

## HYDROGEN ATOM REVISITED

- Fine structure and hyperfine structure

When we studied the hydrogen atom, we chose

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

However, there are additional corrections, in order of decreasing magnitude:-

- Fine structure: relativistic corrections and spin-orbit coupling.
- Lamb shift: associated with the quantization of the electric field.
- Hyperfine structure: interactions between magnetic dipole moments of the electron and proton.

We will take a closer look at two of these using perturbation theory.

# FINE STRUCTURE

## Relativistic correction

[G7.3.1, H7.1.3]

In H<sub>0</sub> we have used the expression

$$T = \frac{p^2}{2m}$$

for the kinetic energy. This is, however, just the lowest order term in the relativistic expression for the kinetic energy

$$\begin{aligned} T &= \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots \end{aligned}$$

for  $p \ll mc$ . Is  $p/mc$  small enough to justify dropping the higher order terms?

For the ground state, we get

$$\begin{aligned} \langle p^2 \rangle &= \int d\vec{r} \psi_{100} (-i\hbar \nabla)^2 \psi_{100} \\ &= \frac{\hbar^2}{a_0^3} \int d\vec{r} \frac{1}{\pi a_0^3} e^{-2r/a_0} = \frac{\hbar^2}{a_0^2}. \end{aligned}$$

Hence,

$$\langle v \rangle/c = \frac{\sqrt{\langle p^2 \rangle}}{mc} = \frac{\hbar}{a_0 mc} = \frac{e^2}{4\pi\epsilon_0 \hbar c}$$

$$\equiv \alpha \approx \frac{1}{137},$$

the fine structure constant.

We will now calculate the corrections due to

$$H_r = -\frac{p^4}{8m^3c^2}.$$

Since  $H_r$  is spherically symmetric, it commutes with  $H_0$ ,  $L^2$  and  $L_z$ , meaning that  $\psi_{nlm}$  are "good" states, and we can use non-degenerate pert. theory.

To first order, we get the correction

$$E_r^1 = \langle \psi | \hat{V}_r | \psi \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 | \psi \rangle \\ = -\frac{1}{8m^3c^2} \langle \psi | [2m(E-V)]^2 | \psi \rangle,$$

where we have used

$$p^2 |\psi\rangle = 2m(E-V) |\psi\rangle,$$

based on the SE for the unperturbed states. Inserting for the Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r},$$

we get

$$E_r^1 = -\frac{1}{2mc^2} \left[ E_n^2 + \frac{2E_n e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right],$$

with Bohr (hydrogen) energy  $E_n$  for the unperturbed states

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2},$$

where  $a_0$  is the Bohr radius.

For the two expectation values,  
we have

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0} \quad [\text{Hemmer pp. 109-110}]$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2}{[2\ell+1]n^3 a_0^2}.$$

Hence, we get

$$\begin{aligned} E_r' &= -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \frac{e^2}{4\pi\epsilon_0 a_0} \frac{1}{n^2} \right. \\ &\quad \left. + \frac{2}{2\ell+1} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^3 a_0^2} \right] \\ &= -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{\ell+1/2} - 3 \right]. \end{aligned}$$

The correction is smaller than  $E_n$   
by a factor

$$\sim \frac{\bar{E}_n}{mc^2} \sim \frac{eV}{MeV} \sim 10^{-5}. \text{ Small!}$$

Some degeneracy has been lifted  
for the  $n^{\text{'th}}$  level, but  $(2\ell+1)$ -fold  
degeneracy in  $m$  remains.

## Darwin term

There is also a relativistic correction to the potential energy,

$$H_D = \frac{\hbar^2 \pi}{2m^2 c^2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \delta(\vec{r}),$$

stemming from the relativistic Dirac equation. Only s-orbitals are affected by the perturbation, since orbitals with  $\ell \neq 0$  have vanishing wavefunctions at  $r=0$ .

To first order we get

$$E'_D = \langle 4|H_D|4\rangle = \frac{\hbar^2 \pi}{2m^2 c^2} \left( \frac{e^2}{4\pi\epsilon_0} \right) |\psi_{nem}(0)|^2.$$

We have:

$$|\psi_{nem}(0)|^2 = \frac{1}{\pi a_0^3 n^3} \quad \text{See.}$$

$$= \frac{e^2 m}{4\pi\epsilon_0 \hbar^2} \frac{1}{\pi a_0^2 n^3} \quad \text{See.}$$

using the definition of the Bohr radius, resulting in

$$E'_D = \frac{1}{2mc^2} \left( \frac{e^2}{4\pi\epsilon_0 a_0} \right)^2 \frac{1}{n^3} \quad (l=0)$$
$$= \frac{2n}{mc^2} E_n^2. \quad (l=0)$$

This correction is of the same order as  $E_r'$ .

### Spin-orbit coupling [G 7.3.2]

Using a classical image, the electron rotates about the proton. However, in the electron's rest frame, the proton rotates about the electron.

