

Ph195c lecture notes, 4/3/02

Fine and hyperfine structure of hydrogen

[Cohen-Tannoudji, Diu, and Laloe Ch. XII]

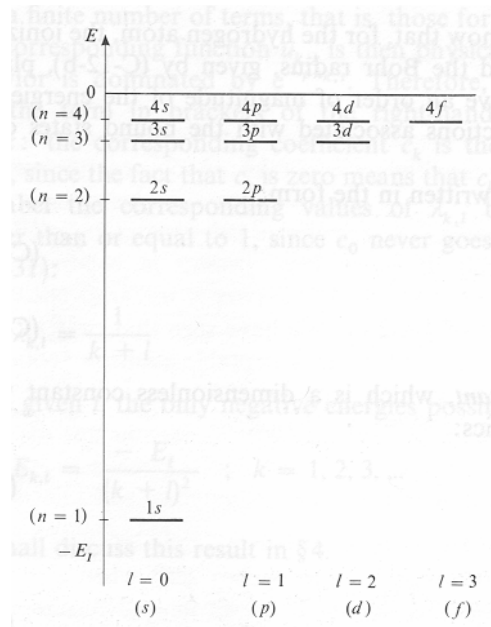
Last time we saw that the eigenstates of the Coulomb potential

$$H_0 = \frac{p^2}{2m} - \frac{Ze^2}{r}$$

can be grouped into 'shells' labelled by a principal quantum number n , which ranges over non-negative integers. The eigenstates in a given shell have energy

$$E_n = -\frac{Z^2 m e^4}{2\hbar^2 n^2}.$$

Within each shell are 'subshells' of orbital angular momentum $l = 0 \dots n - 1$, each of which is itself $(2l + 1)$ -fold degenerate.



As one might imagine, this simple picture is only a first approximation to the level structure of real hydrogen atoms.

In order to obtain a more accurate energy spectrum, we need to add three things to our physical model:

1. relativistic effects
2. electron spin
3. nuclear spin

The first two items combine to contribute what are known as the *fine-structure* terms in the atomic Hamiltonian, while addition of the third produces *hyperfine* terms.

A note of warning: below we will follow the convention of Cohen-Tannoudji *et al* by writing

$$\frac{q^2}{4\pi\epsilon_0} \equiv e^2.$$

The fine-structure Hamiltonian

In relativistic quantum theory, the dimensionless coupling constant between charged matter and electromagnetic fields is

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}.$$

Thanks to the smallness of this parameter (compared to 1), perturbation methods can successfully be applied in atomic physics and quantum electrodynamics. For the hydrogen atom, α also appears as the ratio v/c of the characteristic electron velocity to the speed of light. The smallness of the ratio indicates that relativistic effects should introduce relatively small corrections to the hydrogen spectrum.

A correct relativistic description of the hydrogen atom (via the Dirac equation) can be used to derive leading-order (in α) corrections to the basic Coulomb Hamiltonian:

$$\begin{aligned} H &= m_e c^2 + \left[\frac{p^2}{2m_e} + V(r) \right] - \left[\frac{p^4}{8m_e^3 c^2} \right] + \left[\frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{\mathbf{L}} \cdot \vec{\mathbf{S}} \right] + \left[\frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V(r) \right] + \dots \\ &\equiv m_e c^2 + H_0 + W_{mv} + W_{SO} + W_D + \dots \end{aligned}$$

It should be noted that here m_e refers to the bare electron mass rather than a reduced mass (Cohen-Tannoudji *et al* mention that there is some significant complication with two-body systems in relativistic theory, on p. 1214). The rest-mass energy term $m_e c^2$ clearly shifts all energy levels equally, and therefore has no effect on the hydrogen spectrum *per se*. The next term in square brackets reproduces the Coulomb Hamiltonian we studied last week. The remaining terms can be assigned specific physical interpretations:

$$W_{mv} = -\frac{p^4}{8m^3 c^2}$$

This term represents relativistic variation of the electron mass with velocity. Starting from the general expression

$$E = c\sqrt{p^2 + m^2 c^2},$$

we can expand to second order in p/mc to obtain

$$\begin{aligned} E &\approx mc^2 \left(1 + \frac{p^2}{2m^2 c^2} - \frac{p^4}{8m^4 c^4} \right) \\ &= mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}. \end{aligned}$$

