Phys 115C 10/1/09 Fine Structure of Hydrogen

The topic for today is the fine structure within the hydrogen energy spectrum, which arises from higher order corrections to the simple Hamiltonian used, initially, in Schrödinger's equation.

Before discussing the fine structure, let's do a quick review of the "coarse" structure.
Solved the Schrödinge equation for the radial part of the wave function (after separating variables into r, θ, φ):

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

where $u(r)$ is a stand-in for the real radial wave function,

$$R(r) = u(r)/r$$

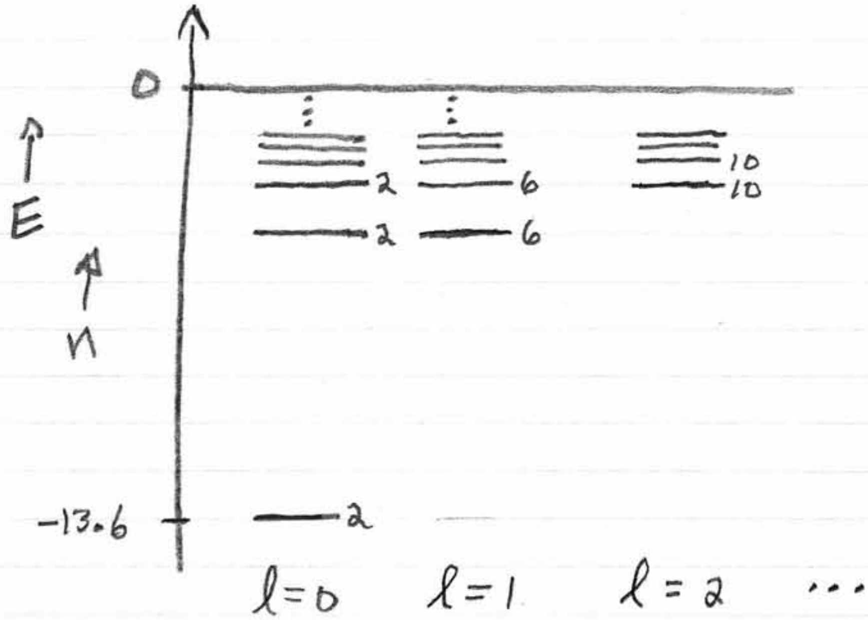
The $\ell(\ell+1)$ term is the so-called "centrifugal term" that brings the effect of angular momentum into an "effective potential."

The energy levels obtained from solving this are:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \qquad n=1,2,3,\ldots$$

$$\doteq -\frac{13.6\,\mathrm{eV}}{n^2}$$

The spectrum is: (not to scale)



Number of degenerate states in red. $= 2 * (2\ell+1)$, where $2 \leftarrow m_s$ and $(2\ell+1) \leftarrow m_\ell$

But, there are also the other quantum numbers:

n = principal $\quad n = 1, 2, 3, \ldots$

ℓ = orbital; magnitude of angular momentum, L
$\quad \ell = 0, 1, 2, \ldots, n-1$

m_ℓ = orbital magnetic; z-component of L, L_z
$\quad m_\ell = -\ell, -\ell+1, \ldots, \ell$

m_s = spin quantum number, $\pm 1/2$

These don't affect E, so far, so they are degenerate.

The energy levels will be perturbed if there are any new terms added to the Hamiltonian. We'll discuss three.

First, the Zeeman effect. (The text puts this last, but it is intuitively simplest for me).

It was first observed in 1896 that some Hydrogen lines split into triplets in a magnetic field.

A $\vec{B}$ field adds a new potential term,

$$V_{ZE} = -\vec{\mu} \cdot \vec{B}$$

where $\vec{\mu}$ is the magnetic dipole moment of the electron, which comes from its orbit and its spin.

$$\vec{\mu} = \vec{\mu}_\ell + \vec{\mu}_s$$

I'll consider only $\vec{\mu}_\ell$ now for simplicity.

What is $\vec{\mu}_\ell$? We can get a crude estimate from a simple argument.

$\vec{\mu} = I\vec{A}$ from electron orbit.

$$= \left(\frac{-e}{T}\right)\pi r^2 = \frac{-e}{2\pi r/v}\pi r^2$$

$$= -\frac{1}{2} e r v$$

$$= \frac{-e}{2m} m r v = \frac{-e}{2m} \vec{L}$$

So,

$$V_{ZE} = -\frac{e}{2m} \vec{L} \cdot \vec{B}$$

$$= -\frac{e}{2m} L_z B$$

What direction is $\vec{L}$? Consider $\vec{B} = B\hat{z}$, so only the L_z part matters.

So, add this term to the Hamiltonian, and resolve the SE. That would be messy, but recall from perturbation theory that

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

I.e., the energy correction, E_n^1, is the expectation value of the correction term in the Hamiltonian, using the unperturbed state.
(The superscript 1 means 1st order, as opposed to E_n^0 being the unperturbed energy).