This circulating positive charge sets up a magnetic field  $\vec{B}$  that exerts a torque on the magnetic moment  $\vec{\mu}$  of the electron:

$$H = -\vec{\mu} \cdot \vec{B}.$$

For the electron we know  $\vec{\mu} \propto \vec{S}$ , and we expect  $\vec{B} \propto \vec{L}$ , since it's related to the orbital motion. From the Dirac equation, one finds for a general potential  $V(r)$ ,

$$H_{SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}$$

which for the hydrogen atom gives

$$H_{SO} = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2c^2 r^3} \vec{L} \cdot \vec{S}.$$

This term does not commute with  $\vec{L}$  and  $\vec{S}$ , so spin and orbital angular momentum are not conserved separately. However,  $H_{SO}$  commutes with

$$\vec{j} = \vec{L} + \vec{S},$$

along with  $\vec{l}^2$  and  $\vec{s}^2$ . Hence,  $\ell$ ,  $s$ ,  $j$  and  $m_j$  are good quantum numbers, while  $m_\ell$  and  $m_s$  are not.

We have

$$\begin{aligned}\vec{j}^2 &= (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S} \\ \Rightarrow \vec{L} \cdot \vec{S} &= \frac{1}{2} [\vec{j}^2 - \vec{L}^2 - \vec{S}^2],\end{aligned}$$

and hence the eigenvalues of  $\vec{L} \cdot \vec{S}$  are

$$\frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)],$$

where  $s = 1/2$  for the electron.

We also have

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2}{\ell(2\ell+1)(\ell+1)\alpha_0^3 n^3} \quad [\text{Hemmer p. 110}]$$

To first order, we therefore get  
the correction ( $\ell > 0$ )

$$\begin{aligned}E_{so}^1 &= \left\langle \psi_{nlm} | \hat{H}_{so} | \psi_{nlm} \right\rangle \\ &= \frac{e^2}{8\pi\epsilon_0} \frac{\hbar^2}{m^2 c^2} \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{\ell(2\ell+1)(\ell+1)\alpha_0^3 n^3} \\ &= \frac{2E_n^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - \frac{3}{4}]}{\ell(2\ell+1)(\ell+1)} \right\}.\end{aligned}$$

Again the correction is of same size.

## Fine structure

Adding all three correction terms, we get the fine structure correction

$$E'_{fs} = -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{\ell+1/2} - 3 \right]$$

$$+ \frac{2n}{mc^2} E_n^2 \delta_{\ell_0}$$

$$+ \frac{\alpha E_n^2}{mc^2} \left\{ \frac{n[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(2\ell+1)(\ell+1)} \right\} (1 - \delta_{\ell_0})$$

$$= \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{\ell+1/2} + 4n \delta_{\ell_0} \right.$$

$$\left. + \frac{4n[j(j+1) - \ell(\ell+1) - 3/4]}{\ell(2\ell+1)(\ell+1)} (1 - \delta_{\ell_0}) \right]$$

We treat the cases  $j = \ell \pm 1/2$  separately:

$$\underline{j = \ell + 1/2} :$$

$$E'_{fs} = \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{j} + 4n \delta_{\ell_0} \right]$$

$$+ \frac{4n}{2j(j+1/2)} (1 - \delta_{\ell_0}) \left] = \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right] \right]$$

If  $j = \ell - \frac{1}{2}$ , which excludes  $\ell = 0$

$$\begin{aligned} E_{fs}^j &= \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4j}{\ell + \frac{1}{2}} \right. \\ &\quad \left. + \frac{2n \cdot (\ell + 1)}{\ell(\ell + \frac{1}{2})(\ell + 1)} \right] \\ &= \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{\ell} \right] = \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{j + \frac{1}{2}} \right] \end{aligned}$$

In either case, we get

$$E_{fs}^j = \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4j}{j + \frac{1}{2}} \right]$$

and thus the new energy levels

$$E_{nj} = -\frac{13.6 \text{ eV}}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right],$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$$

is the fine structure constant.

We see that the fine structure breaks the degeneracy in  $\ell$  — for a given  $n$  not all  $\ell$  have the same energy — but we still have degeneracy in  $j$ .

$m_l$  and  $m_s$  are no longer good quantum numbers, and the stationary states are linear combinations of states with different  $m_l$  and  $m_s$ . The good quantum numbers are  $n, l, s, j$  and  $m_j$ .

We have already seen examples of how to construct such states with  $\ell=1$  in problem set 9.

# HYPERFINE STRUCTURE

[ G 7.5 ]

We have seen that both the proton and electron have a magnetic dipole moment:

$$\vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p$$

$$\vec{\mu}_e = -\frac{g_e e}{2m_e} \vec{S}_e = -\frac{e}{m_e} \vec{S}_e$$

where  $g_p \approx 5.59$  and  $g_e \approx 2$ . Since  $m_p \gg m_e$  by a factor of  $\approx 2000$ ,  $|\vec{\mu}_p| \ll |\vec{\mu}_e|$ .

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

$$\vec{B} = \frac{\mu_0}{4\pi r^3} \left[ 3(\vec{\mu} \cdot \hat{r}) \hat{r} - \vec{\mu} \right] + \frac{2\mu_0}{3} \vec{\mu} \delta(r)$$

at position  $\vec{r}$  relative to  $\vec{\mu}$ .

