

Fine Structure of Hydrogen

We have previously solved for the stationary states and energies of the Hydrogen atom. The energy formula was

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \approx \frac{-13.6 \text{ eV}}{n^2}$$

First I will introduce a new constant, called the Fine Structure Constant:

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$$

With the definition we can rewrite the Bohr energies as $E_n = -\frac{1}{2}mc^2\frac{\alpha^2}{n^2}$. It turns out that there are a series of corrections to the simplified Bohr Hamiltonian that change these energies, and the fine structure constant provides an effective way to gauge their scale. The first correction we will consider is called the fine structure, which is actually a combination of two distinct causes: a relativistic correction and spin-orbit coupling. The second correction is known as the Lamb shift, and is caused by the quantization of the electric field. Finally, hyperfine structure is caused by coupling between the electron spin and the nuclear magnetic moment of the proton. The energy scales are as follows:

Bohr energies	of order	$\alpha^2 mc^2$	1
Fine Structure	of order	$\alpha^4 mc^2$	5×10^{-5}
Lamb Shift	of order	$\alpha^5 mc^2$	4×10^{-7}
Hyperfine Structure	of order	$(m/m_p)\alpha^4 mc^2$	3×10^{-8}

As stated earlier, the fine structure is caused by two different mechanisms: a relativistic correction and spin orbit coupling. We will consider the relativistic correction first. In special relativity, kinetic energy is given by $T = \sqrt{p^2c^2 + m^2c^4} - mc^2 = mc^2 \left[\sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1 \right]$. If we

assume that $p \ll mc$ and take a binomial expansion we get

$$T \approx mc^2 \left[1 + \frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 + \dots - 1 \right] \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

Therefore the relativistic correction consists of a perturbation $\hat{H}'_r = -\frac{\hat{p}^4}{8m^3c^2}$. Using first-order perturbation theory we get a first order correction term of

$$E_r^1 = \frac{-1}{8m^3c^2} \langle \psi_{nlm}^0 | \hat{p}^4 | \psi_{nlm}^0 \rangle = \frac{-1}{8m^3c^2} \langle \hat{p}^2 \psi_{nlm}^0 | \hat{p}^2 \psi_{nlm}^0 \rangle$$

which takes advantage of the fact that $\hat{p}$ is hermitian. But of course the time-independent Schrödinger equation for the unperturbed state tells us that $\hat{p}^2 \psi_{nlm}^0 = 2m(E - V) \psi_{nlm}^0$. This means that $\langle \hat{p}^2 \psi_{nlm}^0 | \hat{p}^2 \psi_{nlm}^0 \rangle = 4m^2 \langle (V - E)^2 \rangle$ where the expectation value is for the unperturbed state ψ_{nlm}^0 . This gives

$$\begin{aligned} E_r^1 &= -\frac{1}{2mc^2} [E^2 - 2E\langle V \rangle + \langle V^2 \rangle] \\ &= -\frac{1}{2mc^2} \left[E^2 + 2E \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right] \end{aligned}$$

For any unperturbed hydrogen stationary state these expectation values are $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2a}$ and $\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+1/2)n^3a^2}$

Therefore

$$E_r^1 = -\frac{1}{2mc^2} \left[E^2 + 2E \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2a} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(l+1/2)n^3a^2} \right]$$

This can be simplified to

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

Now this energy shift was calculated using non-degenerate perturbation theory, which seems problematic because the hydrogen energy

levels are highly degenerate. However, because the perturbation is spherically symmetric it commutes with both $\hat{L}^2$ and $\hat{L}_z$. These two operators break the degeneracy fully. Therefore, we are lucky that the ψ_{nlm}^0 states that we typically use are in fact “good” states to use in perturbation theory. Another phrase is that n , l , and m are “good quantum numbers”.

That determines the fine structure correction for relativistic reasons. There is another mechanism that gives a term of the same order of magnitude. This is spin-orbit coupling. An electron orbits the proton nucleus. But, from the perspective of the electron, the proton is orbiting it. This creates a magnetic field at the position of the electron. It is the interaction between this magnetic field and the magnetic moment of the electron that provides the perturbation for this section.

First we treat the orbiting proton as a steady current. The magnetic field will equal $\frac{\mu_0 I}{2r}$ where $I = \frac{e}{T}$ with T being the orbital period. The angular momentum of the electron is $L = mvr = 2\pi mr^2/T$, which we will use to eliminate T . This gives

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}$$

where we have used $\mu_0 = \frac{1}{\epsilon_0 c^2}$ and the fact that the electrons angular momentum and the effective magnetic field felt by the electron will point in the same direction. Further, the magnetic dipole moment of the electron is given by $\vec{\mu}_e = -\frac{e}{m} \vec{S}$ where I am treating the electron g -factor as 2. The problem with what we have done so far is that we moved into the reference frame of the electron, which is problematic because it is accelerating. This can be corrected by considering Thomas precession, which yields a factor of 1/2.

