From the unperturbed Sch Eq we know that:

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

Unperturbed energies of Ch. 4.

Then, we arrive to:

$$E_r^1 = -\frac{1}{2mc^2}\langle(E - V)^2\rangle = -\frac{1}{2mc^2}[E^2 - 2E\langle V\rangle + \langle V^2\rangle]$$

Now specifically for the hydrogen atom potential V= $-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$
and for the state "*n*":

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

Detail: index *n* missing in this formula,
and *n* is actually (*n*,*l*,*m*) for *H*.

It can be shown that (*no need to verify*):

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

Then, we arrive to the result:

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

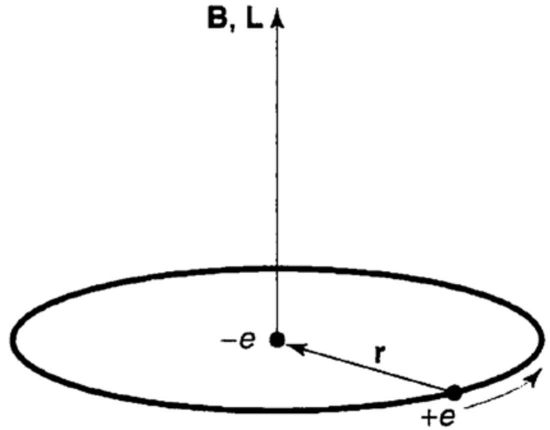
Using formulas of Ch. 4 for the Bohr radius "*a*" and for E_n :

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \qquad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

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

Example: for ground state use n=1, l=0, E_1 = -13.6 eV, m mass of electron, and c speed of light. Result ~ 10^{-3} eV (small!).

7.3.2 Spin-orbit coupling:



From the perspective of the electron, the proton is orbiting around:

From classical electromagnetism a loop of current creates a magnetic field at the center:

$$B = \frac{\mu_0 I}{2r}$$

$$c = 1/\sqrt{\epsilon_0 \mu_0}$$

where the permeability μ_0 of free space and the permittivity of free space ε_0 are related via:

Unrelated: next page comments and URL of video of this amazing E&M formula.

The current relates with the period *T* via:

$$I = e/T$$

$\omega = 2\pi/T$

and the period *T* relates with the angular momentum *L* via:

$$L = I\,\omega = m\,r^2\,2\pi/T$$

$$c = 1/\sqrt{\epsilon_0 \mu_0}$$

Side comment: This formula contains the essence of why the speed of light is **the same** for any pair of reference frames moving one with respect to the other at constant velocity.

A priori this is counterintuitive and before Einstein nobody thought about this . But it was contained in Maxwell's equations, where the above formula was derived.

Just imagine two rockets moving between galaxies (so that gravities can be neglected entirely) at different speeds. In both you measure the Coulombic static force between two charges and their distance and from there find ε_0 using Coulomb's law. Obviously, in both rockets you will find the same result. Same with experiments on both rockets that provides μ_0 measuring current and magnetic field and previous page formula for a loop wire with a current. In both rockets you will get the same ε_0 and μ_0 by common sense, thus the same speed of light c.

See URL https://www.youtube.com/watch?v=FSEJ4YLXtt8
Minutes 6.15 for Maxwell and minute 11.33 for Einstein and c constant.

From study of spins in magnetic fields (Ch. 4), in general:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}$$

From previous study of spin:

$$\mu_e = -\frac{e}{m}\mathbf{S}$$

From previous page:

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

Then, overall, classically we obtain the correction called spin-orbit coupling:

$$H = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}$$

Repeating via rigorous math (including the fact that the electron inertia system is accelerating, etc.) leads just to a factor 2 difference:

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

Important statement, without proof: Because of the **S.L** term, the Hamiltonian no longer commutes with S_z (quantum number m_s) and L_z (quantum number m_l) but still commutes with L^2 and S^2 and with the total angular momentum J^2 and its projection J_z (quantum number m_j).

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$$

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

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

Change of basis required: from basis with (n, l, s, m_l, m_s) as quantum numbers to basis with (n, l, s, j, m_j) as quantum numbers.

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

Fixed to $\frac{3}{4}$ for electrons

Moreover, the expectation value of $1/r^3$ using H wave functions is:

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

$$\langle H'_{so} \rangle = \langle \left(\frac{e^2}{8\pi\epsilon_0}\right) \frac{1}{m^2c^2r^3} \mathbf{S}\cdot\mathbf{L} \rangle$$

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

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

First order in perturbation theory

$$E^1_{so} = \langle H'_{so} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2} \frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3a^3}$$

Eqs. from Ch 4 for the Bohr radius "*a*" and for E_n :

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

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

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

In spite of their very different origins, the relativistic and spin-orbit corrections have the same number in front. I.e. they are of the "same order".

