

**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

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

\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

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

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

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

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

$$\hat{\vec{M}}_I = \frac{g_P \mu_n \hat{\vec{I}}}{\hbar}, \quad \mu_n = \frac{q_P \hbar}{2M_P} \quad (6.5)$$

Fine structure of the $n = 2$ level

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

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

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

$$\hat{W}_f = \hat{W}_{mv} + \hat{W}_{SO} + \hat{W}_D \quad (6.7)$$

$$\hat{W} = \hat{W}_f + \hat{W}_{hf} \quad (6.8)$$

Matrix representation of \hat{W}_f

16 × 16 matrix

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

$$(W_f)_{n=2} = \begin{array}{cc} & \begin{array}{c} 2s \\ 2p \end{array} \\ \begin{array}{c} 2s \\ 2p \end{array} & \begin{array}{|c|c|} \hline \text{dark} & 0 \\ \hline 0 & \text{dark} \\ \hline \end{array} \end{array}$$

1. $2s$ subshell

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

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

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

$$\begin{aligned}\langle \hat{W}_{mv} \rangle_{2s} &= \langle n = 2; l = 0, m_L = 0 | -\frac{\hat{P}^4}{8m_e^3 c^2} | n = 2; l = 0, m_L = 0 \rangle \\ &= -\frac{13}{128} m_e c^2 \alpha^4\end{aligned}\tag{6.9}$$

$$\begin{aligned}\langle \hat{W}_D \rangle_{2s} &= \langle n = 2; l = 0, m_L = 0 | \frac{\hbar^2}{8m_e^2 c^2} \Delta V(R) | n = 2; l = 0, m_L = 0 \rangle \\ &= \frac{1}{16} m_e c^2 \alpha^4\end{aligned}\tag{6.10}$$

and since $l = 0$

$$\langle \hat{W}_{SO} \rangle = 0 \quad (6.11)$$

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

$$\langle \hat{W}_{mv} \rangle + \langle \hat{W}_D \rangle + \langle \hat{W}_{SO} \rangle = -\frac{5m_e c^2 \alpha^4}{128} \quad (6.12)$$

2. $2p$ subshell

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

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

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a multiple of a unit matrix

$$\langle \hat{W}_{mv} \rangle_{2p} = -\frac{7}{384} m_e c^2 \alpha^4 \quad (6.13)$$

$$\langle \hat{W}_D \rangle_{2p} = 0 \quad (6.14)$$

(See Complement BXII)

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

various elements:

$$\langle n = 2; l = 1; s = \frac{1}{2}; m'_L; m'_S | \xi(R) \hat{\vec{L}} \cdot \hat{\vec{S}} | n = 2; l = 1; s = \frac{1}{2}; m_L; m_S \rangle$$
$$\xi(R) = \frac{e^2}{2m_e^2 c^2} \frac{1}{R^3} \quad (6.15)$$

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

$$\xi_{2p} \langle l = 1; s = \frac{1}{2}; m'_L; m'_S | \hat{\vec{L}} \cdot \hat{\vec{S}} | l = 1; s = \frac{1}{2}; m_L; m_S \rangle \quad (6.16)$$