The perturbation is then

$$\hat{H}'_{so} = -\vec{\mu}_e \cdot \vec{B} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

Once we add this term, the Hamiltonian no longer commutes with $\hat{L}_z$ or $\hat{S}_z$. Therefore m_l and m_s are no longer good quantum numbers to use to describe the stationary states. Luckily, we can define $\vec{J} = \vec{L} + \vec{S}$ as the total angular momentum. The spin and orbital angular momenta add to give $\vec{J}$ just like any addition of angular momentum using Clebsch-Gordan tables. We know that $|l - s| \leq j \leq l + s$, which means that $j = \frac{1}{2}$ for $l = 0$ and j can be either of $l \pm \frac{1}{2}$ for all other l . $\hat{J}^2$ and $\hat{J}_z$ do in fact commute with the Hamiltonian as well as $\hat{L}^2$ and $\hat{S}^2$.

$\vec{L} \cdot \vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$ which means that the eigenvalues of $\vec{L} \cdot \vec{S} = \frac{1}{2}(j(j+1) - l(l+1) - \frac{3}{4})$ which of course uses the fact that $s = \frac{1}{2}$. The only remaining task is to determine $\left\langle \frac{1}{r^3} \right\rangle$ which can be shown to be

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3}$$

Therefore

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

This can be added to the relativistic correction achieve the total first-order energy correction, which is

$$E_{\text{fine structure}}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right)$$

This is added to the standard Bohr energy E_n to get

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

Notice that when spin-orbit coupling is included the energy of a level depends on n and j . The good quantum numbers are n , l , s , j , and m_j . These quantum numbers define each stationary state.

The Zeeman Effect

Another perturbation that we might consider is the Zeeman effect, that arises when we apply an external magnetic field to an atom. From classical physics, we would say that this adds a perturbation of $\hat{H}'_Z = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{\text{ext}}$ where $\vec{\mu}_l$ and $\vec{\mu}_s$ are (respectively) the magnetic dipole moments due to orbital and spin angular momenta. These are given by

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L} \quad \text{and} \quad \vec{\mu}_s = -\frac{e}{m}\vec{S}$$

where you will notice that the factor of 2 in the denominator of the first equation is missing in the second. This is because the “g-factor” for orbital angular momentum is $g_l = 1$ while that for spin is $g_s \approx 2$ (really slightly higher, ≈ 2.0023). Together, this gives us

$$\hat{H}'_Z = \frac{e}{2m}(\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}}$$

How we apply the Zeeman effect in perturbation is going to depend on how strong the external magnetic field is compared to the internal magnetic field that gave rise to the spin-orbit coupling in the fine structure. When the external magnetic field is small we treat it as a small perturbation upon the energy levels already determined from the fine structure. When the external magnetic field is very large we instead treat the fine structure term as the perturbation. These two approaches will differ as to which quantum numbers are the good ones.

Weak Field Zeeman Effect

We start by treating the external magnetic field as small. Therefore $\hat{H}'_Z$ is the perturbation while $\hat{H}_{\text{Bohr}} + \hat{H}_{\text{fine structure}}$ is the unperturbed Hamiltonian $\hat{H}^0$. The fine structure used n, l, j , and m_j as its quantum numbers. Therefore we use these for our unperturbed states $|\psi_{nljm_j}\rangle$

with unperturbed energies

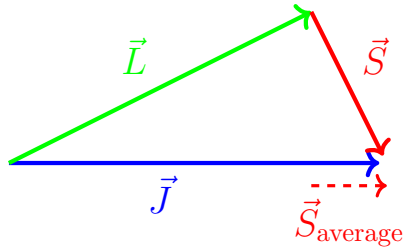
$$E_{nj} = \frac{-13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + 1/2} - \frac{3}{4} \right) \right]$$

These energies are still degenerate, as they depend only on n and j and do not depend on l or m_j . We are very lucky that these remain good quantum numbers. We can know that they remain good quantum numbers because the operators $\hat{L}^2$ and $\hat{J}_z$ (which together describe the state completely, including the quantum numbers l and m_j that do not affect the energy) both commute with the perturbation $\hat{H}'_Z$. Therefore we can assume that the external magnetic field is pointing along the z -axis and give the first-order Zeeman energy correction term as

$$E_Z^1 = \langle \psi_{nljm_j} | \hat{H}'_Z | \psi_{nljm_j} \rangle = \frac{e}{2m} B_{\text{ext}} \hat{k} \cdot \langle \vec{L} + 2\vec{S} \rangle$$

