HYDROGEN FINE AND HYPERFINE STRUCTURE

We already saw that the hydrogen Hamiltonian is less simple than it looks. Its most basic form is:

$$H = \frac{p^2}{2m} + \frac{e^2}{4\pi\varepsilon_0 r}$$

Solutions of corresponding Schroedinger's equation:

$$\psi_{n\ell m}(r, \theta, \varphi) = R_n^\ell(r)\, Y_\ell^m(\theta, \varphi)$$

$$E_n = -\frac{13.6\ \text{eV}}{n^2}$$

these are the Henkel's functions of the first type, seen in scattering problems

But we saw that there are additional contributions, namely the spin-orbit interaction, which breaks (partially) the n^2 degeneracy of the energy levels (for each n, $\ell = 0, .., n$ and $m = \underbrace{-\ell, -\ell+1, .., \ell-1, \ell}_{2\ell+1 \text{ states}}$: hence, we have $\sum_{\ell=0}^{n-1} 2\ell+1 = n^2$ states, all with the same energy E_n).

$$H_{\substack{\text{spin-}\\\text{orbit}}} = \frac{e^2}{8\pi\varepsilon_0} \cdot \frac{1}{m^2 c^2 r^3} \cdot \vec{S} \cdot \vec{L}$$

Now the states with $\ell \neq 0$ split: the new quantum number that defines the energy (beside n, of course) is j, corresponding to $\vec{J} = \vec{L} + \vec{S}$.

We also saw that the magnitude of the spin-orbit correction, calculated in perturbation theory, is α^2 smaller than the Bohr energy, where α = FINE-STRUCTURE CONSTANT = $e^2/4\pi\varepsilon_0 \hbar c = 1/137$.

Let us now investigate two additional terms that contribute to a modification of the hydrogen energy (and define its <u>fine</u> and <u>hyperfine</u> structure):

1) relativistic correction: $\propto \alpha^2 \cdot$ Bohr energy (same as spin-orbit: they <u>both</u> contribute to fine structure)

2) hyperfine splitting: $\propto \alpha^4 \cdot$ Bohr energy (this term defines the hydrogen hyperfine structure)

1) relativistic conection

The kinetic energy of our electron is not really $\frac{1}{2}mv^2 = p^2/2m$. Its relativistic expression is a bit more complicate:

$$T = \text{kinetic energy} = \underbrace{\sqrt{(pc)^2+(mc^2)^2}}_{\text{total energy}} - \underbrace{mc^2}_{\text{energy of mass at rest}}$$

Expanding the expression above in the limit $p \ll mc$, we get:

$$T = mc^2\left(1+\left(\frac{p}{mc}\right)^2\right)^{1/2} - mc^2 \approx mc^2\left(1+\frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \dots\right) - mc^2$$

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

this is our relativistic conection!

The first-order conection to the energy is therefore:

$$E^1_{\substack{\text{relativistic}\\ \text{conection}}} = \langle \psi_{nlm} | -\frac{p^4}{8m^3c^2} | \psi_{nlm} \rangle$$

We can use a simple trick to evaluate the integral above. ψ_{nlm} are the eigenstates of the unperturbed Hamiltonian H^0:

$$H^0 = \frac{p^2}{2m} + V(r) \xrightarrow[\text{therefore}]{} p^2 = 2m(H^0 - V(r))$$

Finally:

$$E^1_{\substack{\text{relativistic}\\ \text{conection}}} = \langle \psi_{nlm} | -\frac{1}{8m^3c^2}(2m)^2(H^0 - V(r))^2 | \psi_{nlm} \rangle =$$

$$= -\frac{1}{2mc^2} \langle \psi_{nlm} | (H^0 - V(r))^2 | \psi_{nlm} \rangle = -\frac{1}{2mc^2} \langle (H^0 - V(r))\psi_{nlm} | (H^0 - V(r))\psi_{nlm} \rangle$$

$$= -\frac{1}{2mc^2}\left(E_n^2 + 2E_n \frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle + \frac{e^4}{16\pi^2\varepsilon_0^2}\left\langle \frac{1}{r^2} \right\rangle\right)$$

