H}_0} \simeq \frac{\hat{W}_D}{\hat{H}_0} \simeq \frac{\hat{W}_{mv}}{\hat{H}_0} \quad \simeq \quad \alpha^2 \simeq \left(\frac{1}{137}\right)^2 \tag{6.2}$$

In addition we will consider hyperfine structure which comes from the interaction of the electron and nuclear magnetic momenta

$$\hat{W}_{hf} \quad = \quad -\frac{\mu_0}{4\pi}\left\{\frac{q}{m_e R^3}\hat{\vec{L}} \cdot \hat{\vec{M}}_I + \frac{1}{R^3}\left[3\left(\hat{\vec{M}}_S \cdot \hat{n}\right)\left(\hat{\vec{M}}_I \cdot \hat{n}\right) - \hat{\vec{M}}_S \cdot \hat{\vec{M}}_I\right]\right. \tag{6.3}$$

$$\left. +\frac{8\pi}{3}\hat{\vec{M}}_S \cdot \hat{\vec{M}}_I \delta\left(\vec{R}\right)\right\} \simeq \frac{\hat{W}_{SO}}{2000} \tag{6.4}$$

$$\hat{\vec{M}}_I = \frac{g_P \mu_n \hat{\vec{I}}}{\hbar}, \;\; \mu_n = \frac{q_P \hbar}{2M_P} \tag{6.5}$$

Fine structure of the $n = 2$ level

$2s$ ($n = 2$, $l = 0$) and $2p$ ($n = 2$, $l = 1$)

$$E = -\frac{E_I}{4} = -\frac{1}{8}\mu c^2\alpha^2 \tag{6.6}$$

Orbital angular momentum $\hat{L}_z$: $l = 0$, $m = 0$ and $l = 1$, $m = +1, 0, -1$
Electron spin $\hat{S}_z$: $m = \pm 1/2$
Nuclear spin $\hat{I}_z$: $m = \pm 1/2$

The perturbation Hamiltonian

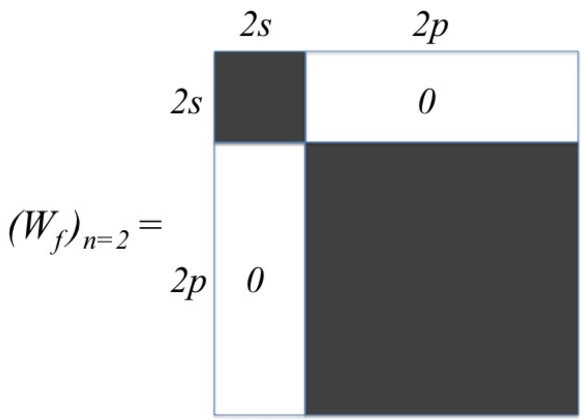
$$\hat{W}_f = \hat{W}_{mv} + \hat{W}_{SO} + \hat{W}_D \tag{6.7}$$

$$\hat{W} = \hat{W}_f + \hat{W}_{hf} \tag{6.8}$$

Matrix representation of $\hat{W}_f$

16×16 matrix

– $\hat{W}_f$ does not act on ths spin variables of the proton
– $\hat{W}_f$ does not connect the $2s$ and $2p$ subshells
– $\hat{L}^2$ commutes with $\hat{W}_f$



1. $2s$ subshell

   $m_s = \pm 1/2 \Rightarrow$ 2 dimensional

   $\hat{W}_{mv}$ and $\hat{W}_D$ do not depend on $\hat{\vec{S}}$

   $\Rightarrow$ they are proportional to a unit matrix and are given as

$$\left\langle \hat{W}_{mv} \right\rangle_{2s} = \langle n = 2; l = 0, m_L = 0| - \frac{\hat{\vec{P}}^4}{8m_e^3c^2}|n = 2; l = 0, m_L = 0\rangle$$

