

Fine Structure

Note Title

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Fine structure comes from relativistic corrections to electronic wavefunctions

→ Think of fine structure correction as Dirac eqn. - Schrodinger eqn

Use the Pauli equation as a starting point (approximation to Dirac equation to lowest order in v/c)

$$H = \underbrace{mc^2}_{\text{rest energy}} + \underbrace{p^2/2m - \frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{non-relativistic}} + \underbrace{H_{FS}}_{\text{fine structure}}$$

$$H_{FS} = \underbrace{\frac{-p^4}{8m^3c^2}}_{\text{kinetic}} + \underbrace{\frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \vec{L} \cdot \vec{S}}_{\text{spin-orbit}} + \underbrace{\frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \delta(\vec{r})}_{\text{"Darwin"}}$$

Kinetic: relativistic correction to kinetic energy

$$E = \sqrt{(mc^2)^2 + (pc)^2}$$

$$KE = E - mc^2 = mc^2 \left(\sqrt{1 + \frac{p^2}{m^2c^2}} - 1 \right) \approx mc^2 \left(1 + \frac{1}{2} \frac{p^2}{m^2c^2} - \frac{1}{8} \frac{p^4}{m^4c^4} - 1 \right)$$

$$KE = \underbrace{\frac{p^2}{2m}}_{\text{regular kinetic energy}} - \underbrace{\frac{1}{8} \frac{p^4}{m^3c^2}}_{\text{correction}}$$

with $p^2 \ll m^2c^2$

Spin-orbit :

Interaction of electron magnetic moment with rotational magnetic field (relativistic $\vec{v} \times \vec{E}$, where $\vec{E}$ is from the nucleus)

$$\begin{aligned}\vec{B} &= -\frac{\vec{v} \times \vec{E}}{c^2} = -\frac{\vec{v}}{c^2} \times (-\vec{\nabla} V) = \frac{\vec{v}}{c^2} \nabla \left(\frac{Ze}{4\pi\epsilon_0 r} \right) \\ &= \frac{\vec{v}}{c^2} \times \frac{\vec{r}}{r} \left(\frac{-Ze}{4\pi\epsilon_0 r^2} \right) = \frac{Ze\hbar}{4\pi\epsilon_0 mc^2 r^3} \vec{L} \quad (\text{since: } \hbar \vec{L} = m \vec{r} \times \vec{v})\end{aligned}$$

only for Hydrogenic atoms

Interaction energy = $-\vec{\mu} \cdot \vec{B}$ where

$$\vec{\mu} = -g \frac{e\hbar}{2m} \vec{S} \quad \text{and} \quad g \approx 2 \quad (\text{for an electron})$$

from Dirac theory
QED - $g \neq 2$

$$* \mu_0 = 1.4 \text{ MHz/gauss} \times \hbar = \frac{e\hbar}{2m} \quad \text{Bohr magneton}$$

Many AND experimentalists like frequencies as units

There is another contribution to the interaction energy from Thomas precession (see Jackson)

- relativistic transformation of vector between frames involves a rotation if the relative accelerations are non-colinear
- observer fixed at the nucleus sees this as an additional magnetic field

Thomas precession cuts the energy in half, so

$$H_{LS} = -\vec{\mu} \cdot \vec{B} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2\hbar^2}{m^2c^2r^3} \vec{L} \cdot \vec{S} \left(\frac{1}{2}\right)$$

More generally: $H_{LS} = \frac{1}{2} \frac{\hbar^2}{m^2c^2} \vec{L} \cdot \vec{S} \frac{1}{r} \left(\frac{dV}{dr} \right)$ — we'll see soon why this may not be $1/2$!

With $\vec{J} = \vec{L} + \vec{S}$, $\vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$
 (remember the triangle inequality! $j = l+s \dots l-s$)

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

 vanishes if $l=0$!

So, to first order in perturbation theory:

$$\Delta E_{LS} = \frac{1}{2mc^2} \frac{Ze^2\hbar^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle [j(j+1) - l(l+1) - s(s+1)]$$

* just for hydrogenic atoms

Darwin term:

hard to understand "Zitterbewegung" - electrons jitter on a length scale $\hbar/mc \sim 400 \text{ fm}$

So, the electron experiences the electric potential averaged over this length scale - getting this calculation right is very hard

$$H_D = \frac{\pi \hbar^2 Z e^2}{2m^2 c^2} \frac{1}{4\pi \epsilon_0} \delta(\vec{r}) \quad \langle H_D \rangle \neq 0 \text{ for } l=0 \text{ only!}$$

