HYDROGEN ATOM REVISITED

– Fine structure and Hyperfine structure

When we studied the hydrogen atom, we chose

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}.$$

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_0 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

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

for $p \ll mc$. 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 ψ_{nlm} are "good" states, and we can use non-degenerate pert. theory.

To first order, we get the correction

$$E_r^1 = \langle \psi | H_r | \psi \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 | \psi \rangle$$

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

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

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r},$$

we get

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + \frac{2E_n e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle\right],$$

with Bohr (hydrogen) energy E_n for the unperturbed state,

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2},$$

where a_0 is the Bohr radius.
For the two expectation values, we have

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0}$$ [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

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n \frac{e^2}{4\pi\varepsilon_0 a_0}\frac{1}{n^2} + \frac{2}{2\ell+1}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^3 a_0^2}\right]$$

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

The correction is smaller than E_n by a factor

$$\sim \frac{E_n}{mc^2} \sim \frac{eV}{MeV} \sim 10^{-5}.$$ Small!

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

Darwin term

There is also a relativistic correction to the potential energy,

$$H_D = \frac{\hbar^2 \pi}{2m^2c^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\delta(\vec{r}),$$

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

$$E_D^1 = \langle\psi|H_D|\psi\rangle = \frac{\hbar^2\pi}{2m^2c^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)|\psi(0)|^2.$$

We have:

$$|\psi_{n\ell m}(0)|^2 = \frac{1}{\pi a_0^3 n^3}\quad \delta_{\ell 0}.$$

$$= \frac{e^2 m}{4\pi\varepsilon_0\hbar^2}\ \frac{1}{\pi a_0^2 n^3}\quad \delta_{\ell 0},$$

using the definition of the Bohr radius, resulting in

$$E_D^1 = \frac{1}{2mc^2}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right)^2 \frac{1}{n^3} \qquad (\ell=0)$$

$$= \frac{2n}{mc^2} E_n^2. \qquad (\ell=0)$$

This correction is of the same order as E_r^1.

<u>Spin-orbit coupling</u> [G 7.3.2]

Using a classical image, the electron rotates about the proton. However, in the <u>electron's rest frame</u>, the proton rotates about the electron. This circulating positive charge sets up a magnetic field $\vec{B}$ that excerts 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

$$H_{so} = \left(\frac{e^2}{8\pi\varepsilon_0}\right) \frac{1}{m^2c^2r^3} \vec{L} \cdot \vec{S}.$$

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, ℓ, s, j and m_j are good quantum numbers, while m_ℓ and m_s are not.

We have

$$\vec{J}^2 = (\vec{L}+\vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S}$$

$$\Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right],$$

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

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

where $s = 1/2$ for the electron.
We also have

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2}{\ell(2\ell+1)(\ell+1)a_0^3 n^3} \quad [\text{Hemmer p. 110}].$$

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

$$E^1_{so} = \langle \psi_{n\ell m} | H_{so} | \psi_{n\ell m} \rangle$$

$$= \frac{e^2}{8\pi\varepsilon_0} \frac{\hbar^2}{m^2c^2} \frac{\left[j(j+1) - \ell(\ell+1) - \frac{3}{4}\right]}{\ell(2\ell+1)(\ell+1)a_0^3 n^3}$$

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

Again the correction is of same size.

Fine structure

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

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

$$+ \frac{2n}{mc^2} E_n^2 \delta_{\ell 0}$$

$$+ \frac{2E_n^2}{mc^2}\left\{\frac{n\left[j(j+1) - \ell(\ell+1) - \frac{3}{4}\right]}{\ell(2\ell+1)(\ell+1)}\right\}(1-\delta_{\ell 0})$$

$$= \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{\ell+1/2} + 4n\,\delta_{\ell 0}\right.$$

$$\left. + \frac{4n\left[j(j+1) - \ell(\ell+1) - 3/4\right]}{\ell(2\ell+1)(\ell+1)}(1-\delta_{\ell 0})\right]$$

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

$j = \ell + 1/2$:

$$E^1_{fs} = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j} + 4n\,\delta_{\ell 0}\right.$$

$$\left. + \frac{4n}{2j(j+1/2)}(1-\delta_{\ell 0})\right] = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right]$$

If $j = \ell - 1/2$; which excludes $\ell = 0$

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

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

In either case, we get

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

and thus the new energy levels

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

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 ℓ — for a given n not all ℓ 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 momen:

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

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

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

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

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

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 <u>spin-spin coupling</u> (we already had $\vec{L}\cdot\vec{S}$) described by the Hamiltonian

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

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

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

We will now focus on the first order correction of the ground state $(nlm) = (100)$.

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 $l=0$), and the "good" states are therefore $|100; s m_s\rangle$:

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

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

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

We then get:

$$E_{hf}^{(1)} = \langle 100; s m_s | H_{hf} | 100; s m_s \rangle$$

$$= \langle s m_s | \int d\vec{r}\, \psi_{100}^* H_{hf} \psi_{100} | s m_s \rangle$$

$$= \frac{\mu_0 g_p e^2}{3 m_p m_e} |\psi_{100}(0)|^2 \langle s m_s | \vec{S}_p \cdot \vec{S}_e | s m_s \rangle,$$

where only the last term in H_{hf} gives a non-zero contribution when $l=0$, see Griffiths pp. 312-313 for details.

We now square $\vec{S}$:

$$\vec{S}^2 = \vec{S}_p^2 + \vec{S}_e^2 + 2\vec{S}_p \cdot \vec{S}_e$$

$$\Rightarrow \vec{S}_p \cdot \vec{S}_e = \frac{\vec{S}^2 - \vec{S}_p^2 - \vec{S}_e^2}{2}.$$

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

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

$$= \frac{1}{2} \langle s m_s | \hbar^2 s(s+1) - \frac{3\hbar^2}{4} - \frac{3\hbar^2}{4} | s m_s \rangle$$

$$= \begin{cases} +1/4 & s=1, \text{ triplet} \\ -3/4 & s=0, \text{ singlet} \end{cases}$$

Hence, gathering all results, using

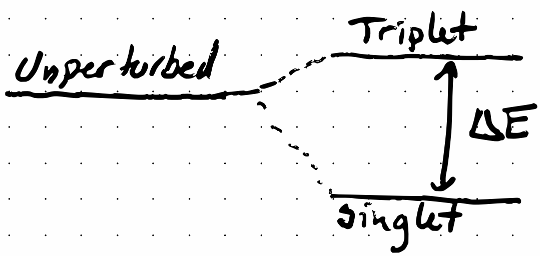
$$|\psi_{nlm_l}(0)|^2 = \frac{1}{\pi a_0^3 n^3}\delta_{l0}$$

from before with $n=1$, $l=m_l=0$, and $\mu_0 = (\varepsilon_0 c^2)^{-1}$, we get

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

Hence, we have a hyperfine splitting of the states

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



When an electron transitions from the triplet to the singlet state, a photon with wavelength $\lambda \approx 21$ 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.