So, the Zeeman effect changes the energy of a state by

$$E_n^{ZE} = \left\langle -\frac{e}{2m} L_z B \right\rangle = -\frac{e}{2m} B \langle L_z \rangle$$

$$= -\frac{e}{2m} B \, m_\ell \hbar$$

$$= -\frac{e\hbar}{2m} m_\ell B$$

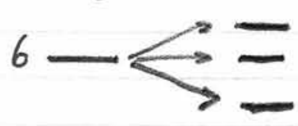
$$= -\mu_B \, m_\ell \, B$$

where $\mu_B \equiv e\hbar/2m_e = 5.788 \times 10^{-5}$ eV/Tesla

is the "Bohr magneton".

So, for a 1 Tesla field, you split the $m_\ell = \pm 1$ states by $O(1 \mu eV)$, and the $m_\ell = 0$ states are unchanged

For $n=2$
$\ell = 1$



The Zeeman Effect is not "fine structure", actually. It is a response to an external $\vec{B}$ field.

There is an internal $\vec{B}$ field that causes splitting, i.e. "fine structure within the normal hydrogen spectra". This field comes from the proton. From the electron's point of view, i.e., in its frame, the proton is a current loop around it.

$$B = \mu_0 I / 2r$$

$$= \frac{\mu_0}{2r}\frac{e}{T} = \frac{\mu_0 e}{2r}\frac{1}{2\pi r/v} = \frac{\mu_0 e}{4\pi r^2} v$$

$$= \frac{\mu_0 e}{4\pi r^2}\frac{mrv}{mr}$$ to put it in terms of L.

$$\vec{B} = \frac{\mu_0 e}{4\pi m r^3}\vec{L} = \frac{\mu_0 \varepsilon_0 e}{4\pi m r^3 \varepsilon_0}\vec{L}$$

$$= \frac{e\,\vec{L}}{4\pi\varepsilon_0 mc^2 r^3}$$ since $c = \frac{1}{\sqrt{\mu_0\varepsilon_0}}$.

Now, what is $\vec{\mu}$? It is not from the electron's orbit, since we are in the electron's rest frame.

But there is a $\vec{\mu}$ from the electron spin.

If we thought of the electron as a spinning <u>ring</u> of charge, then $\mu = IA$ gives

$$\mu = \frac{q}{T}\pi r^2 = \frac{-e}{2\pi r/v}\pi r^2 = \frac{-e}{2} r v$$

$$= -\frac{e}{2m} L$$

In fact if it was a sphere, built up from rings, you'd get the same thing.

Treating $\vec{L}$ as $\vec{S}$, the spin of the electron,

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

This is wrong, because our picture is naive, but we'll deal with that soon.

So, this coupling between the spin of the electron and its orbit adds a "spin-orbit coupling" term to the Hamiltonian:

$$V_{so} = -\vec{\mu}_e \cdot \vec{B}_{orbit} = -\left(\frac{-e}{2m}\vec{S}\right)\cdot\left(\frac{e\,\vec{L}}{4\pi\varepsilon_0 m c^2 r^3}\right)$$

$$= \frac{e^2}{8\pi\varepsilon_0 m^2 c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$

This is actually correct despite two errors...

First, the naive model of a spinning ball of charge doesn't match a real electron.
Properly calculating $\vec{\mu}_e$ requires relativistic quantum mechanics, i.e., Dirac's equation.
That gives,

$$\vec{\mu}_e = g\left(\frac{-e}{2m}\right)\vec{S}$$

where $g = 2$ plus some corrections.

$$g = 2 + \frac{\alpha}{\pi} + \ldots \quad \text{where} \quad \alpha = \frac{1}{137}$$

$$= 2.0023193043615 \pm 6\times10^{-13}$$

So, we were wrong by about a factor of two!

But wait, there's more...
Treating the proton as a current loop is naive; because the electron is <u>accelerating</u> around the proton it is not an inertial system.
If we did that correctly, it changes the result by a factor of $1/2$.

These "two naive" effects cancel, and we have a pretty good (missing the $\alpha/\pi + \ldots$) answer.

Now, we can use perturbation theory to calculate the energy shift from V_{so}.

$$E^1_{so} = \langle H_{so} \rangle = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2} \langle \frac{1}{r^3} \vec{S}\cdot\vec{L} \rangle$$

Finding $\langle \vec{S}\cdot\vec{L} \rangle$ is tricky because H doesn't commute with $\vec{L}$ and $\vec{S}$, they are not the appropriate quantities to use. Instead, we should use the total angular momentum,

$$\vec{J} \equiv \vec{S} + \vec{L} \quad \text{from which we can get } \vec{S}\cdot\vec{L}$$

$$\Rightarrow \quad J^2 = S^2 + L^2 + 2\vec{S}\cdot\vec{L}$$

$$\Rightarrow \quad \vec{S}\cdot\vec{L} = \tfrac{1}{2}(J^2 - S^2 - L^2)$$

From addition of angular momentum, J^2 has eigenvalues of $j(j+1)\hbar^2$, L^2 has eigenvalues $l(l+1)\hbar^2$ and $j = l \pm 1/2$, and of course, S^2 has eigenvalues of $s(s+1)$ but $s = \frac{1}{2}$.

