2 ATOMS

2.1. Single (active) electron atoms!)

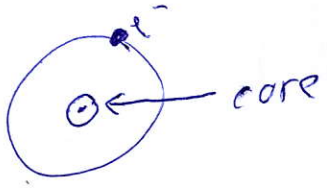
See section 1.2.3. for most basic: Hydrogen atom
What about all others?

- Directly applies to Hydrogenic atoms
  - deuterium, tritium (just heavier, electron behaves same)
    $pn + e^-$ $pnn + e^-$

- Next simplest, hydrogenic ions
  He^+, Li^{++}, etc $Z > 1$ in 1.2.3

- Also almost applicable to Alkali-atoms
  Li, Na, K, Rb, Cs (mainly single valence electron important)

- Rydberg states ($n \gg 10$)

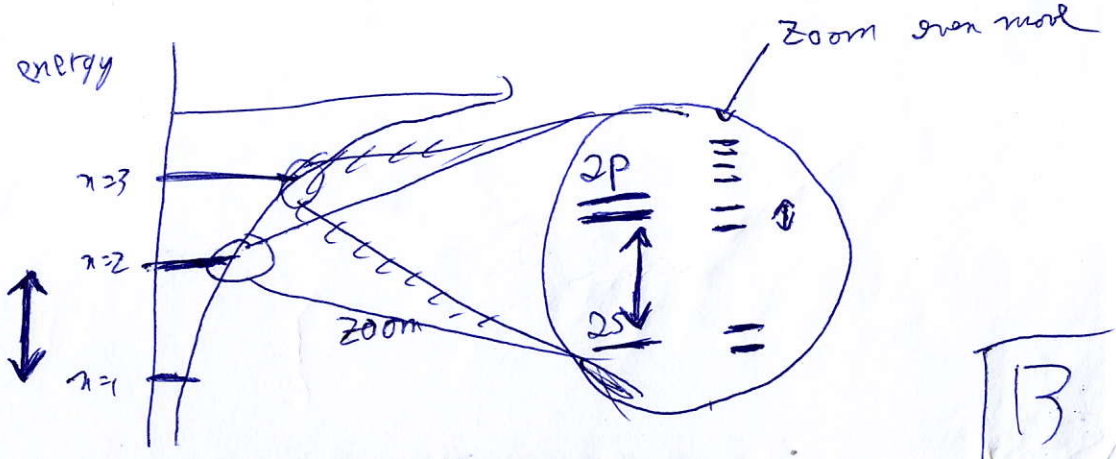


- Now first more detailed look at spins & E/B fields. & relativistic corrections. In 1.2.3. just added m_s quantum number without consequences.

- Hydrogen energy levels

indep of ℓ!

(ask why)



2.12. Effect of Spins, Fine ~~and Hyperfine~~ structure

- Spins arise naturally in relativistic QM
- Calculations in 1.2.3 are also fully non-relativistic, i.e. use $H = \frac{p^2}{2m}$ not $H = \sqrt{p^2c^2 + m_0^2c^4}$ *

FINESTRUCTURE

Start from relativistic wave-equation (Dirac-equation), expand for $v \ll c$? of e^-

and get as in 1.2.3, Hydrogen

$$\hat{H} = \hat{H}_0 + \hat{H}'_{FS}$$

where

$$\hat{H}'_{FS} = \hat{H}'_1 + \hat{H}'_2 + \hat{H}'_3 \quad \text{with}$$

Relativistic corrections:

$$\hat{H}'_1 = -\frac{p^4}{8m^3c^2}$$ relativistic correction to kinetic energy (expand * in p)

$$\hat{H}'_2 = \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}}_{\equiv \varphi(r)} \hat{L}\cdot\hat{S}$$ spin-orbit coupling (2.1) (for later)

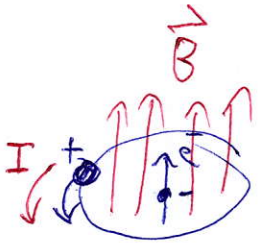
$$\hat{H}'_3 = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(\vec{r})$$ Darwin-term

Comments on $\hat{H}'_1$: Taylor (*)

Comments on spin orbit coupling:

Atom "cartoon":

Rest frame of e^-



proton moves with $-\vec{v}$ ($\vec{v}$ e^- velocity)

Spin-energy?