With a bit of effort, one can calculate that:

$$\left\langle \frac{1}{r} \right\rangle = \langle \psi_{nlm} | \frac{1}{r} | \psi_{nlm} \rangle = \frac{1}{n^2 a} \quad \text{and} \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+\frac{1}{2})n^3 a^2}$$

where a is the Bohr radius

Finally:

$$E'_{\substack{\text{relativistic}\\ \text{correction}}} = -\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+1/2}-3\right)$$: about a factor α^2 smaller than E_n ⇒ perturbation theory applies safely

2) Hyperfine structure

We shall note that the hydrogen nucleus, a proton, does have a magnetic momentum, albeit way smaller than the electron. In fact:

$$\vec{\mu}_p = \frac{g_p \cdot e}{2m_p}\vec{S}_p \qquad \vec{\mu}_e = \frac{-g_e e}{2m_e}\vec{S}_e$$

$g_p = 5.59$, while $g_e = 2$, but $m_p \cong 2000 \cdot m_e$!

We need to find the magnetic field $\vec{B}$ generated by the proton magnetic momentum (it is a magnetic dipole). The electron spin will interact with it. The Hamiltonian Term describing this interaction is:

$$H' = -\vec{\mu}_e \cdot \vec{B} = +\frac{\mu_B}{\hbar}\vec{S}_e \cdot \vec{B}$$ where μ_B = Bohr magneton = $\frac{e\hbar}{2m_e}$ $= 50\,\mu eV/T$ (microelectronvolt/Tesla)

The complicate business is finding $\vec{B}$. Classical electrodynamics says that:

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

is the $\vec{B}$ field generated by a magnetic dipole momentum $\vec{\mu}_p$. Let us note the $\delta^3(\vec{r})$ term: we can anticipate that if $l \neq 0$ that term will not have any effect: $\psi_{nlm}(0) = 0$ if $l \neq 0$.

Using the definition of $\vec{B}$ and $\vec{\mu}_p$ in H', we obtain:

$$\underset{\text{hyperfine}}{H'_{HF}} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e r^3}\left(3\cdot(\vec{S}_p\cdot\hat{r})(\vec{S}_e\cdot\hat{r}) - \vec{S}_p\cdot\vec{S}_e\right) + \frac{\mu_0 g_p e^2}{3 m_p m_e}\delta^3(r)\,\vec{S}_p\cdot\vec{S}_e$$

According to perturbation theory, we have:

$$E'_{HF} = \langle \psi_{nlm} | H'_{HF} | \psi_{nlm} \rangle$$

Let us focus on a case of critical usefulness: the ground state ψ_{100}. We will not perform the calculations explicitly, but it can be shown that, since $l=0$ and the state is spherically symmetric, the first term of H'_{HF} does <u>not</u> contribute. We are left with one integral to evaluate:

$$E'_{HF} = \frac{\mu_0 g_p e^2}{3 m_p m_e} \underbrace{\langle \psi | \vec{S}_p \cdot \vec{S}_e | \psi \rangle}_{\substack{\text{this expectation value} \\ \text{is computed using only} \\ \text{the spin part of } \psi \\ \text{(which now must also} \\ \text{contain the proton spin)}}} \underbrace{|\psi(0)|^2}_{\substack{\text{this is the result of the integral} \\ \text{with } \delta^3(\vec{r}),\ \vec{r}=0 \text{ is the position of the} \\ \text{proton}}}$$

Let us use the same trick used with the spin-orbit case: from using eigenstates of the electron and proton spins separately, let us use eigenstates of the total spin $\vec{S} = \vec{S}_e + \vec{S}_p$. We can therefore write:

$$\vec{S}_e \cdot \vec{S}_p = \frac{S^2 - S_e^2 - S_p^2}{2}$$

Since $|\psi_{100}(0)|^2 = 1/\pi a^3$, we obtain:

$$E'_{HF} = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \cdot \langle \psi | \frac{S^2 - S_e^2 - S_p^2}{2} | \psi \rangle$$

Which values can the operator S^2 have, as eigenvalues? Both electron and proton have spin $1/2$, hence the total spin can be either 0 or $\hbar^2(1+1)\cdot 1 = 2\hbar^2$ (the corresponding quantum numbers for S are 0 or 1).