We already saw that the energy of a dipole  $\vec{\mu}$  in a field  $\vec{B}$  is given by

$$H = -\vec{\mu} \cdot \vec{B}.$$

Hence, the energy of the electron will be affected by the magnetic field  $\vec{B}_p$  due to the magnetic moment of the proton. We get a spin-spin coupling (we already had  $\vec{L} \cdot \vec{S}$ ) described by the Hamiltonian

$$H_{hf} = -\vec{\mu}_e \cdot \vec{B}_p$$

$$= \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left[ 3(\vec{s}_p \cdot \hat{r}) (\vec{s}_e \cdot \hat{r}) - \vec{s}_p \cdot \vec{s}_e \right] \frac{1}{r^3}$$

$$+ \frac{\mu_0 g_p e^2}{3m_p m_e} \vec{s}_p \cdot \vec{s}_e \delta(\hat{r}).$$

We will now focus on the first order correction of the ground state ( $n_{lm} = (100)$ .

The hydrogenic Hamiltonian  $H_0$  does not take the spin of the proton and electron into account at all.

The states  $|100; m_p, m_e\rangle$ ,  $m_p, m_e = \pm \frac{1}{2}$  are therefore degenerate, all with energy  $E_1$ .

We could then use degenerate perturbation theory directly, or we can look for "good" states. In this case the operators  $\vec{S}^2$  and  $S_z$  for the total spin

$$\vec{S} = \vec{S}_e + \vec{S}_p$$

commute with both  $H_0$  and  $H_{SF}$  (for  $\ell=0$ ), and the "good" states are therefore  $|100; s m_s\rangle$ :

$$|100; 1 m_s\rangle, m_s = -1, 0, 1 \quad (s=1, \text{ triplet})$$

$$|100; 0 0\rangle, \quad (s=0, \text{ singlet})$$

and we can perform non-degenerate first-order perturbation theory.

We then get:

$$\begin{aligned} E_{hf}^{(1)} &= \langle 100; sm_s | H_{hf} | 100; sm_s \rangle \\ &= \langle sm_s | \int d\vec{r} \Psi_{100}^* H_{hf} \Psi_{100} | sm_s \rangle \\ &= \frac{\mu_0 g_p e^2}{3m_p m_e} |\Psi_{100}(0)|^2 \langle sm_s | \vec{S}_p \cdot \vec{S}_e | sm_s \rangle, \end{aligned}$$

where only the last term in  $H_{hf}$  gives a non-zero contribution when  $\ell=0$ , since  $\int d\phi \int d\theta \sin\phi (\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) = \frac{4\pi}{3} \vec{S}_p \cdot \vec{S}_e$ , see Griffiths pp. 312-313 for details.

We now square  $\vec{S}$ :

$$\begin{aligned} \vec{S}^2 &= \vec{S}_p^2 + \vec{S}_e^2 + 2 \vec{S}_p \cdot \vec{S}_e \\ \Rightarrow \vec{S}_p \cdot \vec{S}_e &= \frac{\vec{S}^2 - \vec{S}_p^2 - \vec{S}_e^2}{2}. \end{aligned}$$

Since  $S_e = S_p = 1/2$ , we get:

$$\langle sm_s | \vec{S}_p \cdot \vec{S}_e | sm_s \rangle$$

$$\begin{aligned} &= \frac{1}{2} \langle sm_s | \hbar^2 s(s+1) - \frac{3\hbar^2}{4} - \frac{3\hbar^2}{4} | sm_s \rangle \\ &= \begin{cases} +1/4 & s=1, \text{ triplet} \\ -3/4 & s=0, \text{ singlet} \end{cases} \end{aligned}$$

Hence, gathering all results, using

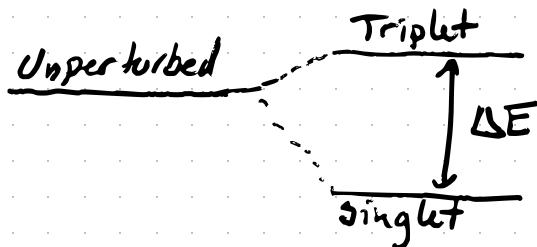
$$|4f_{nem_c}(0)|^2 = \frac{1}{\pi a_0^3 n^3} \delta_{c0}$$

from before with  $n=1$ ,  $\ell=m_c=0$ ,  
and  $\mu_0 = (\epsilon_0 c^2)^{-1}$ , we get

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} \begin{cases} +1/4, & \text{triplet} \\ -3/4, & \text{singlet.} \end{cases}$$

Hence, we have a hyperfine splitting  
of the states

$$\Delta E = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} = 5.88 \cdot 10^{-6} \text{ eV.}$$



When an electron transitions from the triplet to the singlet state, a photon with wavelength  $\lambda \approx 21 \text{ cm}$  is emitted.  
Since there is an abundance of

hydrogen in the universe, the 21-cm line is a pervasive form of radiation. By measuring the spectrum of electromagnetic radiation in different parts of our galaxy, it is for instance possible to calculate the relative speeds of the arms of our galaxy from the Doppler shifts in the 21-cm line.