

Atoms - Electronic States

(much of this from
Tennyson "Astronomical Spectra")

An atom with charge Z (i.e. Z protons) and N electrons obeys the time independent Schrödinger equation:

$$\left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \vec{\nabla}_i^2 - \frac{Ze^2}{r_i} \right) + \sum_{i=1}^N \sum_{j=i+1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - E \right] \psi = 0$$

↳ note really should be " μ "

where $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$ describes the state of the electrons.

This system is very complicated! It can be simplified by using the "central field model," which separates it into N equations (one for each electron) each with some potential $V_i(r_i)$ determined by other $N-1$ electrons

$$\left[-\frac{\hbar^2}{2m_e} + V_i(r_i) \right] \phi_i(\vec{r}_i) = E_i \phi_i(\vec{r}_i)$$

And furthermore that:

$$\psi = \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \dots \phi_N(\vec{r}_N)$$

"orbital
approximation"
"orbitals"

Because $V(r_i)$ is central the form of $\phi_i(\vec{r}_i)$

that solve Schrödinger can be written as:

$$\phi_i(\vec{r}_i) = R_{n_i l_i}(\vec{r}_i) Y_{l_i m_i}(\theta_i, \phi_i)$$

$n=1, 2, \dots$
 $l=0, \dots, n-1$
 $m=-l, \dots, l$

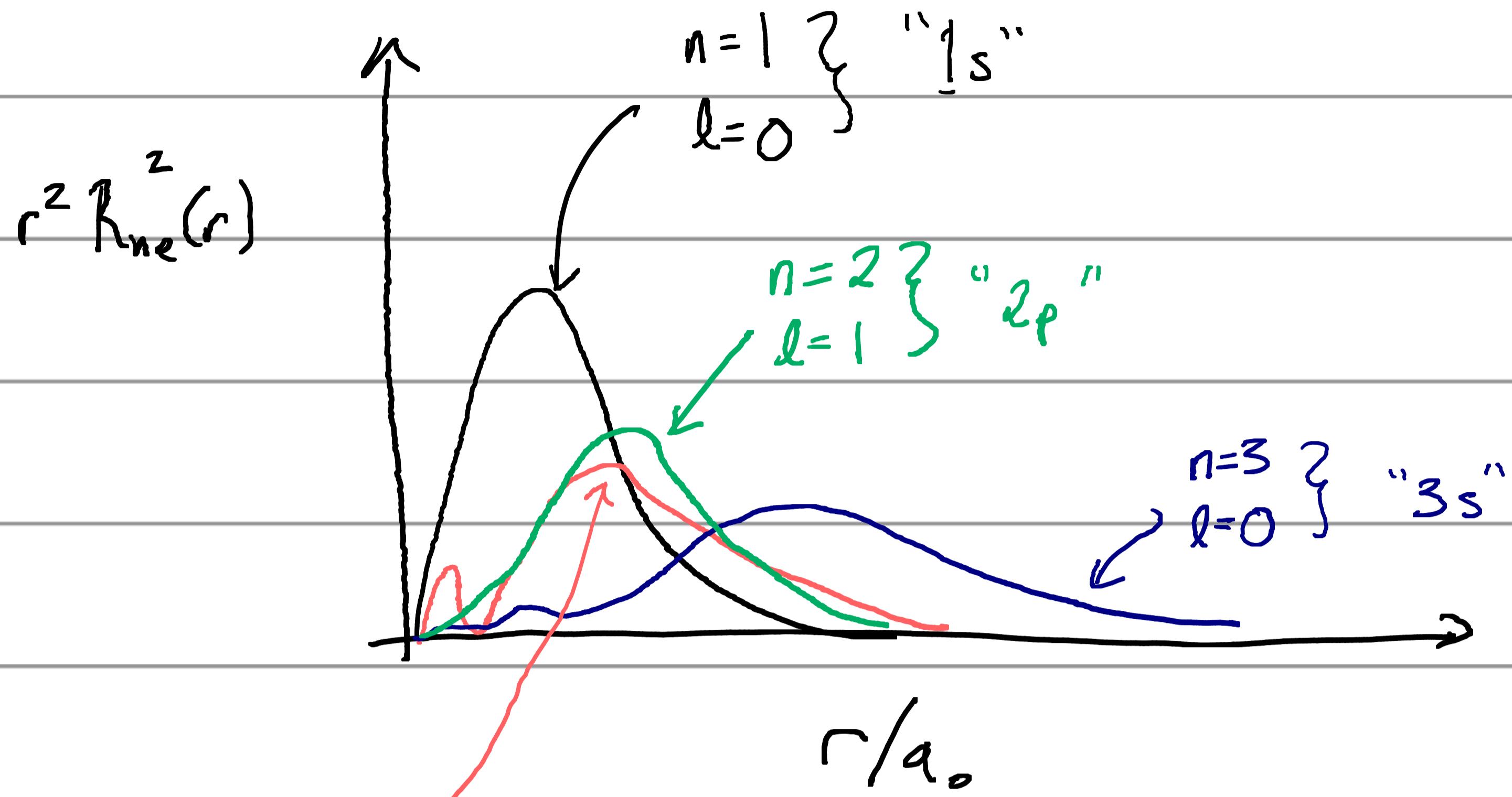
some radial basis function spherical harmonic

So possible states are defined by n, l, m .

But also the spin of the electron can be
 $s = \frac{1}{2}, -\frac{1}{2}$, so then it really is n, l, m, s .

Full system wave function is some combination
of orbitals including spin for each electron: $\{(n_i, l_i, m_i, s_i)\}$

Hydrogen is a simple one. In this case, R_{ne} are the Laguerre polynomials and have forms like



"2s" $\{ n=2$
 $l=0$

$$a_0 = \frac{\hbar^2}{2me^2} = \text{"Bohr radius"}$$

l can be
interpreted as
an angular mom.
state of electron

Nomenclature is "nl"
number letter $\rightarrow l=0 \rightarrow s$

$$1 \rightarrow p$$

$$2 \rightarrow d$$

$$3 \rightarrow f$$

$$4 \rightarrow g$$

$$\vdots \quad \vdots$$

Note that this will all hold
for any atom w/ N=1

Energy levels associated w/ n for H

$$E_n = -\frac{\mu e^2 c^4}{2 \hbar^2} \frac{1}{n^2}$$



Note $\frac{m_e c^4}{2 \hbar^2} = 13.6 \text{ eV}$

These levels do split according to angular momentum state.

Ang. momenta involved are:

electron orbit - l

electron spin - s

nuclear spin - i (total of nucleus)

l and s add to j total electron a.m.

j and i add to f final ang. mom.

Under the rules of addition of ang. mom.

Recall that classically:-

$$|l-s| \leq |\vec{l} + \vec{s}| \leq l+s$$

depending on relative alignment of vectors

In quantum mechanics, the allowed range is the same but only integers are allowed

$$\text{Eg. } l_1 = 2, \quad l_2 = 1 \rightarrow |l_1 + l_2| = 1, 2, 3$$

The notation used to describe these states is as follows:

<u>Configuration</u>	<u>l</u>	<u>s</u>	<u>j</u>	<u>only</u>	<u>for H</u>	<u>more general</u>	<u>Term</u>	<u>Level</u>
nS	0	$\frac{1}{2}$	$\frac{1}{2}$		$ns_{\frac{1}{2}}$		n^2S	$n^2S_{\frac{1}{2}}$
np	1	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$		$np_{\frac{1}{2}}, np_{\frac{3}{2}}$		$n^2P^{(o)}$	$n^2P_{\frac{1}{2}}, n^2P_{\frac{3}{2}}, n^2P_{\frac{5}{2}}$
nd	2	$\frac{1}{2}$	$\frac{3}{2}, \frac{5}{2}$		$nd_{\frac{3}{2}}, nd_{\frac{5}{2}}$		n^2D	$n^2D_{\frac{3}{2}}, n^2D_{\frac{5}{2}}$
nf	3	$\frac{1}{2}$	$\frac{5}{2}, \frac{7}{2}$		$nf_{\frac{5}{2}}, nf_{\frac{7}{2}}$		$n^2F^{(o)}$	\dots

you will often see
leading n omitted

Term $\rightarrow 2S+1 \begin{cases} (p) \\ L \end{cases}$

Level $\rightarrow 2S+1 \begin{cases} (p) \\ J \end{cases}$

$p = \text{parity} = (0) \text{ if odd}$
 $= " " \text{ if even}$

$J = \text{total electron ang. mom.}$

$S = \text{total electron spin}$

$\hookrightarrow 2S+1$ is "spin multiplicity" \rightarrow always 2 for H-like atoms