Adding both terms naively leads to a long expression

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

Consider j=l+1/2 first. Then j(j+1) = (l+1/2)(l+3/2). Careful algebra leads to

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

Consider now j=l-1/2. Then j(j+1) = (l-1/2)(l+1/2). Careful algebra leads to the **same**

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

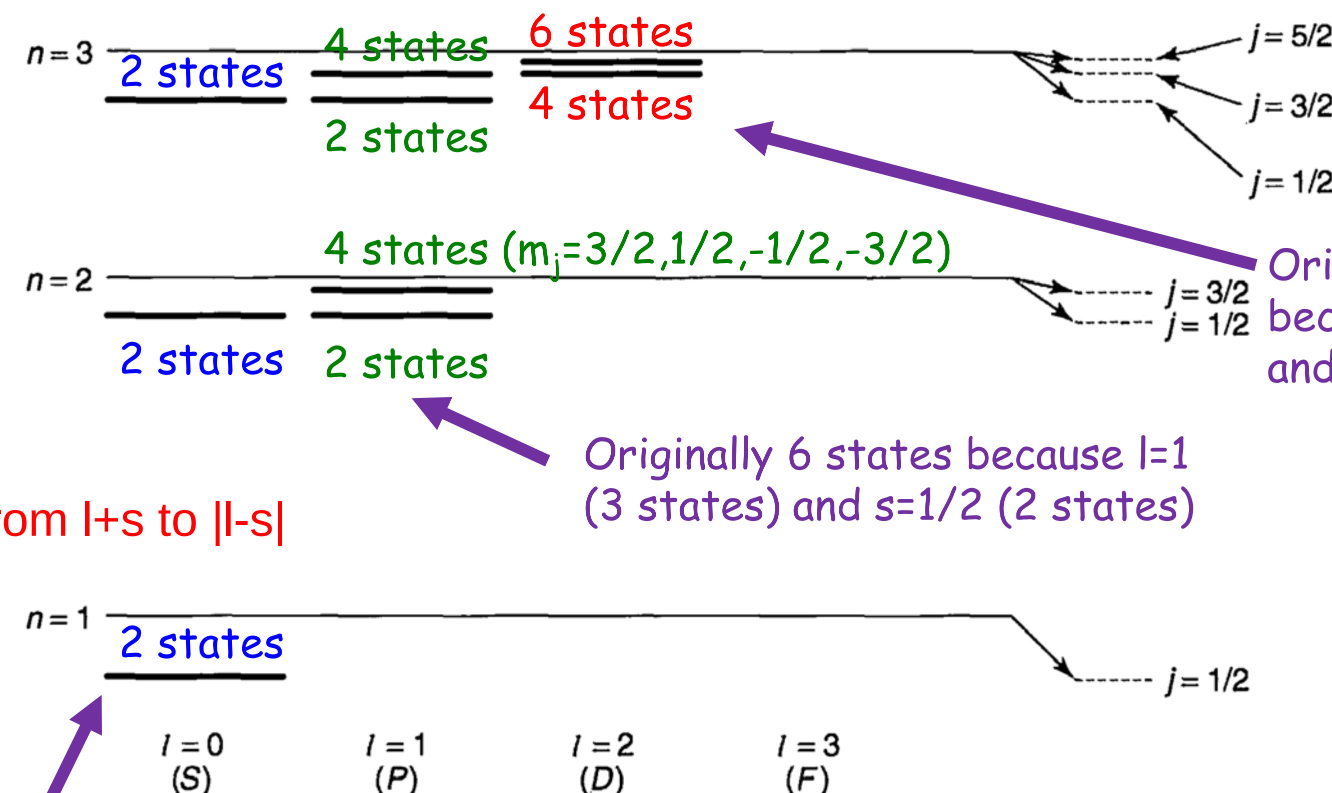
It can be shown that order 0 + order 1 gives:

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

where

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

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



Originally 10 states because l=2 (5 states) and s=1/2 (2 states)

Originally 6 states because l=1 (3 states) and s=1/2 (2 states)

j runs from l+s to |l-s|

NOTE: this is for the H atom. For He and beyond, the e-e repulsion plays a more important role than the fine structure.

Originally 2 states, because l=0 is 1 state but spin s=1/2 makes it 2 states.