So,

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

$$= \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right) \quad s(s+1) = \tfrac{1}{2}\cdot\tfrac{3}{2}$$

We also need $\langle \frac{1}{r^3} \rangle$, which I'll simply state without derivation:

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

So, the energy shift from the spin orbit coupling is

$$E_{so} = \frac{e^2 \hbar^2}{16\pi\varepsilon_0 m^2 c^2 n^3 a^3} \cdot \frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell+\frac{1}{2})(\ell+1)}$$

Plugging in

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

and

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

We can write E_{so} as

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

Note that if $\ell = 0$ we get $0/0$ because in the numer, $j(j+1) = s(s+1) = 3/4$. But with $\ell = 0$ we don't expect a spin orbit coupling anyway.

For $l = 1$, we get $j = 1 + \frac{1}{2}$ or $j = 1 - \frac{1}{2}$, and

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

The $\frac{E_n^2}{mc^2}$ factor is

$$\frac{(13.6\,eV)^2}{511{,}000\,eV} = 3.6 \times 10^{-4}\,eV$$

The rest is $\quad \frac{2}{3}\left[\frac{3}{2} \cdot \frac{5}{2} - 2 - \frac{3}{4}\right] = \frac{2}{3}$

or $\quad \frac{2}{3}\left[\frac{1}{2} \cdot \frac{3}{2} - 2 - \frac{3}{4}\right] = -4/3$

which push the (otherwise degenerate) states up and down a little bit.

The next correction we'll consider is a relativistic effect from v_e. The Schrödinger equation uses

$$\left(\frac{p^2}{2m} + V\right)\psi = E\psi$$

where, of course $p = \frac{\hbar}{i}\nabla$ is an operator.
But the $p^2/2m$ comes from kinetic energy

$$T + V = E$$

The fully relativistic kinetic energy is

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 \qquad \text{i.e. } E - mc^2$$

$$= mc^2\sqrt{\frac{p^2c^2}{m^2c^4} + 1} - mc^2$$

$$= mc^2\left[-1 + \sqrt{1 + \left(\frac{p}{mc}\right)^2}\right]$$

Expanding for small p/mc, we get

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

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

Where this is the correction to the Hamiltonian.
It will shift the energy by $E_r^1 = \left\langle -\frac{p^4}{8m^3c^2}\right\rangle$

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

Using a trick where $p^4 = \overleftarrow{p^2}\cdot\overrightarrow{p^2}$
But we know what p^2 does from the Schrödinger equation.

$$\frac{p^2}{2m}\psi + V\psi = E\psi$$

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

and

$$\langle\psi|p^4|\psi\rangle = \langle 4m^2(E-V)^2\rangle$$
$$= 4m^2\langle E^2 - 2EV + V^2\rangle$$
$$= 4m^2\left[E^2 - 2E\langle V\rangle + \langle V^2\rangle\right]$$
$$= 4m^2\left[E_n^2 - 2E_n\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$

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

So,

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

Plugging in $a = 4\pi\varepsilon_0\hbar^2/me^2$

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

For $n=2$, $\ell=1$,

$$E_r^1 = -\frac{(E_n)^2}{mc^2} \cdot \frac{1}{2} \cdot \left[\frac{8}{3/2} - 3\right]$$

$$= -\frac{(E_n)^2}{mc^2} \cdot \frac{7}{6}$$

$$= -4 \times 10^{-4}\ \text{eV}$$

which is similar to the E_{so}^1 result.

Very different sources, but they are both of order $(E_n)^2/mc^2$.

In fact, they can be added, and simplified using the fact that $j = \ell \pm \frac{1}{2}$ to get

$$E_{fs}^1 = E_r^1 + E_{so}^1 = \frac{(E_n)^2}{mc^2}\left(3 - \frac{4n}{j+1/2}\right)$$

The levels at a given ℓ split, but the j's remain degenerate.

Now, let's rewrite this in terms of α, which is called the fine structure constant.

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0 \hbar c} \cong \frac{1}{137}$$

Note all the universal constants combined: EM, relativity, QM.

Then,

$$E_n + E'_{fs} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

So, α is what we are expanding E in.

There is actually an α^2 in the 13.6 eV

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} = -\frac{1}{2}\alpha^2 mc^2 \cdot \frac{1}{n^2}$$

The fine structure adds another α^2/n^2

There is also "hyperfine splitting" that is proportional to $\alpha^4 mc^2$, like the fine structure, but with a m_e/m_p factor.

We also saw α in g. $g = 2 + \alpha/\pi + \dots$

And, the electron velocity is $\frac{v_e}{c} \approx \alpha$.

Rather important number!