$L = \text{total electron orbital ang. mom.} \rightarrow$

- $L=0 \rightarrow S$
- $=1 \rightarrow P$
- $=2 \rightarrow D$
- $=3 \rightarrow F$

Fine structure

l and s couple to produce slightly different energies based on their relative orientation

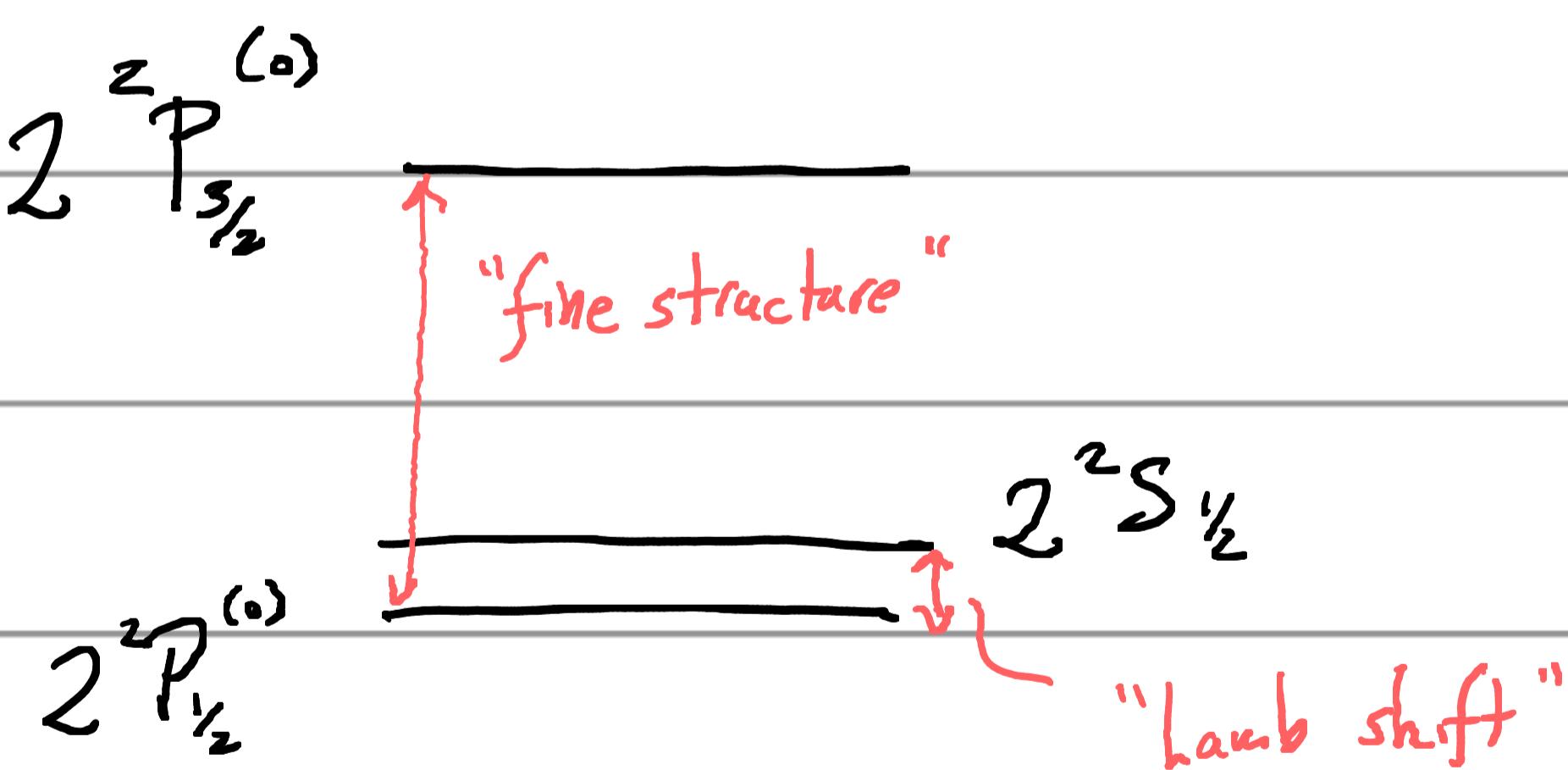
Therefore "levels" have slightly different energies.

Eg.

$2p$ configuration has levels :

$$2^2P_{\frac{1}{2}}^{(o)}, 2^2P_{\frac{3}{2}}^{(o)}$$

separated in energy by $\Delta E \approx 4.5 \times 10^{-5} \text{ eV}$



Hyperfine Structure

$$f = j \pm \frac{1}{2} \quad \leftarrow \text{for H, } i = \frac{1}{2}$$

m

energy difference due to magnetic effects

(~21 cm)

Zeeman Splitting

Each level has some J , and is degenerate

with $2J+1$ "sublevels" $M_J = -J, \dots, J$

In a magnetic field these acquire different energies,
leading to Zeeman effect.

Many Electron Atoms

Even the orbital approximation looks super complex if electrons can be in whatever states. A general wave function would be:

$$\psi(1, 2, \dots, N) = \phi_1(1) \phi_2(2) \dots \phi_N(N)$$

Luckily atoms are better behaved for several reasons.

Recall Pauli. Only observable thing is:

$$|\psi|^2$$

and particles are indistinguishable. Therefore

$$|\psi(1, 2)|^2 = |\psi(2, 1)|^2$$

$$\psi(1, 2) = \pm \psi(2, 1)$$

for Fermions:

$$\psi(1, 2) = -\psi(2, 1)$$

For two electrons:

$$\psi(2,1) = -\psi(1,2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]$$

If $a=b \rightarrow$ ie. electron 1 & 2 are in same state, $\psi(2,1) = -\psi(1,2) = 0 \rightarrow$ not allowed.

This is the Pauli exclusion principle, which has profound consequences for atomic structure.

Each choice n corresponds to a "shell."

Angular orbital has $2(2l+1)$ options for (n, l, m_l, s) so can have that many electrons.

Note low l orbitals have lower energy, because they penetrate further into less shielded environment:

$$E(1s) < E(2s) < E(2p) < E(3s) < (E3p) < E(3d) \approx E(4s)$$

		<u>2</u>		
H	1	1s		how many electrons at this Q
He	2	1s 2		
Li	3	K	2s	
B _c	4	K	2s ²	
B	5	K	2s ² 2p	
C	6	K	2s ² 2p ²	
N	7	K	2s ² 2p ³	
O	8	K	2s ² 2p ⁴	
F	9	K	2s ² 2p ⁵	
N _e	10	K	2s ² 2p ⁶	
Ne	11	K	L	3s
Mg	12	K	L	3s ²
Al	13	K	L	: 3p
Si	14	K	L	: 3p ²
P	15	K	L	: :
S	16	K	L	: :
Cl	17	K	L	: :
Ar	18	K	L	: : :
K	19	K	L	: : 4s
Ca	20	L	L	: : 4s ²

In astrophysics we will be concerned with excited states. This typically happens to one of the outer electrons.

Eg He ($1s^2$) can have excited configurations like $1s2s$, $1s2p$, $1s3s$, ...

↑

and note can be $2p_{1/2}$, $2p_{3/2}$ states

Of course atoms may be partially ionized; generally will happen from highest energy electrons on down.

The angular momenta of the configurations lead to energy differences due to H fine structure.

The closed shells all have $L=0$, $S=0$ so only the partially filled shells matter.

$$\text{S. } \vec{L} = \sum_i \vec{l}_i, \quad \vec{S} = \sum_i \vec{s}_i, \quad \vec{J} = \vec{L} + \vec{S}$$

For $[O\text{III}]$ (i.e. O^{++}) the outer shell will be:

$1s^2 2s^2 2p^2$ in ground state

Consider excited state:

$1s^2 2s^2 2p 3d$

$L=0$	$L=0$	$L=1$	$L=2$	$L=1, 2, 3$
$S=0$	$S=0$	$S=\frac{1}{2}$	$S=\frac{1}{2}$	$S=0, 1$
		$\delta=\frac{1}{2}$		$J=0, \dots, 4$

L	S	J	
1	0	1	${}^1P_1^{(o)}$
1	1	0, 1, 2	${}^3P_0^{(o)}, {}^3P_1^{(o)}, {}^3P_2^{(o)}$
2	0	2	${}^1D_2^{(o)}$
2	1	1, 2, 3	${}^3D_1^{(o)}, {}^3D_2^{(o)}, {}^3D_3^{(o)}$
3	0	3	${}^1F_3^{(o)}$
3	1	2, 3, 4	${}^3F_2^{(o)}, {}^3F_3^{(o)}, {}^3F_4^{(o)}$

Twelve levels for this configuration.