Here we recognize the electron rest-mass energy, the non-relativistic kinetic energy term,

and the first relativistic correction W_{mv} . Using the characteristic scale

$$\frac{v}{c} = \frac{p}{mc} \approx \alpha$$

we may estimate

$$\frac{W_{mv}}{H_0} \simeq -\frac{\frac{p^4}{8m^3c^2}}{\frac{p^2}{2m}} = -\frac{p^2}{4m^2c^2} \approx \alpha^2 \approx \left(\frac{1}{137}\right)^2.$$

Hence this is indeed a smallish correction.

$$W_{SO} = \left[\frac{1}{2m_e^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{\mathbf{L}} \cdot \vec{\mathbf{S}} \right]$$

As the electron orbits the nucleus it moves rapidly through the electrostatic field created by the proton. Accordingly the electron in its rest frame sees a magnetic field \vec{B}' , given to first order in v/c by

$$\vec{B}' = -\frac{1}{c^2} \vec{v} \times \vec{E}.$$

The electron has an intrinsic spin, and therefore a magnetic moment

$$\begin{aligned} \vec{\mu} &= \gamma \vec{\mathbf{S}} \\ &= \frac{q}{m} \vec{\mathbf{S}} \end{aligned}$$

that interacts with the magnetic field B' to yield an energy correction

$$W' = -\vec{\mu} \cdot \vec{B}'.$$

The electrostatic field seen by the electron can be written

$$\vec{E} = -\frac{1}{q} \frac{1}{r} \frac{dV(r)}{dr} \frac{\vec{r}}{r},$$

where $V(r) = -e^2/r$ is the Coulomb potential. Hence

$$\vec{B}' = \frac{1}{qc^2} \frac{1}{r} \frac{dV(r)}{dr} \frac{\vec{p}}{m} \times \vec{r},$$

which explains the presence of the operator

$$\vec{\mathbf{p}} \times \vec{\mathbf{r}} = -\vec{\mathbf{L}}$$

in the quantum-mechanical Hamiltonian

$$\begin{aligned} W' &= -\frac{q}{m} \vec{\mathbf{S}} \cdot \frac{1}{qc^2} \frac{1}{r} \frac{dV(r)}{dr} \frac{\vec{\mathbf{p}}}{m} \times \vec{\mathbf{r}} \\ &= \frac{1}{m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{\mathbf{S}} \cdot \vec{\mathbf{L}} \\ &= \frac{e^2}{m^2c^2} \frac{1}{r^3} \vec{\mathbf{L}} \cdot \vec{\mathbf{S}}. \end{aligned}$$

As it turns out the actual spin-orbit term W_{SO} differs from this by a factor of 1/2, which is due to the curved orbit of the electron.

We know that L and S are of order \hbar , and r will tend to be of order $a_0 = \hbar^2/me^2$, so we may estimate

$$\frac{W_{SO}}{H_0} \simeq \frac{\frac{e^2}{2m^2c^2} \frac{1}{r^3} \vec{\mathbf{L}} \cdot \vec{\mathbf{S}}}{\frac{e^2}{r}} = \frac{\hbar^2}{2m^2c^2r^2} \approx \frac{e^4}{\hbar^2c^2} = \alpha^2.$$

$$W_D = \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V(r)$$

The so-called 'Darwin term' W_D is harder to rationalize. Apparently the leading terms in v/c from the relativistic quantum model provide this contribution, which looks like a non-local sampling of the potential $V(r)$ in a domain of size $\sim \hbar/mc$ around the position r of the electron. (Note that the Dirac equation itself is strictly local – this apparent non-local sampling is an artifact of the series expansion in v/c .) The length scale \hbar/mc is known as the electron's Compton wavelength, corresponding to the wavelength of a photon with energy equal to the electron's rest mass.