Electrodynamics $\vec{B} = -\frac{e\mu_0}{4\pi}\frac{\vec{v}\times\vec{r}}{r^3}$ ($q = +e$, $\vec{v} = -\vec{v}$)

(Done: $\vec{B} = \frac{\mu_0}{4\pi}\frac{q\vec{v}\times\vec{r}}{r^2}$)

$c = \frac{1}{\sqrt{\varepsilon_0\mu_0}}$

cgs $\frac{1}{4\pi\varepsilon_0} = 1$

$\Rightarrow \frac{\mu_0}{4\pi} = \frac{1}{4\pi\varepsilon_0 c^2}$

$\mu_0 \overset{cgs}{=} \frac{4\pi}{c^2}$

Energy of spin in mag field

$\hat{H}_{mag} = -\hat{\vec{\mu}}\cdot\vec{B}$ $\quad \hat{\mu} \sim -\hat{S}$ (qco)

$\hat{H}_{mag} = +g_s\frac{\mu_B}{\hbar}\vec{B}\cdot\hat{\vec{S}}$ (2.2)

gyromagnetic factor $g_s \approx 2$

Bohr-magneton $\mu_B = \frac{e\hbar}{2m_e}$ (e>0 here)

$$\hat{H}_{mag} = +g_s^{=2}\,\underbrace{\frac{\mu_e}{\hbar}}_{=\frac{e}{2m_e}}\left(\underbrace{-\frac{\mu_0 e}{4\pi m_e}\frac{\vec{p}\times\vec{r}}{r^3}}_{\vec{B}}\right)\cdot\hat{S} \qquad \vec{L}=\vec{r}\times\vec{p}$$

$$= \frac{\overbrace{g_s}^{=2}\,\overbrace{\mu_0\varepsilon_0}^{=\frac{1}{c^2}}}{2m_e^2}\left(\frac{e^2}{4\pi\varepsilon_0 r^3}\right)\hat{L}\cdot\hat{S} = 2\,\hat{H}_2' \qquad (2.1)$$

$\left(\frac{e^2}{4\pi\varepsilon_0 r^3} = \frac{1}{r}\frac{dV}{dr}\right)$

up to factor 2

[e^- rest frame not inertial, see Shankar]

Comments on Darwin term:

- Further consequence of relativistic QM is the exirtence of anti-particles (e^+ here). Can have $\gamma \to e^+ + e^-$ for time $\Delta E\cdot\Delta t \sim \hbar$.
  These vacuum fluctuations interact with e^- and cause Zitterbewegung: ~~~~~~ $\vec{v}$ (Amplitude $\frac{\hbar}{2m_e c} = \frac{\lambda_c}{2\pi}$, freq. $\frac{2m_0c^2}{\hbar}$)
  Compton wavelength $2.4\cdot10^{-12}\,m$
- Effectively smears out nuclear position

  $r \to$ ⊘
- This is origin of Darwin term.

Calculation of energy shift in perturbation theory:

- Eq. (1.20) $\Delta E_1 = \langle\phi_{nlm}|\hat{H}_1'|\phi_{nlm}\rangle$ (see book, can use non-deg cause $\hat{H}_1'$ diagonal in l, m) here
  (as assignment 1 with $p^2 \to p^4$)
- Second term, rewrite (since $\hat{H}_2'$ no longer commute with $\hat{L}, \hat{S}$)

Define total angular momentum of electron (see section 1.2.2)

$$\hat{J} = \hat{L} + \hat{S} \qquad (2.3)$$

New eigen functions

$|\phi_{nljm_j}\rangle$

Eigen Values

$j = \frac{1}{2}$ $(l=0,\ s=\frac{1}{2})$

$j = l \pm \frac{1}{2}$ $(\text{for } l>0,\ s=\frac{1}{2})$

$\hat{J}^2|\phi\rangle = \hbar^2 j(j+1)|\phi\rangle$

$J_z|\phi\rangle = \hbar m_j|\phi\rangle$

see chapter 4, but need for j, m_j values

Now write: $\hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{1}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2\right)$