Parity

It must always be that:

$$|\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 = |\psi(-\vec{r}_1, -\vec{r}_2, \dots, -\vec{r}_N)|^2$$

$$\text{So } \psi(\vec{r}_1, \dots) = \pm \psi(-\vec{r}_1, \dots)$$

If \oplus "even" parity

\ominus "odd" parity

Parity is $(-1)^{\sum_i l_i}$ for all electrons.

All closed shells $\sum_i l_i = \text{even}$ so only outer electrons matter.

Eg for O^{III} in $1s^2 2s^2 2p^3 3d$, $\sum_i l_i = 1 + 2 = 3$

\hookrightarrow parity = -1 "odd"

Of great consequence: electric dipole transitions only occur between opposite parity states. "Laporte rule"

Energies of Terms & Levels

He :

Configuration

term

level

parity

↳ ground state : $1s^2 \rightarrow ^1S - ^1S_0$ even
 first excited $1s2s$ $^1S, ^3S$ $^1S_0, ^3S_1$ even

second excited $1s^2 p$ $^1P^{(G)}$ 1P_0 odd
 $^3P^{(G)}$ 3P_0
 3P_1 3P_2
 $\delta, 1, 2$

Recall configuration energy order $E(1s) < E(2s) < E(2p) \dots$

(Within configuration the total L & S determine an energy eigenstate, the term. (Note this pictures fairly at high z)).

Hund's rules: (1) higher S \rightarrow lower energy \leftarrow primary effect
 (2) higher L \rightarrow lower energy

(Hund's rules only apply in ground state).

Finally, the levels arise from spin-orbit coupling. This can be characterized by J because it is related to $\vec{S} \cdot \vec{L}$, and:

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

Hund's 3rd Rule:

$$\Delta E_{so} \propto \underbrace{(J(J+1) - L(L+1) - S(S+1))}_{\text{remember } J^2 \rightarrow J(J+1)}$$

Levels are sorted by J

"Landé interval rule"

\rightarrow increasing E w/ J if shell $< \frac{1}{2}$ full

\rightarrow decreasing E w/ J if shell $> \frac{1}{2}$ full

If shell is exactly $\frac{1}{2}$ full, $L=0$ in ground state

$S=0$ $S=0, L=1$ $'P_0$

$2p$ ————— $S=1$ $S=1, L=1$ ${}^3P_0, {}^3P_1, {}^3P_2$

S

L

$S-L$

$\underbrace{\quad}_{\text{in}}$

(+ remember $M_J = -J \dots J$,
degenerate except in \vec{B} field)

"fine structure"

Carbon

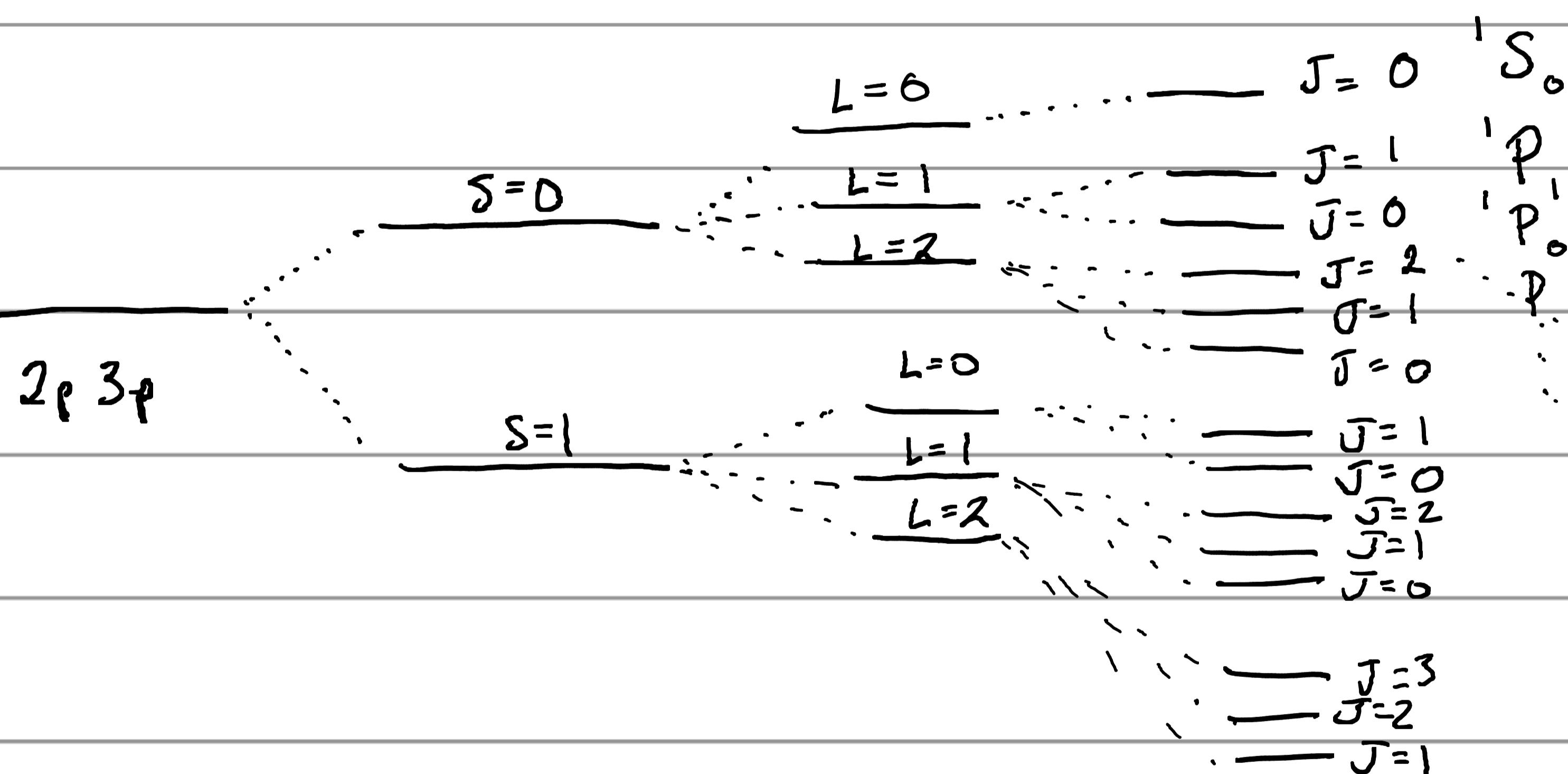
Ground state is $1s^2 2s^2 2p^2$

Consider the excited state: $1s^2 2s^2 2p\ 3p$

$$l=1 \quad l=1$$

Possibles are $S=0, 1$

$L=0, 1, 2$



Note that ground state is trickier because the two $2p$ electrons can be in the same (n, l, m, s) state and so would not be possible.

Can show $L+S = \text{even}$ is required.

Emission & absorption result from transitions from state to state. These radiative transitions are not all equally likely. We calculated classically from the Thomson model the transition rate $\Gamma(\omega)$ that would be associated with a transition for a harmonic oscillation. This rate is \sim right for "electric dipole" transitions; but not all transitions can proceed as electric dipole transitions. Rules are set by the semiclassical model (wave is classical, atom is quantum).