$$= -\frac{13}{128}m_e c^2 \alpha^4 \tag{6.9}$$

$$\left\langle \hat{W}_D \right\rangle_{2s} = \langle n = 2; l = 0, m_L = 0|\frac{\hbar^2}{8m_e^2c^2}\Delta V(R)|n = 2; l = 0, m_L = 0\rangle$$

$$= \frac{1}{16}m_e c^2 \alpha^4 \tag{6.10}$$

and since $l = 0$

$$\left\langle \hat{W}_{SO} \right\rangle = 0 \tag{6.11}$$

Thus the fine structure terms lead to shifting the $2s$ subshell as a whole by an amount

$$\left\langle \hat{W}_{mv} \right\rangle + \left\langle \hat{W}_{D} \right\rangle + \left\langle \hat{W}_{SO} \right\rangle = -\frac{5m_e c^2 \alpha^4}{128} \tag{6.12}$$

2. $2p$ subshell

(a) $\hat{W}_{mv}$ and $\hat{W}_D$ terms

– commute with $\hat{\vec{L}}$ and do not act on spin $\hat{\vec{S}}$ variables

$\Downarrow$

a multiple of a unit matrix

$$\left\langle \hat{W}_{mv} \right\rangle_{2p} = -\frac{7}{384} m_e c^2 \alpha^4 \tag{6.13}$$

$$\left\langle \hat{W}_D \right\rangle_{2p} = 0 \tag{6.14}$$

(See Complement BXII)

(b) $\hat{W}_{SO}$

various elements:

$$\langle n=2; l=1; s=\frac{1}{2}; m_L'; m_S' | \xi(R) \hat{\vec{L}} \cdot \hat{\vec{S}} | n=2; l=1; s=\frac{1}{2}; m_L; m_S \rangle$$

$$\xi(R) = \frac{e^2}{2m_e^2c^2}\frac{1}{R^3} \tag{6.15}$$

In $\{|\vec{r}\rangle\}$ representation, we can separate the radial part of the matrix elements from the angular and spin parts:

$$\xi_{2p} \langle l=1; s=\frac{1}{2}; m_L'; m_S' | \hat{\vec{L}} \cdot \hat{\vec{S}} | l=1; s=\frac{1}{2}; m_L; m_S \rangle \tag{6.16}$$

$$\xi_{2p} = \frac{e^2}{2m_e^2c^2} \int_0^\infty \frac{1}{r^3} |R_{21}(r)|^2 r^2 \mathrm{d}r = \frac{1}{48\hbar^2} m_e c^2 \alpha^4 \tag{6.17}$$

Problem: the diagonalization of the $\xi_{2p} \hat{\vec{L}} \cdot \hat{\vec{S}}$ operator

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Basis $\{|l = 1; s = 1/2; m_L; m_S\rangle\}$
– common eigenstates of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, $\hat{S}_z$

Introducing the total angular momentum

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} \tag{6.18}$$

$$\left\{|l = 1; s = \frac{1}{2}; J, m_J\rangle\right\} \tag{6.19}$$

Addition of angular momentum: $J = 1 + 1/2 = 3/2$ and $J = 1 - 1/2 = 1/2$

$$\hat{J}^2 = \left(\hat{\vec{L}} + \hat{\vec{S}}\right)^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\vec{L}} \cdot \hat{\vec{S}} \quad (6.20)$$

then

$$\xi_{2p}\hat{\vec{L}} \cdot \hat{\vec{S}} = \frac{1}{2}\xi_{2p}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \quad (6.21)$$

$$\begin{aligned} & \xi_{2p}\hat{\vec{L}} \cdot \hat{\vec{S}}|l = 1; s = \frac{1}{2}; J, m_J\rangle \\ = \; & \frac{1}{2}\xi_{2p}\hbar^2\left[J(J+1) - 2 - \frac{3}{4}\right]|l = 1; s = \frac{1}{2}; J, m_J\rangle \end{aligned} \quad (6.22)$$