Now can again use non-deg PT (in J basis)

$$\Delta E_2 = \langle \phi_{n\ell j m_j} | \hat{H}_2' | \phi_{n\ell j m_j} \rangle$$

$$= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right], \qquad \ell(\ell+1)$$

from $\hat{J}^2$ etc

where we used shorthand $\hat{H}_2' = \xi(r)\,\hat{L}\cdot\hat{S}$

$$\langle \xi(r) \rangle = \int d^3r\, \phi^*_{n\ell j m_j}(\vec{r})\, \xi(\vec{r})\, \phi_{n\ell j m_j}(\vec{r})$$

- ~~From (1.18) we see that Darwin-term affects only states (others are 2~~

- Darwin-term:

$$\Delta E_3' = \langle \phi_{n\ell j m_j} | \hat{H}_3' | \phi_{n\ell j m_j} \rangle = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right) |\phi_{n\ell j m_j}(0)|^2$$

From (1.18) we see that this shifts $\ell = 0$ states only (others have $|\phi(0)|^2 = 0$).

All together:

Finestructure energy shifts:

$$E_{nj} = E_n \left(1 + \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right) \qquad (2.4)$$

E_n ↗ Eq (1.19)

- Here $\alpha = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} \approx \frac{1}{137}$ is the fine-structure constant

- Now degeneracy of energy in ℓ is lifted

- Note $E_n < 0$, sign of shift depends on n, j, but mostly towards lower energies.

23. LAMB-SHIFT

So far, even when discussing interactions of spins, we always used classical formulae for electric & magnetic fields/ interaction potentials.

Fundamentally, elm-fields & interactions are due to discrete quanta, photons, as described by quantum electro-dynamics (QE

The resulting vacuum fluctuations of γ, e^+, e^- cause a further

Lamb shift:

$$\Delta E_{Lamb} = \alpha^5 m_e c^2 \begin{cases} \frac{1}{4n^3}\left[k(n,\ell) \pm \frac{1}{\pi(j+\frac{1}{2})(\ell+\frac{1}{2})}\right] & \ell \neq 0 \quad j = \ell \pm \frac{1}{2} \\ \frac{1}{4n^3} k(n,0) & \ell = 0 \end{cases} \quad (2.5)$$

$k(n,\ell) < 0.05$

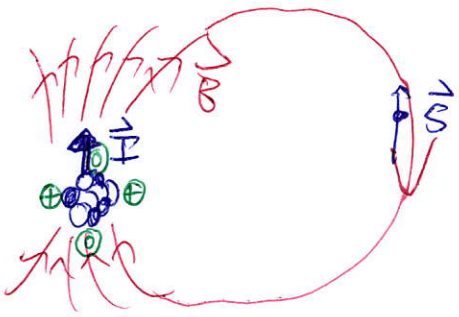
This lifts the degeneracy between S & P! (so might cause splitting not only shift)

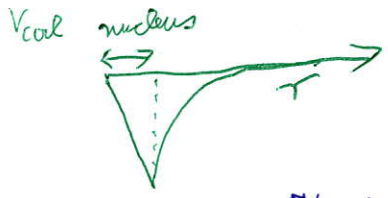
- Finestructure > Lamb-shift

2.4 HYPERFINE-STRUCTURE

Other details neglected so far:

- nuclear spin $\hat{I}$
- finite nuclear extension
  - ↳ correction of Coulomb-law at short r
- electric quadrupole-moment





We discuss here zero-quadrupole moment only

Now $\hat{H} = \underbrace{\hat{H}_0'}_{\text{incl Fine-structure}} + \hat{H}_{HFS}'$ $\left(\hat{H}_0' = \hat{H}_0 + \hat{H}_{FS}'\right)$

Hamiltonian of Hyperfine Interactions: (anisotropic PD) $(r \neq 0)$

$$\hat{H}_{HFS}' = \frac{\mu_0}{4\pi}\frac{2}{\hbar} g_I \mu_B \mu_N \frac{1}{r^3}\left[\hat{L}\cdot\hat{I} - \hat{S}\cdot\hat{I} + 3\frac{(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^2}\right] \quad (2.6)$$