We can sketch the ideas w/out a detailed derivation of the rules; the transition rate should be:

$$\sim \left| \langle f | (\vec{A} \cdot \vec{p}) | i \rangle \right|^2 \quad \vec{A} = \vec{A}(t) e^{i\vec{k} \cdot \vec{r}}$$

$$\sim \left| \langle f | e^{i\vec{k} \cdot \vec{r}} \vec{\nabla} | i \rangle \right|^2 \quad \vec{p} \rightarrow -i\hbar \vec{\nabla}$$

$$\sim \left| \int d^3x \phi_f^* e^{i\vec{k} \cdot \vec{r}} \vec{\nabla} \phi_i \right|^2$$

represents coupling of photon to electron w.f.

$$\vec{k} \cdot \vec{r} \sim k a_0 \sim \frac{2\pi a_0}{\lambda} \sim \frac{a_0 h\nu}{\hbar c} \sim \frac{e^2}{\hbar c} \sim \frac{1}{137} \text{ "x"}$$

$$h\nu \sim \frac{e^2}{d_0} \sim 27.2 \text{ eV}$$

So $e^{i\vec{k} \cdot \vec{r}} \approx 1 + i\vec{k} \cdot \vec{r} + \frac{1}{2} (\vec{k} \cdot \vec{r})^2 + \dots$

"Dipole" approximation is

$$\sim | \int d^3x \phi_f^+ \vec{\nabla} \phi_i |^2$$

Which it turns out can be rewritten as:

$$\sim \Delta E | \int d^3x \phi_f^+ \vec{r} \phi_i |^2$$

↑
thus "dipole"

So the matrix element with the dipole represents the strongest absorption component. If $|\langle f | \vec{r} | i \rangle|^2 = 0$ between two states, then higher order components come in, related to electric quadrupole & magnetic dipole.

The general statement is that this approach allows the calculation of B_{dip} (ie absorption), and thus B_{dip} and A_{dip} through the Einstein coefficients' relationships.

It leads to a set of selection rules for allowed transitions.

<u>Electric Dipole</u>	<u>Electric Quad</u>	<u>Magnetic Dipole</u>
<i>strictly obeyed</i>		"forbidden"
$\left\{ \begin{array}{l} \Delta J = 0, \pm 1 \\ (\text{but never } J=0 \rightarrow 0) \end{array} \right.$	$\Delta J = 0, \pm 1, \pm 2$ (never $0 \rightarrow 0, \frac{1}{2} \rightarrow \frac{1}{2}, 0 \rightarrow 1$)	$\Delta J = 0, \pm 1$ (never $0 \rightarrow 0$)
$\left\{ \Delta M_J = 0, \pm 1 \right.$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1$
Parity must change	Parity must <u>not</u> change	Parity not change
$\left\{ \Delta S = 0 \right.$	$\Delta S = 0$	$\Delta S = 0$
$\left\{ \Delta \ell = \pm 1 \text{ (one electron)} \right.$	$\Delta \ell = 0, \pm 2$	no n, l change
$\left\{ \Delta L = 0, \pm 1 \right.$ Not $L=0 \rightarrow 0$	$\Delta L = 0, \pm 1, \pm 2$ Not $\rightarrow 0 \rightarrow 0, 0 \rightarrow 1$	$\Delta L = 0$
"forbidden" if violated		

Parity rule is especially easy to see, because of matrix element form for electric dipole:

$$\int d^3x \phi_f^* \vec{r} \cdot \vec{\phi}_i$$

if $\vec{r} \rightarrow -\vec{r}$, if parity doesn't change between "f" and "i" states then:

$$\int d^3x \phi_f^*(-\vec{r})(-\vec{r}) \phi_i(-\vec{r}) = - \int d^3x \phi_f^* \vec{r} \cdot \vec{\phi}_i \approx 0$$

Strengths of other transitions as well as propensity & selection rules are set by matrix elements.

The dipole operator can be written in terms of $Y_{lm} \propto l=1$, and this means that ΔL must be $-1, 0, +1$.

Detailed strengths of other transitions involve detailed calculations. But strengths depend on term differences. So level differences in strength are just degeneracy multiplicity differences

Transitions that obey all electric dipole rules are called "allowed" $\rightarrow A > 10^6 \text{ s}^{-1}$

Magnetic dipole transitions $\rightarrow A \sim 10^3 \text{ s}$

Electric quadrupole $\rightarrow A \sim 1 \text{ s}$

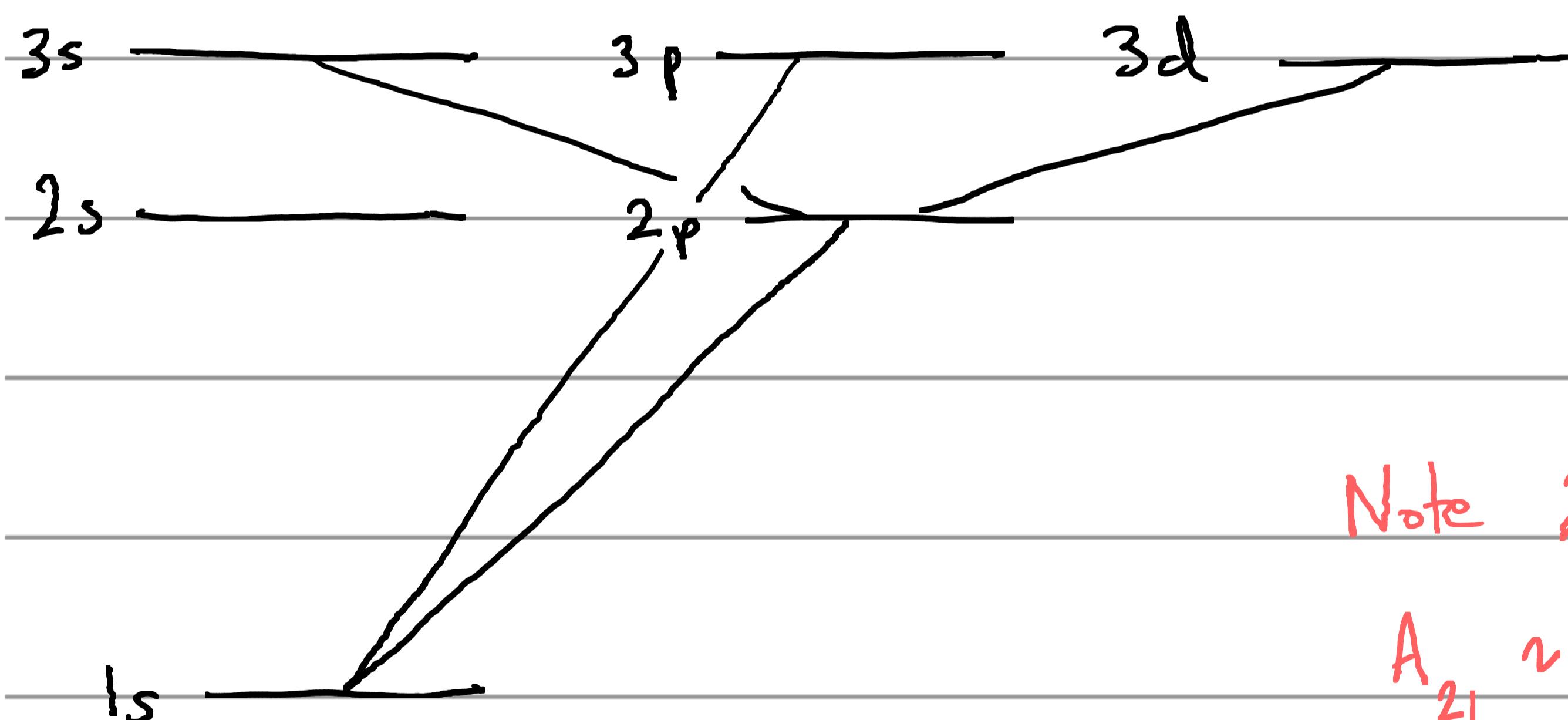
The forbidden lines are hard to study terrestrially, because states are quickly de-excited by collisions before the radiative transition can occur. But extremely important in astrophysics!!