Using $V(r) = -e^2/r$ and $\nabla^2(1/r) = -4\pi\delta(r)$, we may write

$$W_D = \frac{\pi e^2 \hbar^2}{2m^2 c^2} \delta(r),$$

which as an operator has mean value

$$\langle W_D \rangle = \frac{\pi e^2 \hbar^2}{2m^2 c^2} |\psi(0)|^2$$

for an atomic state with electron wave-function ψ . We know that the value of $|\psi(0)|^2$ can only be non-zero for an s state, and should be of order a_0^{-3} since ψ must be normalized and extends over a spatial volume of radius $\sim a_0$. Hence we may estimate

$$\frac{W_D}{H_0} \simeq \frac{\frac{\pi e^2 \hbar^2}{2m^2 c^2} a_0^{-3}}{-e^2/a_0} \approx \frac{\hbar^2}{m^2 c^2 a_0^2} = \frac{\hbar^2}{m^2 c^2} \frac{m^2 e^4}{\hbar^4} = \frac{e^4}{\hbar^2 c^2} = \alpha^2.$$

Finally then, we see that our overall Hamiltonian may be broken-down in the fashion

$$H = mc^2 + H_0 + W_f,$$

$$H_0 = \frac{p^2}{2m} + V(r),$$

$$W_f = W_{mv} + W_{SO} + W_D,$$

with

$$\frac{H_0}{mc^2} \simeq \frac{e^2/a_0}{mc^2} = \frac{e^2}{mc^2} \frac{me^2}{\hbar^2} = \frac{e^4}{\hbar^2 c^2} = \alpha^2,$$

$$\frac{W_f}{H_0} \simeq \alpha^2.$$

We will henceforth ignore the electron rest-mass energy, since this shifts all atomic levels by an equal amount, and proceed with a *perturbative* treatment of W_f relative to H_0 .

Fine structure of the hydrogen $n = 2$ shell

As an application of perturbation theory, and in order to see how W_f is able to partially lift the degeneracy of the Coulomb potential, let's look at the fine structure of the $n = 2$ shell in hydrogen.

Recall that this shell consists of two subshells: the $2s$ subshell with $l = 0$ and the $2p$ subshell with $l = 1$. Taking into account the electron spin, the $2s$ subshell has degeneracy 2 and the $2p$ subshell has degeneracy $2 \times (2 + 1) = 6$. Thus in order to compute first-order energy corrections in W_f we will have to use degenerate perturbation theory in the eight-dimensional Hilbert space corresponding to $n = 2$.

So to begin, we must diagonalize the restriction of W_f in this subspace. Looking at the overall form of the fine-structure Hamiltonian

$$W_f = -\frac{p^4}{8m_e^3c^2} + \frac{1}{2m_e^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{\mathbf{L}} \cdot \vec{\mathbf{S}} + \frac{\hbar^2}{8m_e^2c^2} \nabla^2 V(r),$$

we note that the presence of an $\vec{\mathbf{L}} \cdot \vec{\mathbf{S}}$ term leads us to use the coupled basis for total angular momentum $\vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}}$. Fortunately, this is enough to do the trick!

First we note that W_f does not connect the $2s$ subshell with the $2p$ subshell. This is evident since \mathbf{L}^2 commutes with every term in W_f . We know that \mathbf{L}^2 commutes with \mathbf{p}^2 (since this appears in H_0 , which commutes with \mathbf{L}^2) and therefore with $\mathbf{p}^4 = (\mathbf{p}^2)(\mathbf{p}^2)$. As a differential operator \mathbf{L}^2 depends only on angular coordinates, therefore it must commute with W_D and also with the radial prefactor of W_{SO} . Finally we recall from earlier days that \mathbf{L}^2 commutes with each of \mathbf{L}_x , \mathbf{L}_y , and \mathbf{L}_z and therefore with $\vec{\mathbf{L}} \cdot \vec{\mathbf{S}} = \mathbf{L}_x \mathbf{S}_x + \mathbf{L}_y \mathbf{S}_y + \mathbf{L}_z \mathbf{S}_z$. Thus we can already see that the restriction of W_f to $n = 2$ has block-diagonal form [Cohen-Tannoudji *et al*, p. 1221]:

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

Inside the $2s$ subshell we know that the 2-fold degeneracy is due to electron spin only. Because $l = 0$ in this subshell we must have $j = s = 1/2$. Hence the basis kets may be written

$$|n = 2, l = 0, s = 1/2, j = 1/2; m_j = \pm 1/2\rangle.$$

Also because of $l = 0$, the restriction of W_{SO} to the $2s$ subshell evaluates to zero since L_x , L_y , or L_z acting on any state with $l = 0$ must yield zero. Neither of the remaining terms in W_f can have non-zero off-diagonal matrix elements, since they act only on orbital degrees of freedom. Hence W_f is proportional to the identity in the $2s$ subshell. Its diagonal matrix elements can be computed using the wave-functions we derived last time, yielding

$$\begin{aligned} \langle W_f \rangle_{2s} &= \langle W_{mv} \rangle_{2s} + \langle W_D \rangle_{2s} \\ &= -\frac{13}{128} mc^2 \alpha^4 + \frac{1}{16} mc^2 \alpha^4 \\ &= -\frac{5}{128} mc^2 \alpha^4. \end{aligned}$$

In the $2p$ subshell we have both the electron spin degeneracy and the essential 3-fold degeneracy of m_l states (as a consequence of the rotational symmetry of H_0). With $l = 1$ and $s = 1/2$, the possible values of j are $3/2$ and $1/2$. Hence the six basis kets may be written

$$\begin{aligned}
&|n = 2, l = 1, s = 1/2, j = 3/2; m_j = +3/2\rangle \\
&|n = 2, l = 1, s = 1/2, j = 3/2; m_j = +1/2\rangle \\
&|n = 2, l = 1, s = 1/2, j = 3/2; m_j = -1/2\rangle \\
&|n = 2, l = 1, s = 1/2, j = 3/2; m_j = -3/2\rangle \\
&|n = 2, l = 1, s = 1/2, j = 1/2; m_j = +1/2\rangle \\
&|n = 2, l = 1, s = 1/2, j = 1/2; m_j = -1/2\rangle.
\end{aligned}$$

This time W_{SO} is non-zero. Using

$$\begin{aligned}
\mathbf{J}^2 &= \mathbf{L}^2 + 2\mathbf{L} \cdot \mathbf{S} + \mathbf{S}^2, \\
\mathbf{L} \cdot \mathbf{S} &= \frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2),
\end{aligned}$$

we see that it is diagonal with matrix elements

$$\langle W_{SO} \rangle_{2p} = \frac{\hbar^2}{2m_e^2 c^2} \left\langle \frac{1}{r} \frac{dV(r)}{dr} \right\rangle \left[j(j+1) - 2 - \frac{3}{4} \right].$$

The radial prefactor can be computed from the Coulomb eigenfunctions, yielding

$$\begin{aligned}
\langle W_{SO} \rangle_{2p} &= \frac{1}{96} mc^2 \alpha^4 \quad j = 3/2, \\
&= -\frac{1}{48} mc^2 \alpha^4 \quad j = 1/2.
\end{aligned}$$

The terms W_{mv} is again proportional to the identity (for the same reason as above), yielding an overall shift