- Here g_I is nuclear g-factor $(g_I \approx -2 \dots 6)$
- $\mu_N = 5\cdot 10^{-27}\,J/T$ is nuclear magneton $(\mu_N \sim 10^{-4}\,\mu_B)$
- $\hat{I}$ is nuclear angular momentum operator.
  (contains pin spins & possibly orbital angular momentum)

Can again use perturbation theory. As for finestructure, it will be useful to change to a coupled spin basis, using

Total angular momentum (of atom)

$$\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}} \quad (2.7)$$

As before, eigen states & eigen values

$$\hat{F}^2|F, m_F\rangle = \hbar^2 F(F+1)|F, m_F\rangle \qquad F = |I-J|, \dots, I+J$$

$$\hat{F}_z|F, m_F\rangle = \hbar m_F |F, m_F\rangle \qquad m_F = -F, \dots, F$$

treating Eq.(2.5) and corrections at $r \approx 0$ using perturbation theory (see book) we find:

Hyperfine energy shift:

$$\Delta E = \frac{1}{2}\frac{m}{m_p} g_I \frac{Z^3\alpha^2}{n^3}\left(\frac{\mu}{m}\right)^3 \frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} \qquad (2.8)$$

atomic units → see section 2.2.

- given for reference
- After considering fine-structure & Lamb shift, Levels are already split according to their different values of j, l.
  - ↳ Now Eq. (2.8) causes additional splitting into different allowed values of F in the range

$$j + I \geq F \geq |j - I|$$

- Finestructure > Lamb-shift > Hyperfine structure

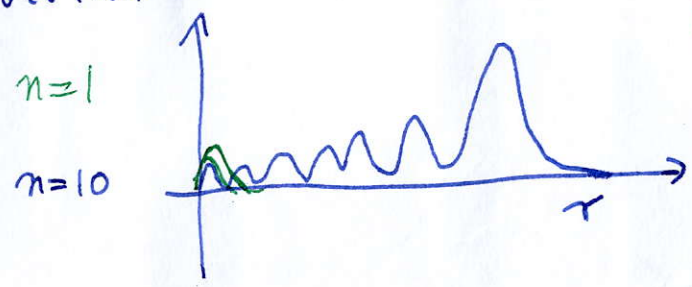
2.1.4. ALKALI ATOMS / RYDBERG ATOMS

Alkali-atoms: Li, Na, K, Rb, Cs → have a single valence electron above fully filled electron shells.

Valence e^- responsible for chemistry and visible spectra.

Consider very highly excited states, e.g. $n \gg 10$. These are called Rydberg states.

From section 1.2.3:



See Assignment:
In fact mean-radius:

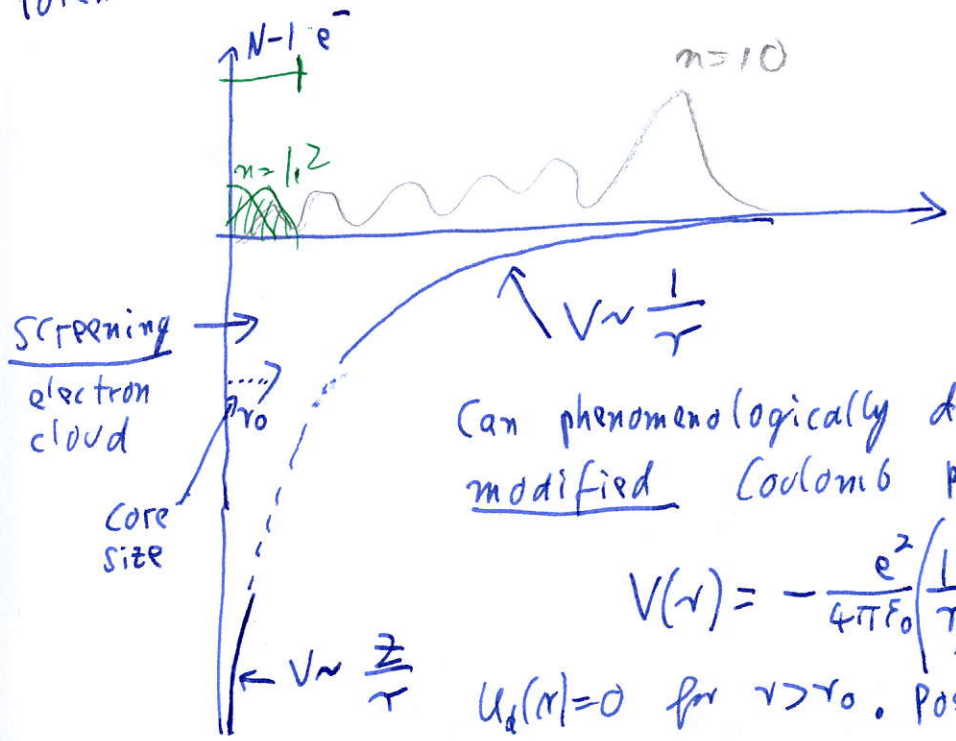
$$\langle \phi_{nlm} | r | \phi_{nlm} \rangle = \ldots \qquad (2.9)$$