How do these rules apply to hydrogen (or any H-like atom)? They reduce to:

$$\Delta l = \pm 1$$

$$\Delta j = 0, \pm 1 \quad (\text{spin can flip})$$

$$\Delta m_j = 0, \pm 1$$



Note 2s state!

$$A_{21} \approx 2s$$

"Grotrian" diagram

+ further constraints on spin states due to Δj conditions

Helium

Recall for H-like atom $E_n = -\frac{\mu Z^2 e^4}{2\hbar^2} \frac{1}{n^2} = -R \frac{Z^2}{n^2}$

So HeII (He^+) has $E_n = -\frac{4\mu e^4}{2\hbar^2} \frac{1}{n^2}$

$$\text{(where } \mu = \frac{2m_e m_p}{2m_p + m_e} = m_e \left(\frac{1}{1 + \frac{1}{2} \frac{m_e}{m_p}} \right) \approx m_e \left(1 - \frac{1}{2} \frac{m_e}{m_p} \right)$$

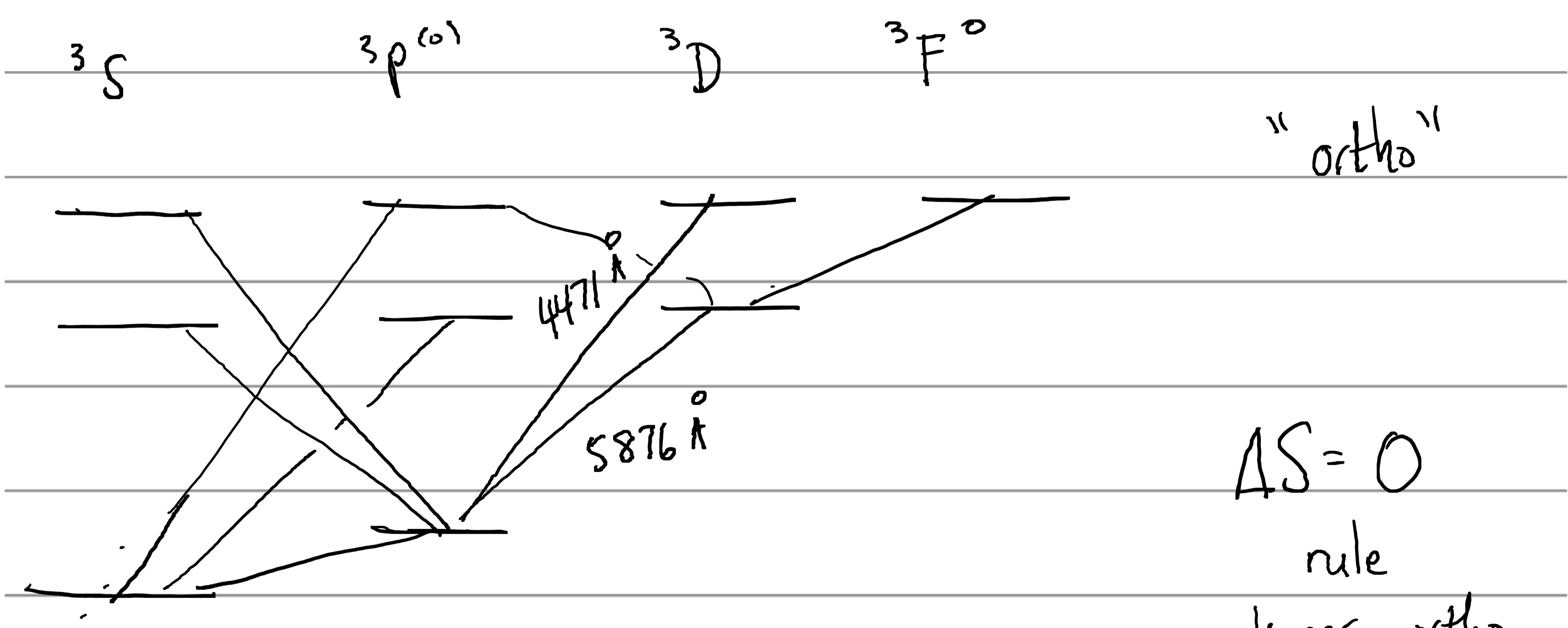
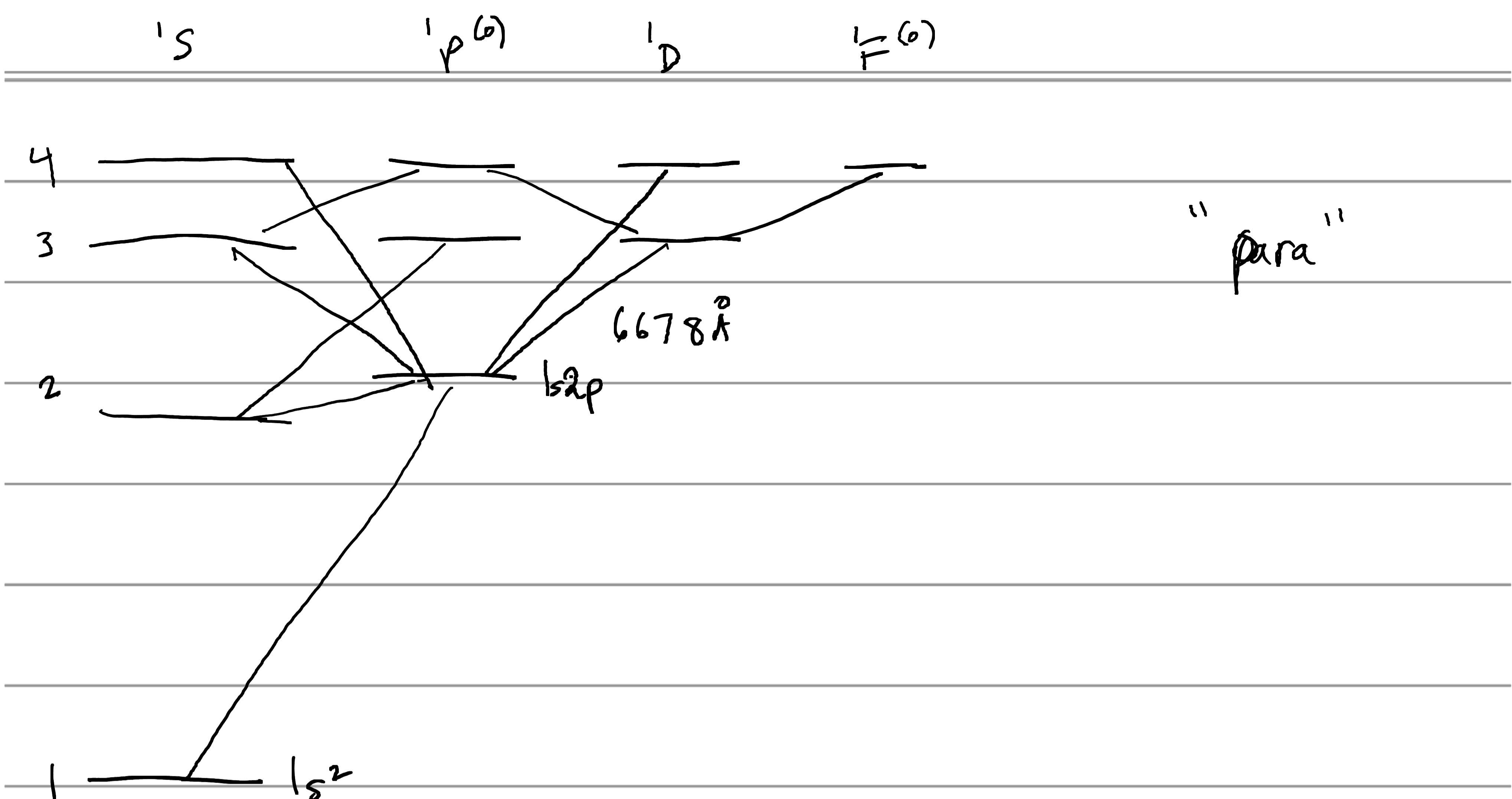
HeI lines require more thought. Excited states involving second electron need to account for screening of first electron. I.e. $V_i(r_i)$ for this electron is

$$-\frac{Ze}{r_i} \quad r_i \ll a_0 \quad \left. \begin{array}{l} \\ \end{array} \right\} \rightarrow \text{quantify}$$

$$-\frac{Z_{\text{eff}} e}{r_i} = -\frac{(Z-N+1)e}{r_i} \quad r_i \gg a_0 \quad \left. \begin{array}{l} \\ \end{array} \right\} \quad E_n = -R \frac{\frac{Z^2}{Z_{\text{eff}}}}{(n - \mu_{\text{eff}})^2}$$

↑
quantum
defect

We've already alluded to dependence of μ_{eff}



k' to $1s^2$ via magnetic dipole
 $A \approx 10^{-4} s^{-1}$

$$\Delta S = 0$$

rule

keeps ortho
& para apart

← n_0 $n=1$ state ($1s^2$) with $S=1$!