The eigenvalues of $\xi_{2p}\hat{\vec{L}} \cdot \hat{\vec{S}}$ depend only on J and not on m_J, and are equal to

$$J = \frac{1}{2}: \qquad \frac{1}{2}\xi_{2p}\left[\frac{3}{4} - 2 - \frac{3}{4}\right]\hbar^2 = -\xi_{2p}\hbar^2 = -\frac{1}{48}m_e c^2 \alpha^4 \tag{6.23}$$

$$J = \frac{3}{2}: \qquad \frac{1}{2}\xi_{2p}\left[\frac{15}{4} - 2 - \frac{3}{4}\right]\hbar^2 = +\frac{1}{2}\xi_{2p}\hbar^2 = \frac{1}{96}m_e c^2 \alpha^4 \tag{6.24}$$

The six-fold degeneracy of the $2p$ level is therefore partially removed by $\hat{W}_{SO}$

The fine structure of the $n = 2$ level: energies

$2s_{1/2}$

$$-\frac{5}{128}m_e c^2\alpha^4 \tag{6.25}$$

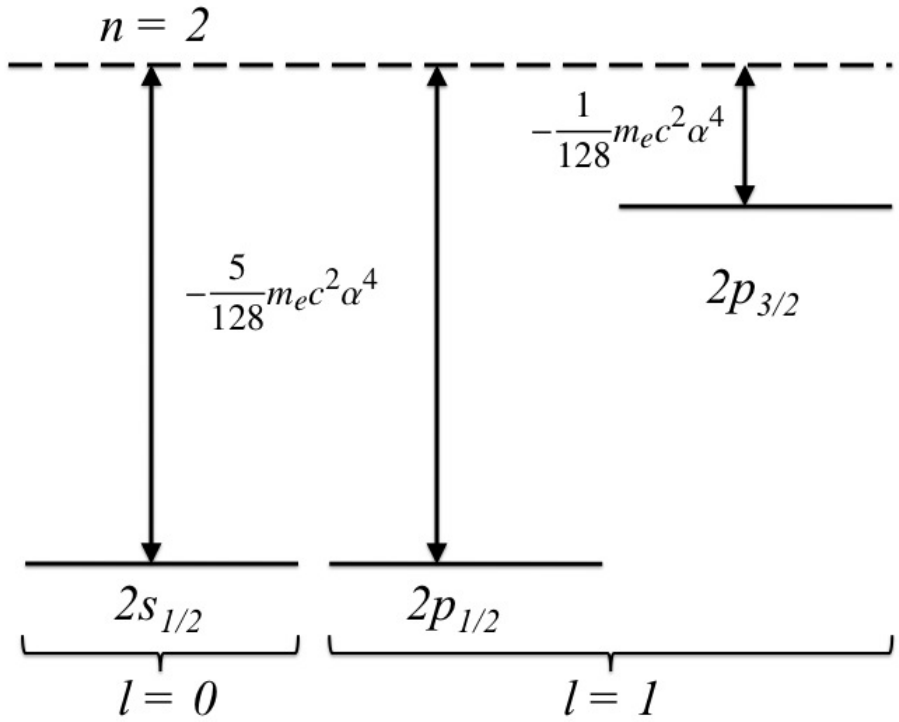
$2p_{1/2}$

$$\left(-\frac{7}{384} - \frac{1}{48}\right)m_e c^2\alpha^4 = -\frac{5}{128}m_e c^2\alpha^4 \tag{6.26}$$

$2p_{3/2}$

$$\left(-\frac{7}{384} + \frac{1}{96}\right)m_e c^2\alpha^4 = -\frac{1}{128}m_e c^2\alpha^4 \tag{6.27}$$

The fine structure of the $n = 2$ level



The hyperfine structure of the $n = 1$ level

a) The degeneracy of the $1s$ level

– no orbital degeneracy ($l = 0$)