$$= a_0 \frac{n^2}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\}$$

roughly $\sim a_0 n^2$ $(l=0, Z=1)$

For, e.g. Li-atom: 3 electrons, two in (1s) outer in (n=10)
→ Valence e^- much farther out than others (= atomic core)

Potential seen by valence electron / let N be the total number of electrons
Z = nuclear charge



Can phenomenologically describe this by modified Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right) + U_d(r)$$

$U_d(r) = 0$ for $r > r_0$. Possible choice

$$U_d(r) = -\frac{e^2}{4\pi\varepsilon_0}\left[(Z-1)\,e^{-a_1 r} - r(a_3 + a_4 r)\,e^{-a_2 r}\right]$$

~~We can fit $a_1 \ldots$ to fit experiments~~
With this $V(r)$, solve again (1.17) radial SE ⇒ get slightly different energies compared to H

Energy levels for Alkali-Atoms ($Z=1$)

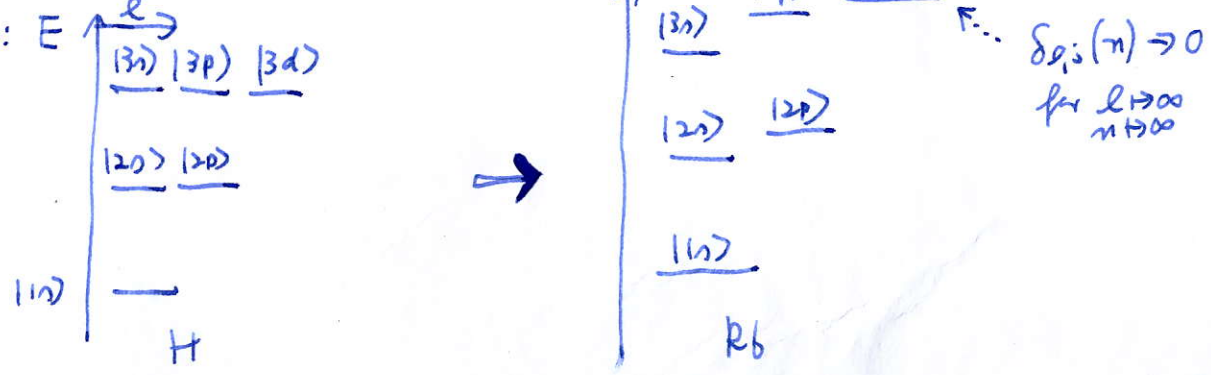
$$E = -\frac{R_y}{(n - \delta_{\ell,j}(n))^2} \qquad (2.10)$$

includes finestructure

$\delta_{\ell,j}(n)$ = quantum defect (due to $U_d(r)$)

- the lower the ℓ, the higher quantum defect, since $\phi_{n\ell m}(r)$ reaches closer to / into the core (less centrifugal barrier).

