Fine-structure:

The H atom spectrum showed "fine structure"
In particular $H\alpha$ showed doublet structure

Perturbations:

- relativistic
- spin-orbit
- Darwin term

- $$H = T + V = \frac{p^2}{2m_e} - \frac{e^2}{r}$$

but relativistic is

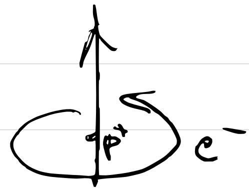
$$T = \sqrt{p^2c^2 + m_e^2c^4} - m_ec^2$$

$$= \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3c^2} + \ldots$$

- spin-orbit

In the frame of the electron the revolving proton produces a magnetic field. The electron spin ~~it~~ interacts with it

Magnetic moment of orbit.




Magnetic moment of electronic orbit

$$M_L = \frac{i\pi r^2}{c} \qquad i = \frac{ev}{2\pi r} \quad \text{current}$$

$$= \frac{1}{2}\frac{evr}{c}$$

$$= \frac{e}{2m_e c} m_e v r \qquad L = m_e v r$$

$$M_L = \frac{e}{2m_e c} L$$

For historical reasons: negative because of $e^-$

$$\vec{M}_L = -\frac{e\hbar}{2m_e c} g_L \frac{\vec{L}}{\hbar}$$

In this case & $g_L$ = orbital g factor = 1

$$\mu_B = \frac{e\hbar}{2m_e c} = \text{Bohr magneton}$$

In a similar fashion

$$\vec{M}_s = -g_s \mu_B \frac{\vec{S}}{\hbar}$$ where $\vec{S}$ = spin angular momentum

$$\frac{\vec{S}}{\hbar} = \pm\frac{1}{2}$$

but $g_s = 2.002318$

In the frame of the electron

$$\vec{B} = \frac{(-Ze\vec{v}) \times \vec{r}}{cr^3}$$

The electron is acted upon ~~by~~ the electrostatic force

$$\vec{E} = \frac{Ze}{r^3}\vec{r}$$

$$\therefore \vec{B} = -\frac{1}{c}\vec{v} \times \vec{E}$$

$-\nabla\Phi$ = force

but $$\vec{E} = \frac{-\nabla\Phi}{e} = \frac{1}{e}\frac{dV}{dr}\frac{\vec{r}}{r}$$

Thus $$\vec{B} = \frac{1}{em_ec}\frac{dV}{dr}\frac{1}{r}\vec{L}$$ $L = m_e\vec{v}\times\vec{r}$

The interaction with electron is

$$E = \left(-\frac{1}{2}\right) \vec{M}_s \cdot \vec{B} \quad \longrightarrow \text{Thomas Precession}$$

$$= \frac{1}{2m_e^2 c} \frac{1}{r} \frac{dV}{dr} \vec{S} \cdot \vec{L}$$

Note $\frac{dV}{dr} \propto \frac{1}{r^3}$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^2}{n^3 a_0^3} \frac{1}{l(l+\frac{1}{2})(l+1)}$$

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

$$\langle H_{so} \rangle = \frac{E_n^2}{m_e c^2} n \left[\frac{j(j+1) - l(l+1) - 3/4}{l(l+\frac{1}{2})(l+1)}\right]$$

For relativistic correction

$$\langle H_r \rangle = \frac{-E_n^2}{2m_e c^2} \left(\frac{4n}{l+\frac{1}{2}} - 3\right)$$

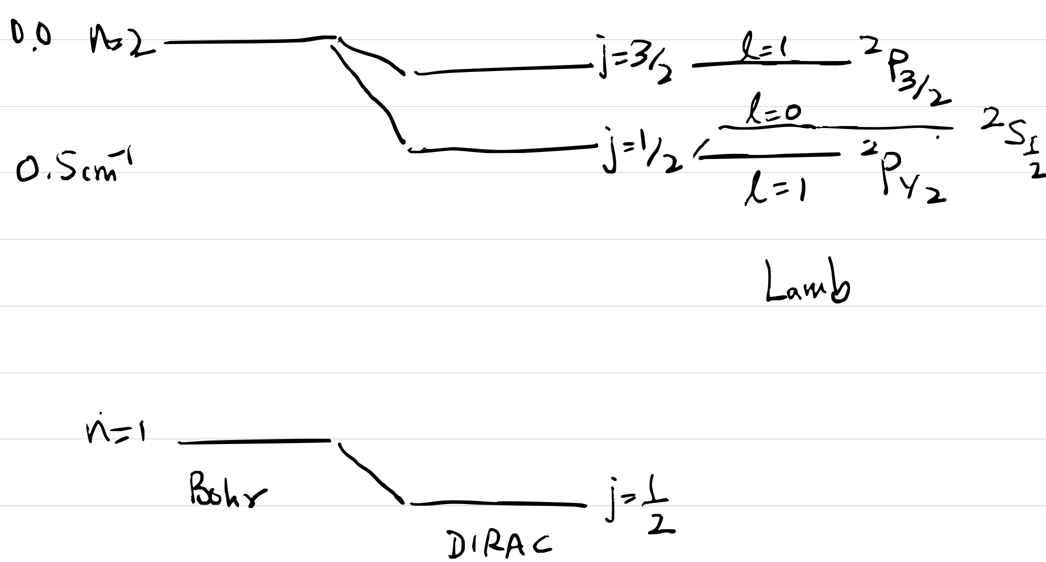
Add the Darwin correction to find

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

note $(Z\alpha)^2$

Dirac Theory:

$$E_{jn} = -m_e c^2\left[1-\left(1+\frac{\alpha^2}{\left(n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^2-\alpha^2}\right)^2}\right)^{-1/2}\right]$$



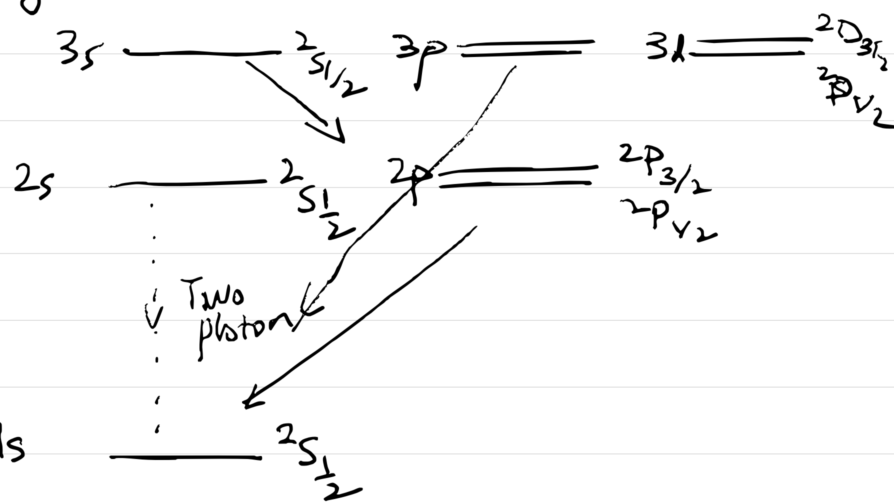
## SPECTROSCOPIC NOTATION

$$^{2S+1}\boxed{L}_J$$

$L = 0, 1, 2, 3$ $\qquad$ $l = 0, 1, 2, \ldots$

$\boxed{L} = S \;\; P \;\; D \;\; F$ $\qquad$ $\boxed{l} = s, p, \ldots$

Hydrogen:




$\Delta l = \pm 1$

Allowed for forbidden $\qquad$ $\Delta j = 0, \pm 1$

Two photon transition $\qquad$ $\Delta n > 0$