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

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

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

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

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

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

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

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

$2s_{1/2}$

$$-\frac{5}{128}m_e c^2 \alpha^4 \quad (6.25)$$

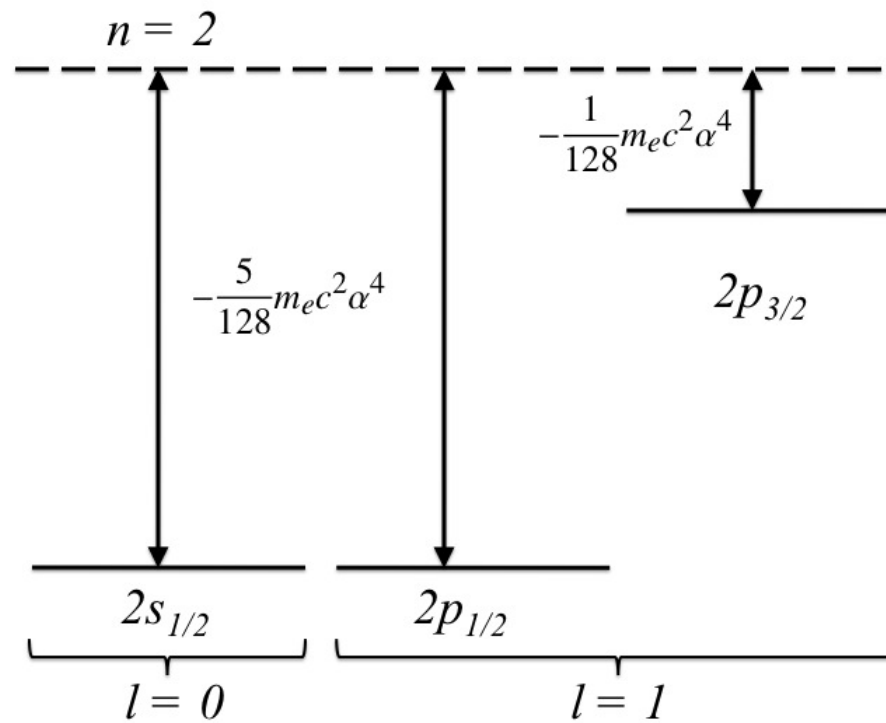
$2p_{1/2}$

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

$2p_{3/2}$

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

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 $\pm 1/2$

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

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

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

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

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

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

\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

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

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

$$\hat{\vec{M}}_I = \frac{g_P \mu_n \hat{\vec{I}}}{\hbar}, \quad \mu_n = \frac{q_P \hbar}{2M_P} \quad (6.34)$$

The matrix elements are

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

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

$$\mathcal{A} \langle m'_S, m'_I | \hat{\vec{I}} \cdot \hat{\vec{S}} | m_S, m_I \rangle \quad (6.35)$$

where

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

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

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

$$\mathcal{A} \hat{\vec{I}} \cdot \hat{\vec{S}} \quad (6.38)$$

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 $F = 1, m_F = 1, 0, -1$

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

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

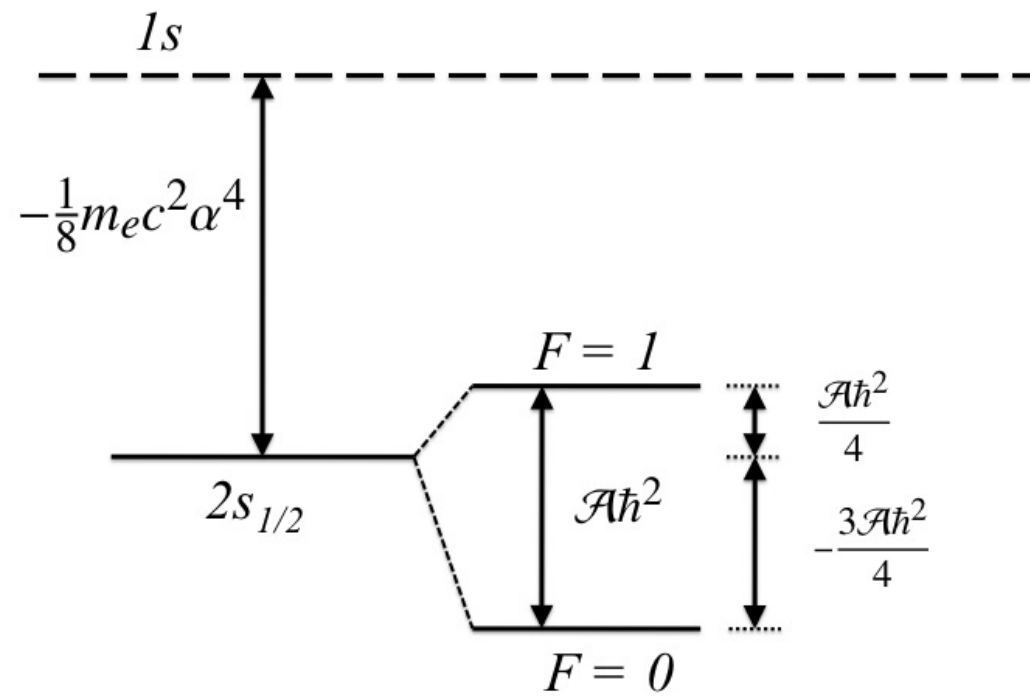
$$\mathcal{A}\hat{\vec{I}} \cdot \hat{\vec{S}}|F, m_F\rangle = \frac{\mathcal{A}\hbar^2}{2} [F(F+1) - I(I+1) - S(S+1)]|F, m_F\rangle \quad (6.40)$$

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

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

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