$\vec{L} + 2\vec{S} = \vec{J} + \vec{S}$. j is still a good quantum number, but s is not, so we wish to remove the $\vec{S}$ from our equation. We know that $\vec{J} + \vec{L} + \vec{S}$ is a constant, but that $\vec{L}$ and $\vec{S}$ will not be. But we only care about the average value of $\vec{S}$ as it precesses around $\vec{J}$. This average value is

$$\vec{S}_{\text{average}} = \frac{\vec{S} \cdot \vec{J}}{J^2} \vec{J}$$



We calculate $\vec{S} \cdot \vec{J}$ by noting that $\vec{L} = \vec{J} - \vec{S}$ which gives $\vec{S} \cdot \vec{J} = \frac{1}{2} (\hat{J}^2 + \hat{S}^2 - \hat{L}^2)$. From this I would claim that

$$\langle \vec{L} + 2\vec{S} \rangle = \left\langle \left(1 + \frac{\vec{S} \cdot \vec{J}}{\hat{J}^2} \right) \vec{J} \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right] \langle \vec{J} \rangle$$

where the term in the brackets at the end is defined as the Landé g-factor g_J . This results in

$$E_Z^1 = \mu_B g_J B_{\text{ext}} m_j$$

where $\mu_B \equiv \frac{e\hbar}{2m}$ is known as the Bohr magneton.

Strong Field Zeeman Effect

When the external magnetic field is very large we start with $\hat{H}_{\text{Bohr}} + \hat{H}'_Z$ as our unperturbed Hamiltonian. Assuming that the external magnetic field is along the z -axis we have $\hat{H}'_Z = \frac{e}{2m} B_{\text{ext}} (\hat{L}_z + 2\hat{S}_z)$. The effect of this on the Bohr energies is simple because our typical states (ψ_{nlm}) will be eigenstates of this. The energies will be $E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s)$. We then add in the fine structure terms (both the relativistic correction and the spin orbit coupling) as perturbations to this while using n , l , m_l , and m_s as our quantum numbers. As before, the energies start as degenerate but we are lucky that these remain good quantum numbers. The relativistic correction remains the same as before: $E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right]$. The spin-orbit correction is $\left(\frac{e^2}{8\pi\epsilon_0} \right)^2 \frac{1}{m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \langle \vec{S} \cdot \vec{L} \rangle$ but now $\langle \vec{S} \cdot \vec{L} \rangle = \hbar^2 m_s m_l$ with these quantum numbers. Putting these together the fine structure term is

$$E_{\text{fine structure}}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right\}$$

which needs to be added to $E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}}(m_l + 2m_s)$ to determine the energy.

Hyperfine Splitting

A proton has a magnetic dipole moment $\vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p$. This will be much smaller than the electron magnetic dipole moment ($\vec{\mu}_e = -\frac{e}{m_e} \vec{S}_e$) because $\frac{m_p}{m_e} \approx 2000$. Also note that the proton g-factor is $g_p \approx 5.59$ which is larger than the simpler value of 2 for the electron because the proton is a composite particle consisting of quarks. The magnetic field created by a magnetic dipole moment is

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

which means that perturbation due to the interaction of the magnetic field created by the proton with the electron spin is given by

$$\hat{H}'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} \vec{S}_p \cdot \vec{S}_e \delta^3(\vec{r})$$

By perturbation theory, the first-order correction is

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle \vec{S}_p \cdot \vec{S}_e \rangle |\psi(0)|^2$$

The expectation value in the first term will be zero for any spherically symmetric state, which means any state with $l = 0$. For the ψ_{100} ground state $|\psi(0)|^2 = \frac{1}{\pi a_0^3}$ giving

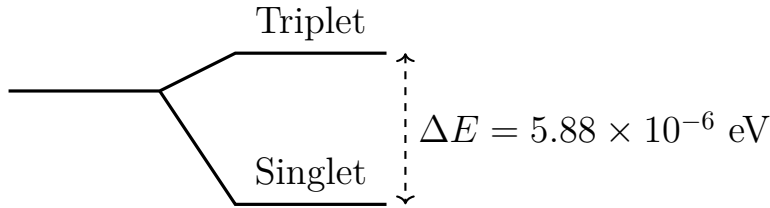
$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a_0^3} \langle \vec{S}_p \cdot \vec{S}_e \rangle$$

Similar to what we have done before, $\vec{S}_p \cdot \vec{S}_e = \frac{1}{2}(\hat{S}_{total}^2 - \hat{S}_p^2 - \hat{S}_e^2)$ which implies that

$$\langle \vec{S}_p \cdot \vec{S}_e \rangle = \begin{cases} +\frac{\hbar^2}{4} & s_{total} = 1 \text{ (triplet)} \\ -\frac{3\hbar^2}{4} & s_{total} = 0 \text{ (singlet)} \end{cases}$$

meaning that

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} \cdot \begin{cases} +\frac{1}{4} & s_{total} = 1 \text{ (triplet)} \\ -\frac{3}{4} & s_{total} = 0 \text{ (singlet)} \end{cases}$$



The splitting between these two states has an energy $\Delta E = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} = 5.88 \times 10^{-6} \text{ eV}$. The microwave radiation emitted in the transition from the triplet to the singlet state has a 21.1 cm wavelength. This wavelength is commonly searched for in radio astronomy studies of the galaxy.