In practice:

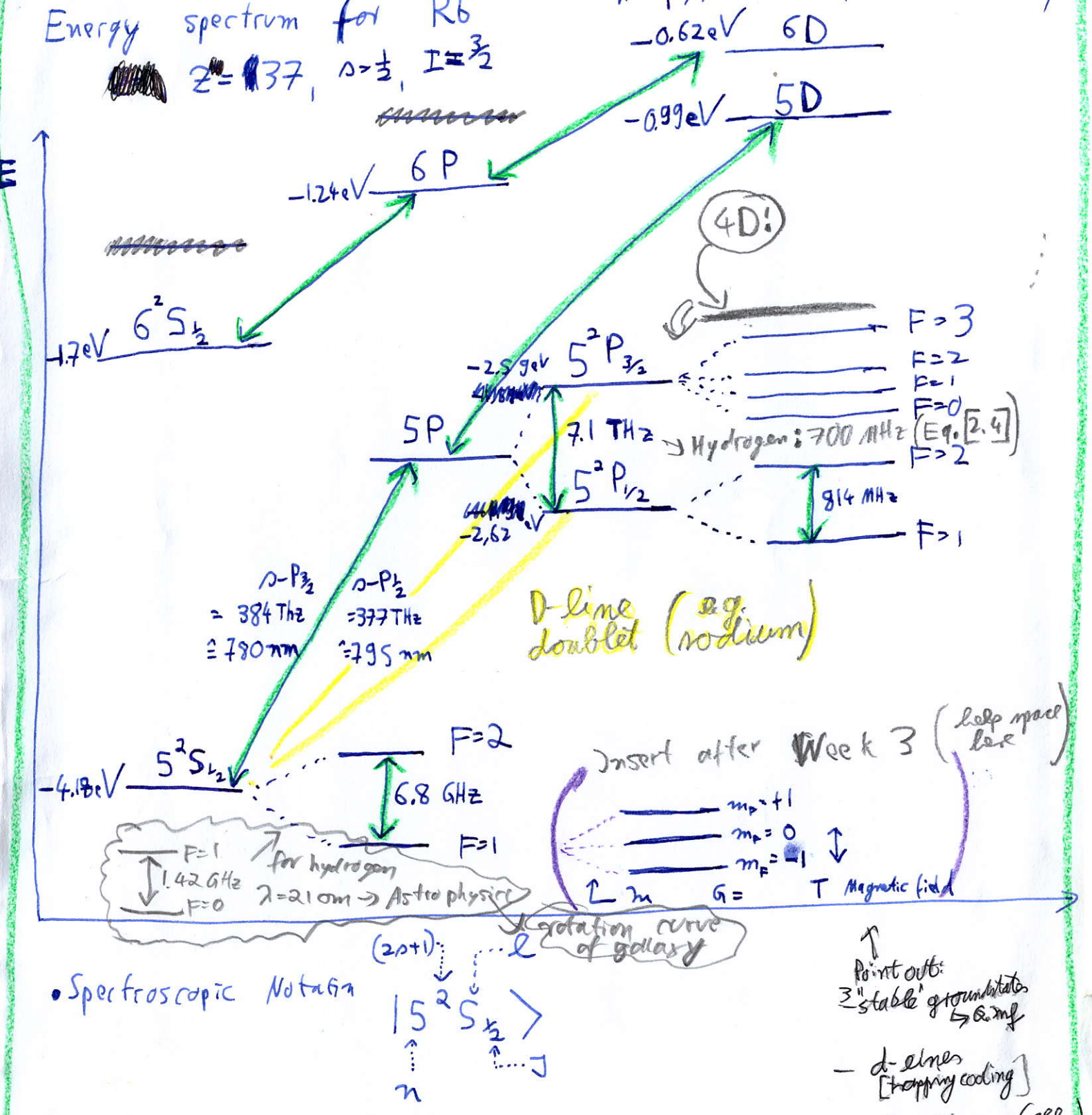


Example for section 2.1

(courtesy Daniel A. Steck http://steck.us/alkalidata)

Energy spectrum for Rb^{87}

$Z = 37$, $s = \frac{1}{2}$, $I = \frac{3}{2}$



- Spectroscopic Notation

$$|n\,(2s+1)\,\ell_J\rangle \quad \text{e.g. } |5\,{}^2S_{1/2}\rangle$$

Point out: 3 "stable" ground states ↳ e.g. ^{87}Rb

- d-lines [trapping cooling]
- descriptions (see books)

- Energy splittings in Hz: $\Delta E = h\nu_{Hz}$

in nm: $\nu \cdot \lambda = c$

- also see: www.nist.gov/pml/atomic-spectra-database