Alkali Atoms

Li, Na, K, Rb are special because they have one electron only outside the closed shells. So are a good place to start understanding the complications.

Na has $Z = 11 \rightarrow 1s^2 2s^2 2p^6 3s^1$ ground state

For the 3s electron, its states are:

$$E_{n,l} = -R \frac{Z_{\text{eff}}^2}{(n - \mu_{\text{core}})^2}$$

$$R = \frac{m_e e^4}{2\hbar^2}$$

$$Z_{\text{eff}} = Z - N + l = 1$$

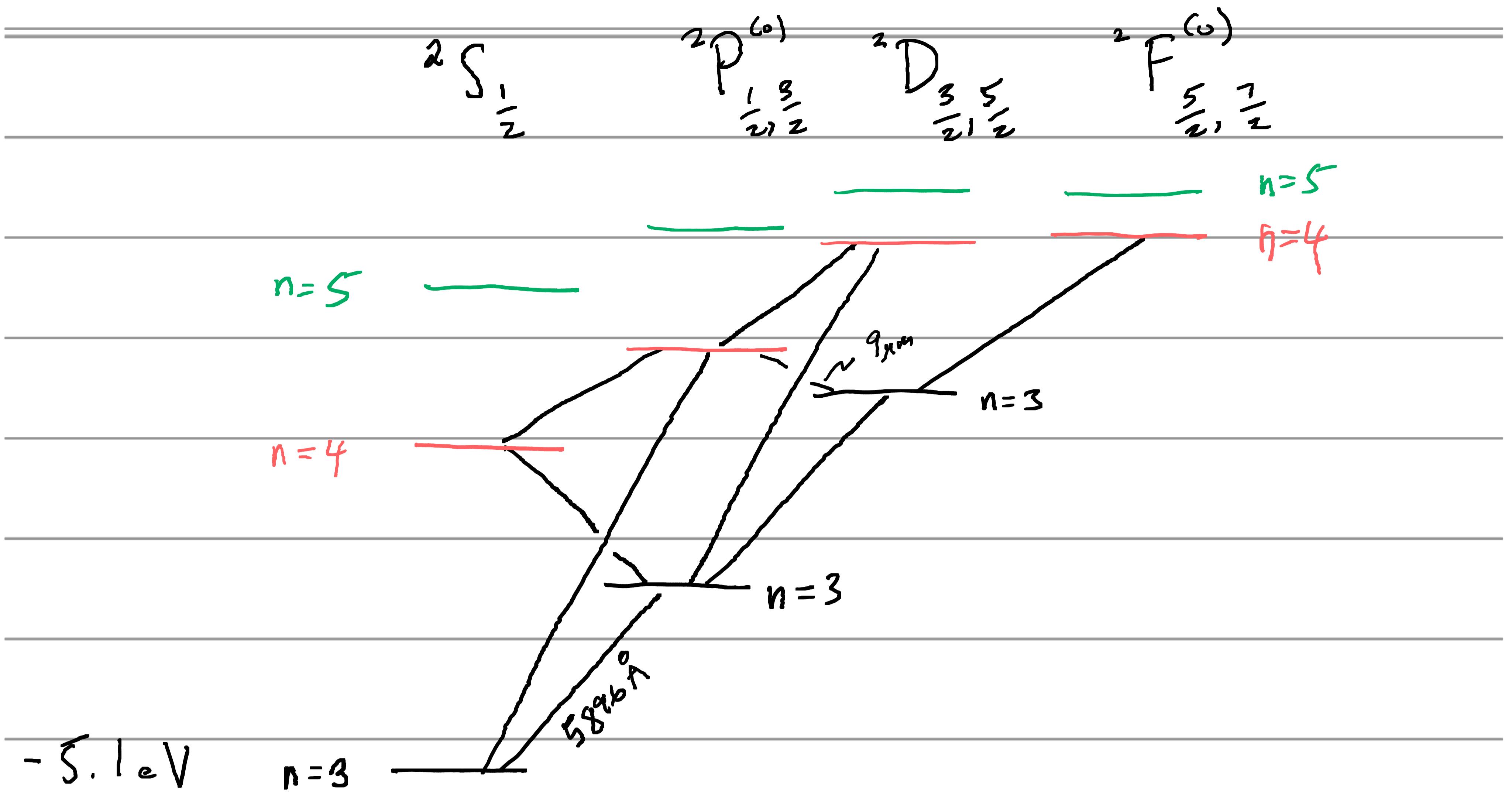
Again, lower l penetrate deeper and have lower energy.

$$\mu_{ns} \approx 1.4$$

$$\mu_{np} \approx 0.9$$

$$\mu_{nd} \approx 0.01$$

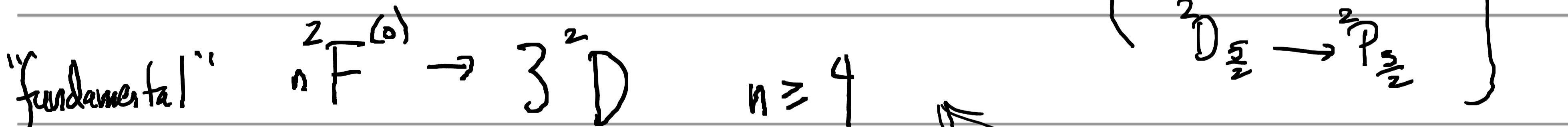
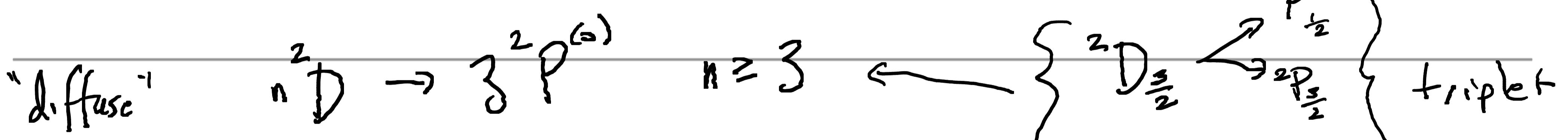
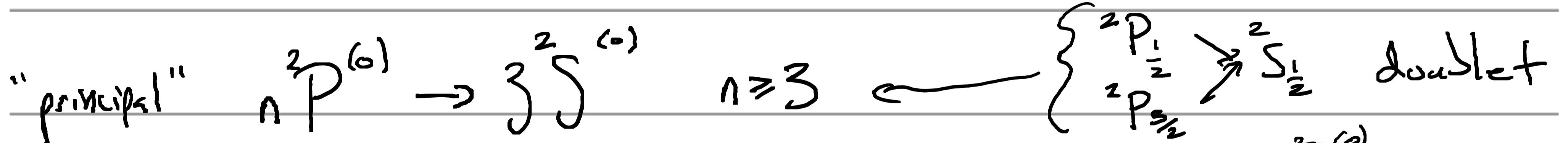
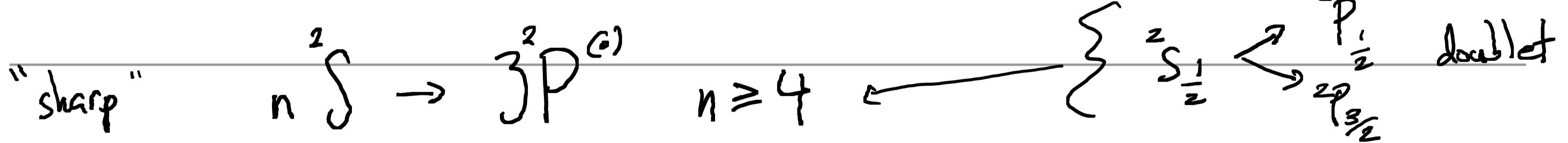
$$\mu_{nf} \approx 0$$



$$\Delta J = 0, \pm 1$$

Consider these series:

Fine structure allowed



\uparrow
initials one
from sodium

series

triplet for same
reason

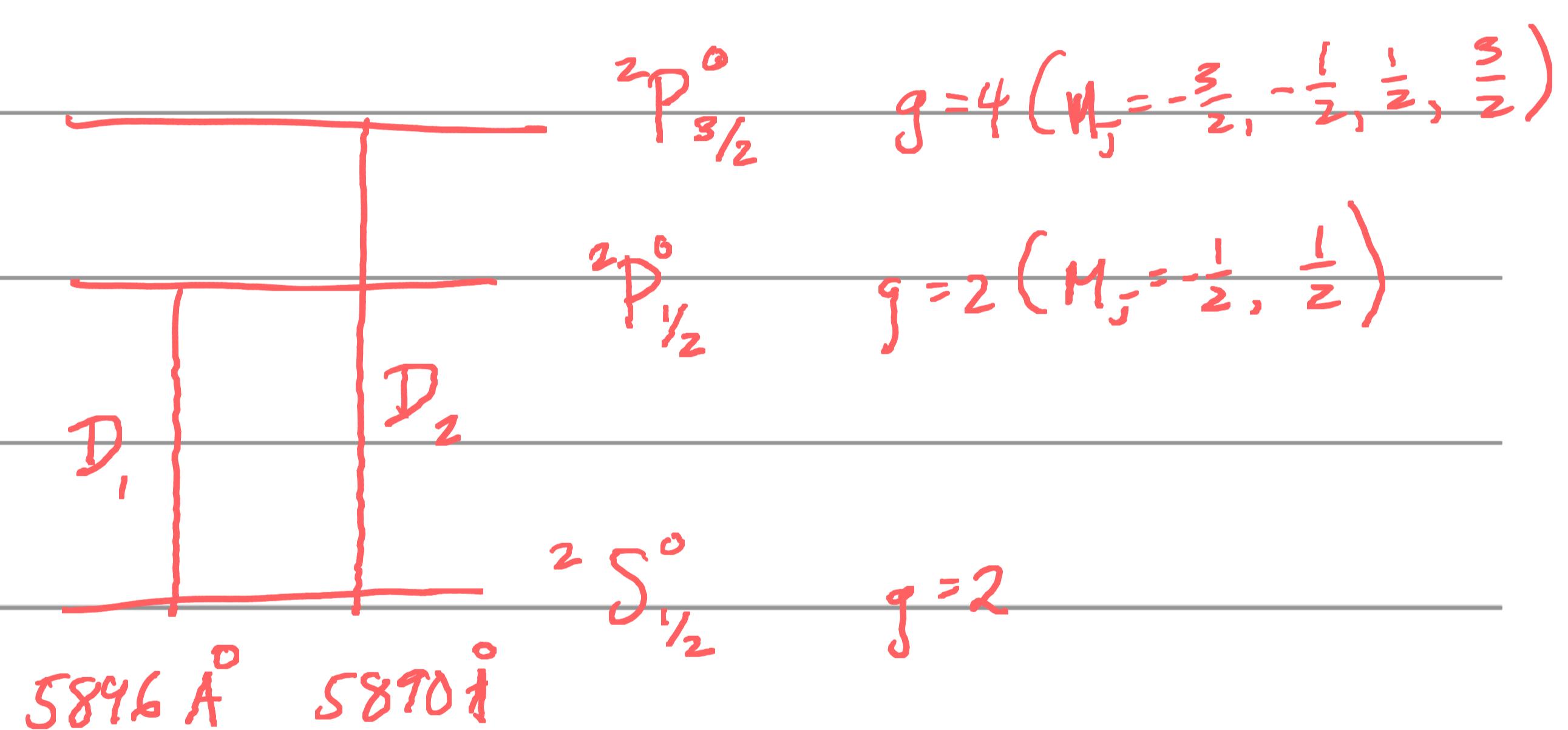
Landé tells us: $\Delta E_{S0} \propto [J(J+1) - L(L+1) - S(S+1)]$

So eg. for doublet $^2S_{\frac{1}{2}} - ^2P_{\frac{1}{2}, \frac{3}{2}}^{(0)}$ (N_a "D")
 ↑ not the same
 "D"!

Splitting is from

$$L=1, S=\frac{1}{2}, J=\frac{1}{2} \rightarrow \Delta E_{S0} \propto -2 \text{ "D}_1$$

$$L=1, S=\frac{1}{2} \rightarrow J=\frac{3}{2} \rightarrow \Delta E_{S0} \propto +1 \text{ "D}_2$$

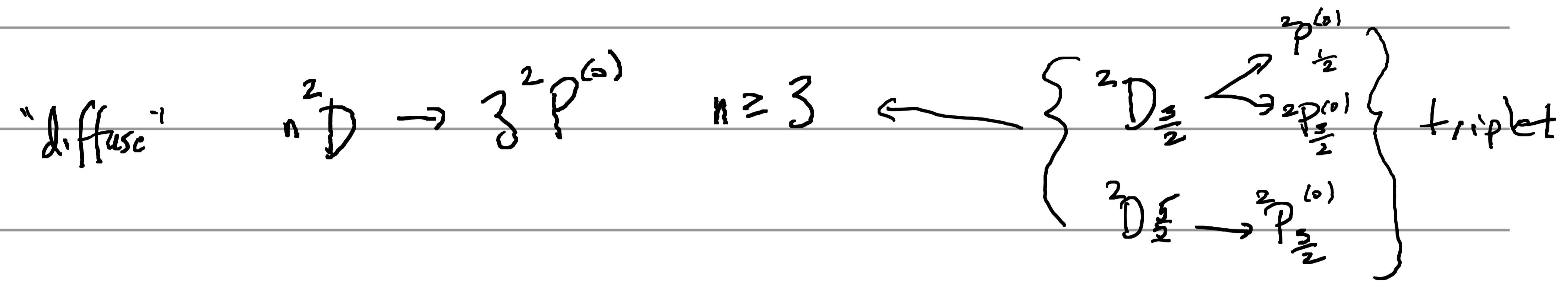


Oscillation strengths determined primarily from term, so within a multiplet the strengths are set strongly by multiplicities (M_J) Ornstein-Burgers sum rules.

Consider transitions from term A to B. Within each term, sum of strengths for each level $\propto 2J+1$
 * only if no non-equivalent electrons

For $\gamma \ll 1$, D_2 should be stronger $\times 2$ than D_1 .

What about triplets? Consider this one:



$${}^2D_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}^{(o)} \quad \begin{matrix} L_1 \\ 2 \end{matrix} \quad \begin{matrix} L_2 \\ 1 \end{matrix} \quad \begin{matrix} J_1 \\ \frac{3}{2} \end{matrix} \quad \begin{matrix} J_2 \\ \frac{1}{2} \end{matrix}$$

$$\hookrightarrow \Delta(\Delta E_{so}) = J_1(J_1+1) - L_1(L_1+1) - J_2(J_2+1) + L_2(L_2+1)$$

$$= - \{$$

$${}^2D_{\frac{3}{2}} - {}^2P_{\frac{3}{2}}^{(o)} \quad \hookrightarrow \Delta(\Delta E_{so}) = -2$$

$${}^3D_{\frac{5}{2}} - {}^2P_{\frac{3}{2}}^{(o)} \rightarrow \Delta(\Delta E_{so}) = 1 \quad \Delta S = 0$$

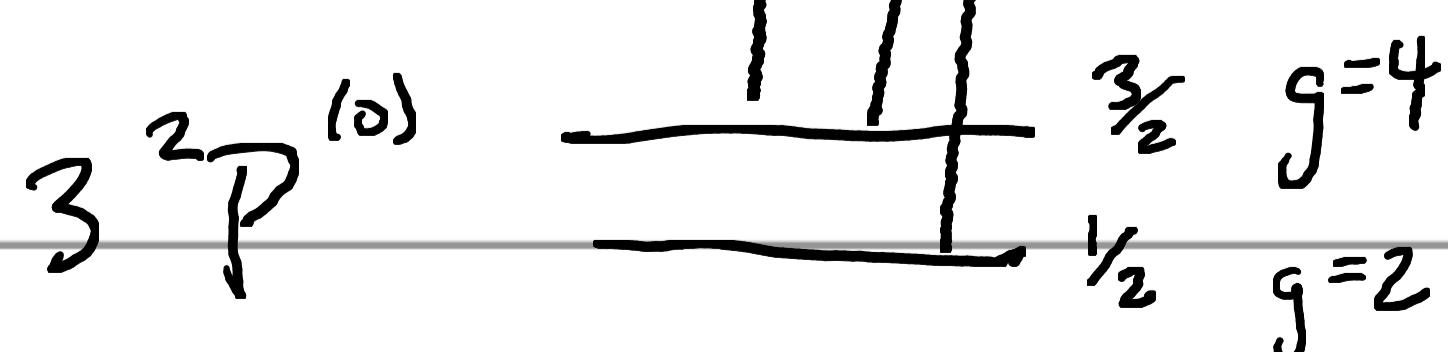
$$\Delta M_J = 0, 1, -1$$



(a) (b) (c)