– $\hat{S}_z$, $\hat{I}_z$: each 2 value $\pm 1/2$

$$\left\{ |n = 1; l = 0; m_L = 0; m_S = \pm\frac{1}{2}; m_I = \pm\frac{1}{2}\rangle \right\} \tag{6.28}$$

b) The $1s$ level has no fine structure

$\hat{W}_f$ does not remove the degeneracy of the $1s$ state

$$\left\langle \hat{W}_{mv} \right\rangle_{1s} = -\frac{5}{8} m_e c^2 \alpha^4 \quad (6.29)$$

$$\left\langle \hat{W}_{D} \right\rangle_{1s} = \frac{1}{2} m_e c^2 \alpha^4 \quad (6.30)$$

$$\left\langle \hat{W}_{SO} \right\rangle_{1s} = 0 \quad (6.31)$$

$\hat{W}_f$ shifts the levels by $-\frac{1}{8} m_e c^2 \alpha^4$

Since $l = 0$ and $s = 1/2$, $J = 1/2 \Rightarrow$ only one fine structure level, $1s_{1/2}$

Matrix representation of $\hat{W}_{hf}$ in the $1s$ level

$$\hat{W}_{hf} = -\frac{\mu_0}{4\pi}\left\{\underbrace{\frac{q}{m_e R^3}\hat{\vec{L}}\cdot\hat{\vec{M}}_I}_{=0 \text{ as } l=0} + \frac{1}{R^3}\underbrace{\left[3\left(\hat{\vec{M}}_S\cdot\hat{n}\right)\left(\hat{\vec{M}}_I\cdot\hat{n}\right) - \hat{\vec{M}}_S\cdot\hat{\vec{M}}_I\right]}_{=0 \text{ due to spherical symmetry of } 1s \text{ state}}\right. \tag{6.32}$$

$$\left. + \underbrace{\frac{8\pi}{3}\hat{\vec{M}}_S\cdot\hat{\vec{M}}_I\delta\left(\vec{R}\right)}_{\neq 0}\right\} \tag{6.33}$$

$$\hat{\vec{M}}_I = \frac{g_P\mu_n\hat{\vec{I}}}{\hbar}, \qquad \mu_n = \frac{q_P\hbar}{2M_P} \tag{6.34}$$

The matrix elements are

$$\langle n=1;l=0;m_L=0;m_s';m_I'|-\frac{2\mu_0}{3}\hat{\vec{M}}_S\cdot\hat{\vec{M}}_I\delta\left(\vec{R}\right)|n=1;l=0;m_L=0;m_s;m_I\rangle$$

In coordinate representation, we separate the orbital and spin parts of the matrix elements

$$\mathcal{A}\langle m_S',m_I'|\hat{\vec{I}}\cdot\hat{\vec{S}}|m_S,m_I\rangle \tag{6.35}$$

where

$$\mathcal{A} = \frac{q^2}{3\epsilon_0 c^2}\frac{g_P}{m_e M_P}\langle n=1;l=0;m_L=0|\delta\left(\vec{R}\right)|n=1;l=0;m_L=0\rangle \tag{6.36}$$

$$= \frac{q^2}{3\epsilon_0 c^2}\frac{g_P}{m_e M_P}\frac{1}{4\pi}\left|R_{10}(0)\right|^2 = \frac{4}{3}g_p\frac{m_e}{M_P}m_e c^2\alpha^4\left(1+\frac{m_e}{M_P}\right)^{-3}\frac{1}{\hbar^2} \tag{6.37}$$

The orbital variables have thus disappeared, and we are left with the problem of two spin 1/2's, coupled by an interaction

$$\mathcal{A}\hat{\vec{I}} \cdot \hat{\vec{S}} \tag{6.38}$$

where $\mathcal{A}$ is a constant.