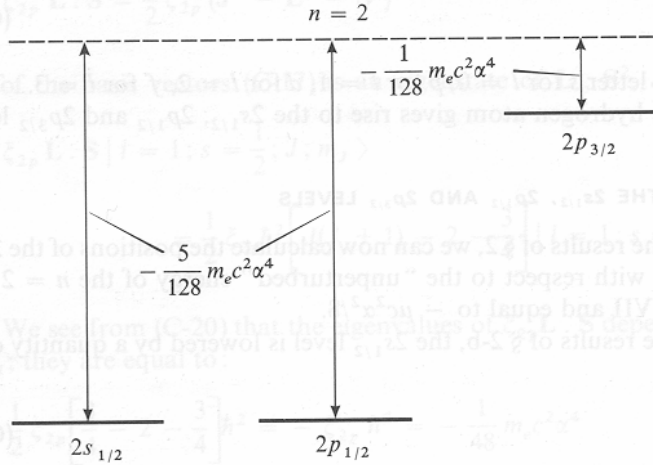
$$\langle W_{mv} \rangle_{2p} = -\frac{7}{384} mc^2 \alpha^4,$$

while $W_D = 0$ since $\psi(0) = 0$ for states with $l > 0$.

Introducing the spectroscopic notation nL_j , we have thus found the fine-structure energy corrections

$$\begin{aligned}
\Delta E_{2s_{1/2}} &= -\frac{5}{128} mc^2 \alpha^4, \\
\Delta E_{2p_{1/2}} &= -\frac{5}{128} mc^2 \alpha^4, \\
\Delta E_{2p_{3/2}} &= -\frac{1}{128} mc^2 \alpha^4.
\end{aligned}$$

[Cohen-Tannoudji *et al* Ch. XII Fig. 2]



Some important notes on this diagram:

1. Although it would appear from the above treatment that the remaining degeneracy between $2s_{1/2}$ and $2p_{1/2}$ might be accidental, it can in fact be shown that this degeneracy is maintained to all orders in W_f . Exact solution of the Dirac equation yields an energy spectrum that depends on j only, and not on l and s independently:

$$E_{n,j} = mc^2 \left[1 + \alpha^2 \left(n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \alpha^2} \right)^{-2} \right]^{-1/2}.$$

2. In real hydrogen, the $2s_{1/2}$ and $2p_{1/2}$ levels are actually split by the “Lamb shift” ~ 1 GHz. This correction is due to interaction of the orbiting electron with vacuum fluctuations of the electromagnetic field.
3. In alkali atoms such as Rb or Cs, the states nS and nP have grossly different energies because of screening effects – although we expect the spectra of such atoms to be hydrogen-like since they have a single valence electron, the electron wave-function for s states dips inside the closed shells of electrons and therefore sees a higher nuclear charge than the net $+e$ seen outside the core.

The hyperfine Hamiltonian

In real hydrogen the nucleus (proton) has an intrinsic spin of $1/2$. The hydrogen nuclear magnetic moment operator may be written

$$\vec{\mu}_I = \frac{g_p \mu_N}{\hbar} \vec{I},$$

where \vec{I} is the usual spin- $1/2$ vector operator, $g_p \approx 5.585$ is the proton “g-factor” (having to do with its internal quark structure) and μ_N is the “nuclear magneton”

$$\mu_N = \frac{q_p \hbar}{2m_p}$$

(where $q_p = -q_e$). It should be noted that μ_N is smaller than the electron’s “Bohr magneton”

$$\mu_B = \frac{q_e \hbar}{2m_e}$$

by a factor of $m_e/m_p \sim 1/2000$. The electron’s magnetic moment operator is

$$\vec{\mu}_S = \frac{g_e \mu_B}{\hbar} \vec{S},$$

with $g_e = 2$.