The state with $S=1$ is called <u>triplet</u> ($m_S = -1, 0, 1$); the state with $S=0$ is a <u>singlet</u>. We started from four states ($m_{S_e} = \pm\frac{1}{2} \times m_{S_p} = \pm 1/2$) all with the same energy; the hyperfine structure splits them into a (degenerate) triplet and a singlet state.

triplet case: $\langle \vec{S}_p \cdot \vec{S}_e \rangle = \frac{1}{2}\hbar^2\left(2 - \frac{3}{4} - \frac{3}{4}\right) = \frac{\hbar^2}{4}$

singlet case: $\langle \vec{S}_p \cdot \vec{S}_e \rangle = \frac{1}{2}\hbar^2\left(0 - \frac{3}{4} - \frac{3}{4}\right) = -\frac{3\hbar^2}{4}$

$\frac{3}{4}\hbar^2 = \hbar^2\left(\frac{1}{2}+1\right)\cdot\frac{1}{2}$

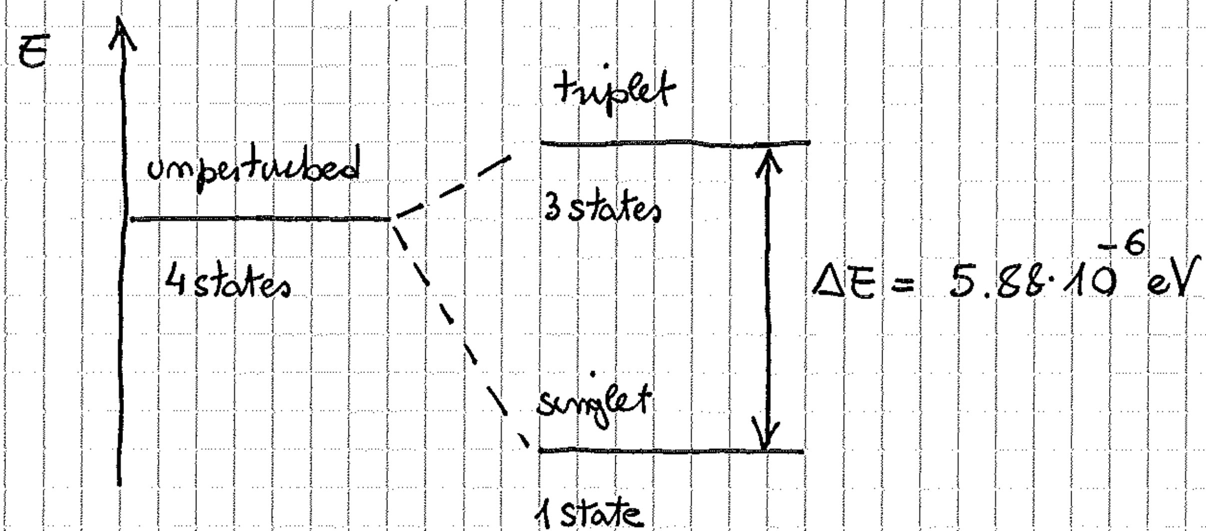
Finally:

$$E'_{HF}\ \text{triplet} = \frac{\mu_0 g_p e^2 \hbar^2}{3 m_p m_e \pi a^3}$$

$$E'_{HF}\ \text{singlet} = -\frac{\mu_0 g_p e^2 \hbar^2}{m_p m_e \pi a^3}$$

order of correction:

$E'_{HF} \propto \alpha^4 E_m$



The transition from triplet to singlet corresponds to a wavelength of 21 cm: this is the most pervasive form of radiation in the whole universe!