Overall: everything is diagonal in $\vec{J}$ basis

$$\Delta E = \langle n l j | H_{KE} + H_{Zs} + H_D | n l j \rangle \quad \text{use 1st order P.T.}$$

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

(surprise - no l dependence)

fine structure constant - correction to energy $\sim \alpha^2$

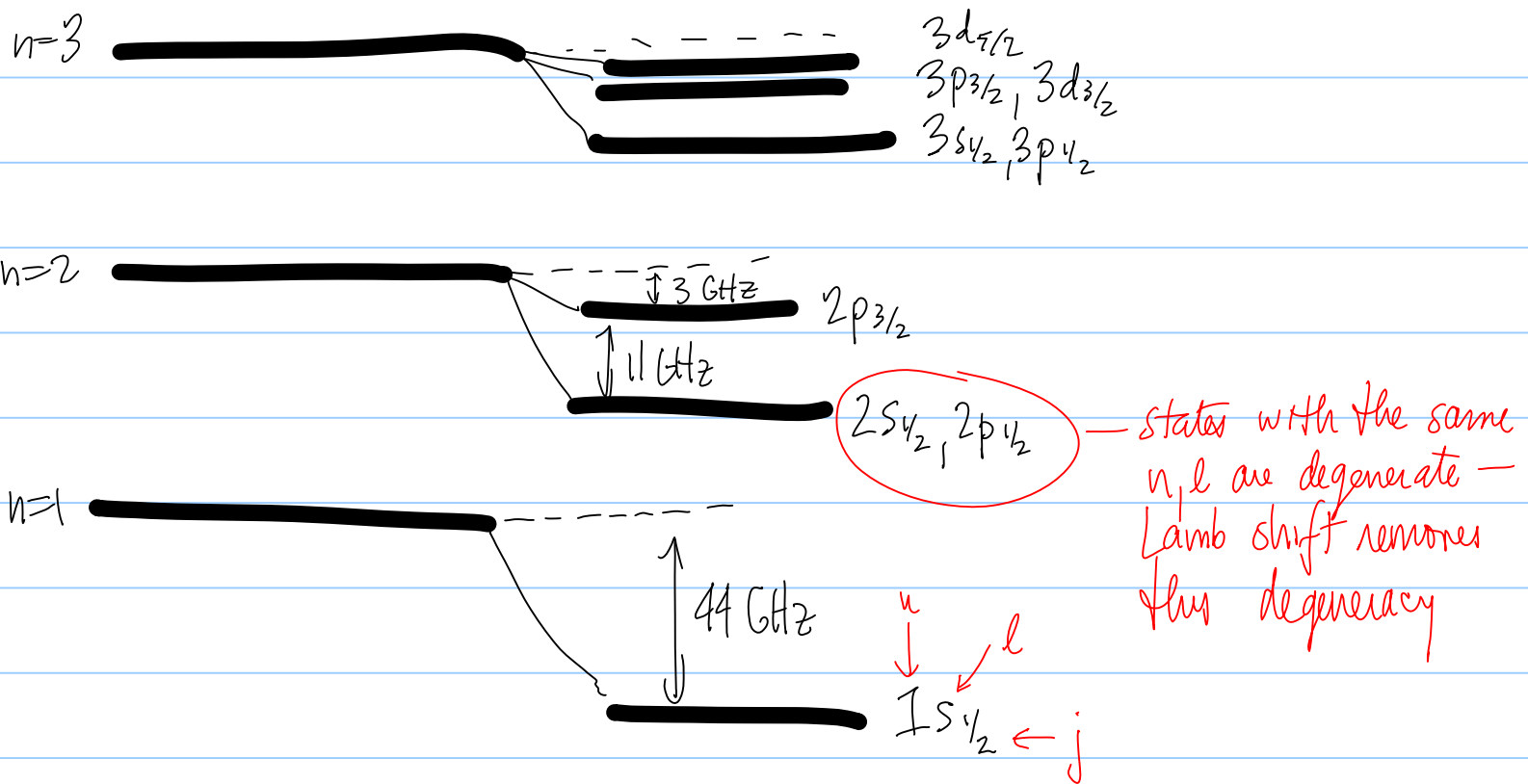
agree to order $(Z\alpha)^2$

Exact result from Dirac equation:

$$E_{nj} = mc^2 \left\{ \left[1 + \left(\frac{Z\alpha}{n - j - 1/2 + \sqrt{(j+1/2)^2 - Z^2 \alpha^2}} \right)^2 \right]^{-1/2} - 1 \right\}$$

(both equations are for hydrogen-like atoms only)

What does Hydrogen look like?



- in Hydrogen, all three terms contribute about equally
- in alkalis, mostly spin-orbit