The hyperfine Hamiltonian is given by

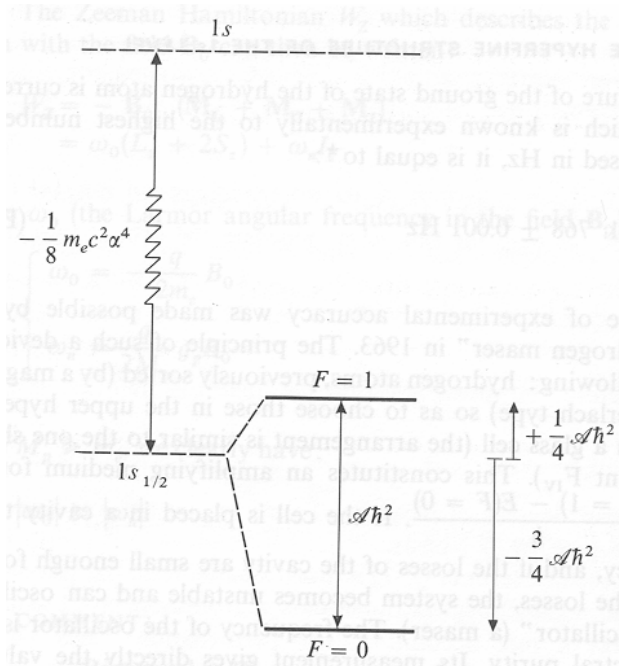
$$W_{hf} = -\frac{\mu_0}{4\pi} \left\{ \frac{q}{m_e r^3} \vec{L} \cdot \vec{\mu}_I + \frac{1}{r^3} [3(\vec{\mu}_S \cdot \hat{n})(\vec{\mu}_I \cdot \hat{n}) - \vec{\mu}_S \cdot \vec{\mu}_I] + \frac{8\pi}{3} \vec{\mu}_S \cdot \vec{\mu}_I \delta(\vec{r}) \right\},$$

where \hat{n} is the unit vector $\vec{r}/|\vec{r}|$. It can be shown that the first two terms here are of order 2000 times smaller than W_{SO} , and the third term is likewise about 2000 times smaller than W_D (which also contains a delta-function). The first term of W_{hf} reflects the interaction of the nuclear magnetic moment with the magnetic field $\sim (\mu_0/2\pi)qL/m_e r^3$ created by the orbiting electron. The second term represents the magnetic dipole-dipole interaction between the nuclear and electronic spins. The third term, known as Fermi's 'contact term,' has to do with the internal magnetic structure of the proton.

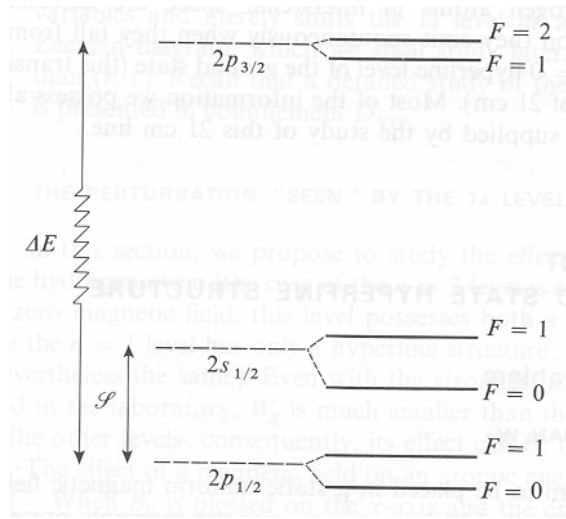
The important thing to note about the hyperfine Hamiltonian is that it leads us to consider coupling of angular momenta between the nuclear spin I and the total electron angular momentum J , yielding

$$\vec{F} = \vec{I} + \vec{J}.$$

The rationale for this coupling scheme (as opposed, e.g., to coupling S and I first and then adding L) is that the spin-orbit coupling is so much larger than the hyperfine interaction. As a result, in the absence of an applied magnetic field, W_{hf} leads to small additional splittings within the nL_j fine-structure levels [Cohen-Tannoudji *et al*, Ch. XII Figs. 3 and 4]:



($\mathcal{A}\hbar/2\pi \approx 1420405751.768 \pm 0.001$ Hz, corresponding to the famous 21 cm line in hydrogen).



We'll see more about all this next time, when we discuss the Zeeman effect.