Eigenstates and eigenvalues

Initial basis $\{|s = 1/2; I = 1/2; m_S; m_I\rangle\}$
– common eigenvectors of $\hat{S}^2$, $\hat{I}^2$, $\hat{S}_z$, $\hat{I}_z$

New basis
– introducing total angular momentum $\hat{\vec{F}} = \hat{\vec{S}} + \hat{\vec{I}}$: $\{|s = 1/2; I = 1/2; F; m_F\rangle\}$
– common eigenvectors of $\hat{S}^2$, $\hat{I}^2$, $\hat{F}^2$, $\hat{F}_z$

$\hat{\vec{F}}$: $F = 0, m_F = 0$ and $F = 1, m_F = 1, 0, -1$

$$\mathcal{A}\hat{\vec{I}} \cdot \hat{\vec{S}} = \frac{\mathcal{A}}{2}\left(\hat{F}^2 - \hat{I}^2 - \hat{S}^2\right) \tag{6.39}$$

The basis states $|F, m_F\rangle$ are eigenstates of $\mathcal{A}\hat{\vec{I}} \cdot \hat{\vec{S}}$:

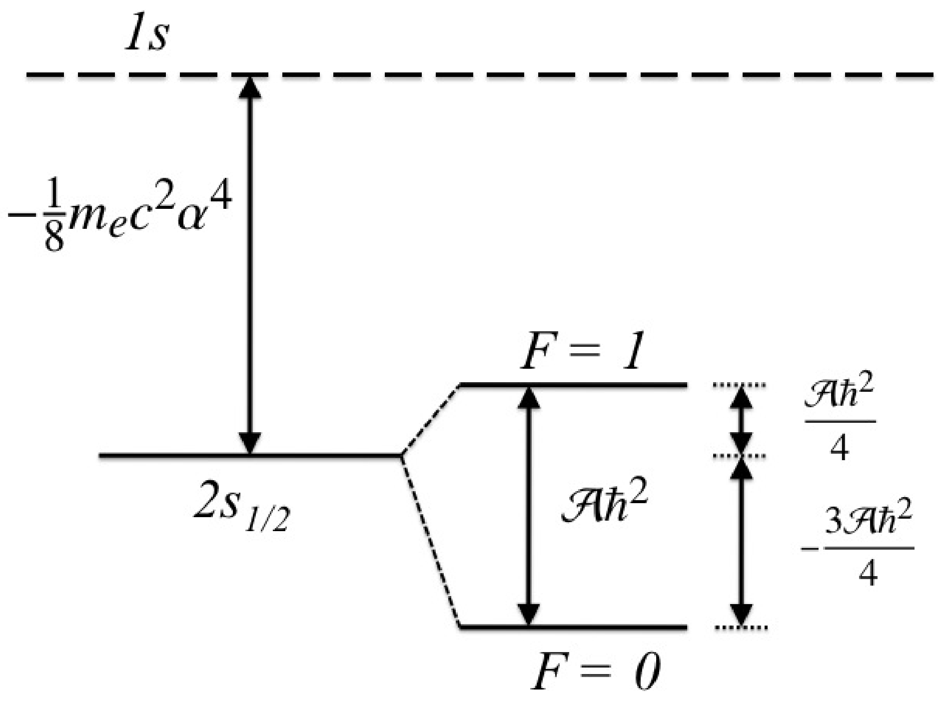
$$\mathcal{A}\hat{\vec{I}} \cdot \hat{\vec{S}}|F, m_F\rangle = \frac{\mathcal{A}\hbar^2}{2}\left[F(F+1) - I(I+1) - S(S+1)\right]|F, m_F\rangle \tag{6.40}$$

$$\Rightarrow F = 1: \quad \frac{\mathcal{A}\hbar^2}{2}\left[2 - \frac{3}{4} - \frac{3}{4}\right] = \frac{\mathcal{A}\hbar^2}{4} \text{ (3-fold degenerate)} \tag{6.41}$$

$$F = 0: \quad \frac{\mathcal{A}\hbar^2}{2}\left[0 - \frac{3}{4} - \frac{3}{4}\right] = -\frac{3\mathcal{A}\hbar^2}{4} \text{ (nondegenerate)} \tag{6.42}$$

The four-fold degeneracy of the $1s$ level is partially removed by $\hat{W}_{hf}$.

The hyperfine structure of the $1s$ level



The $n = 2$ level