(a) : (b) + (c) 6:4

(a) + (b) : (c) 4:2



(a) : (b) : (c) 9:1:5

(Note I think Terayson gets this wrong)

Ca^{II} is a highly important species - alkali-like

$$Z = 20$$

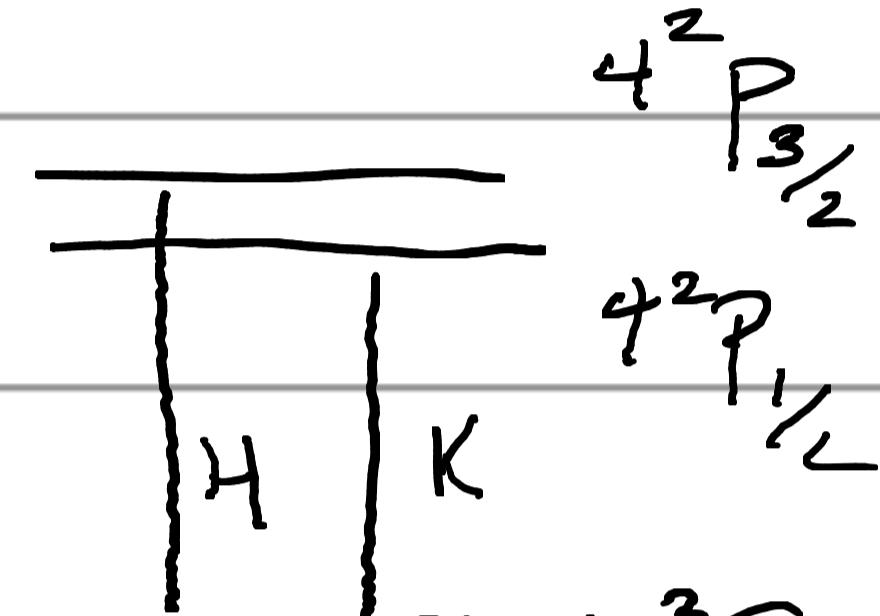
$$N = 19$$

"potassium-like"

ionization potential $\sim 6.1 \text{ eV}$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s$ in ground state

Doublet: $4^2S_{1/2} - 4^2P_{1/2}$ "H" 3968 \AA



$4^2S_{1/2} - 4^2P_{3/2}$ "K" 3934 \AA

Triplet: $4^2P_{3/2}^0 - 3^2D_{3/2}$ 8498 \AA

$4^2P_{3/2}^0 - 3^2D_{5/2}$ 8542 \AA

$4^2P_{1/2}^0 - 3^2D_{3/2}$ 8662 \AA

Mg II

$Z = 12$ } \rightarrow "Na-like"
 $N = 11$

$$3^2S_{\frac{1}{2}} - 3^2P_{\frac{1}{2}}^{(6)} - 2800 \text{ \AA}$$

$$3^2S_{\frac{1}{2}} - 3^2P_{\frac{3}{2}}^{(o)} - 2796 \text{ \AA}$$

$$- 4^2P_{\frac{1}{2}}^{(o)} - 1240.4 \text{ \AA}$$

$$- 4^2P_{\frac{3}{2}}^{(o)} - 1239.9 \text{ \AA}$$

Present in absorption & emission in ISM

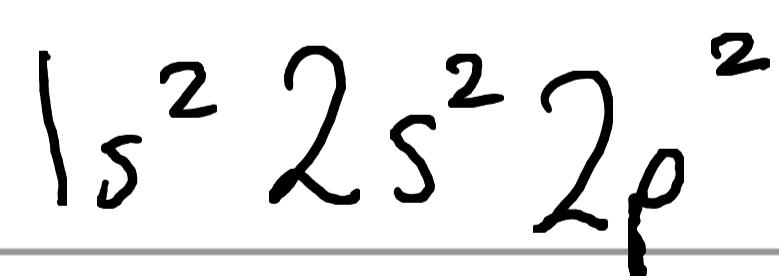
Note it is a "permitted" line so tends to
be strong.

Observations of forbidden transitions

Emission of forbidden lines requires atoms to stay in upper level sufficiently long. This they will not do at high density, because they will encounter another atom relatively quickly.

Below some density (the "critical density") they will last long enough that most of their transitions out are radiative. But in the ISM, much gas is at these very low densities!

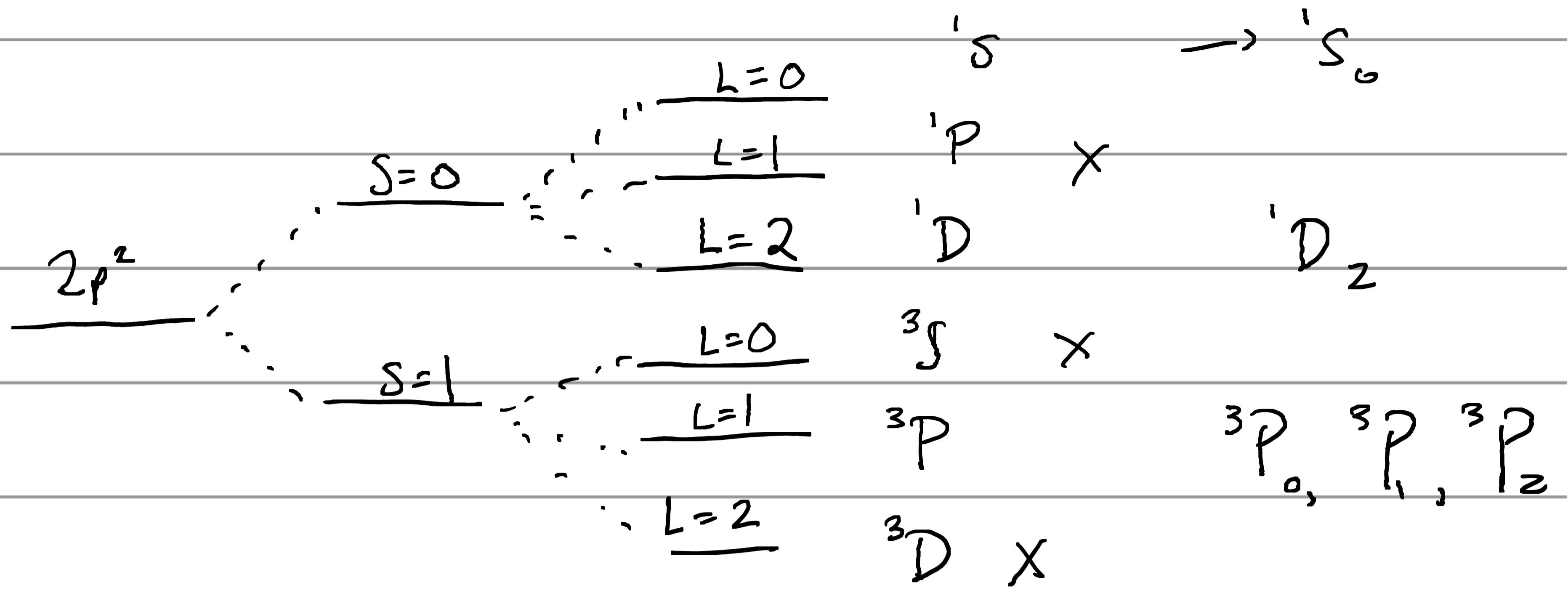
A good example is O^{III} (O^{++}). This has a ground state configuration:



The two $2p$ electrons can total: $S = 0, 1$
 $L = 0, 1, 2$

"C-like"

Without changing the configuration we can have
(ignoring Pauli):



But these must be formed by choices for m_s & m_l , which do not violate Pauli.

(n, l, m_l, m_s) must be distinct

Clearly $S=1, L=2$ is ruled out, since it would lead to disallowed state $m_{l1}=1, m_{l2}=1, m_{s1}=m_{s2}=\frac{1}{2}$

It is subtler to show 3S_0 & 1P also can't exist.

Basically:

3S_0 would require a state like

$$m_{l1}=1, m_{l2}=-1, m_{s1}=\frac{1}{2}, m_{s2}=\frac{1}{2}$$

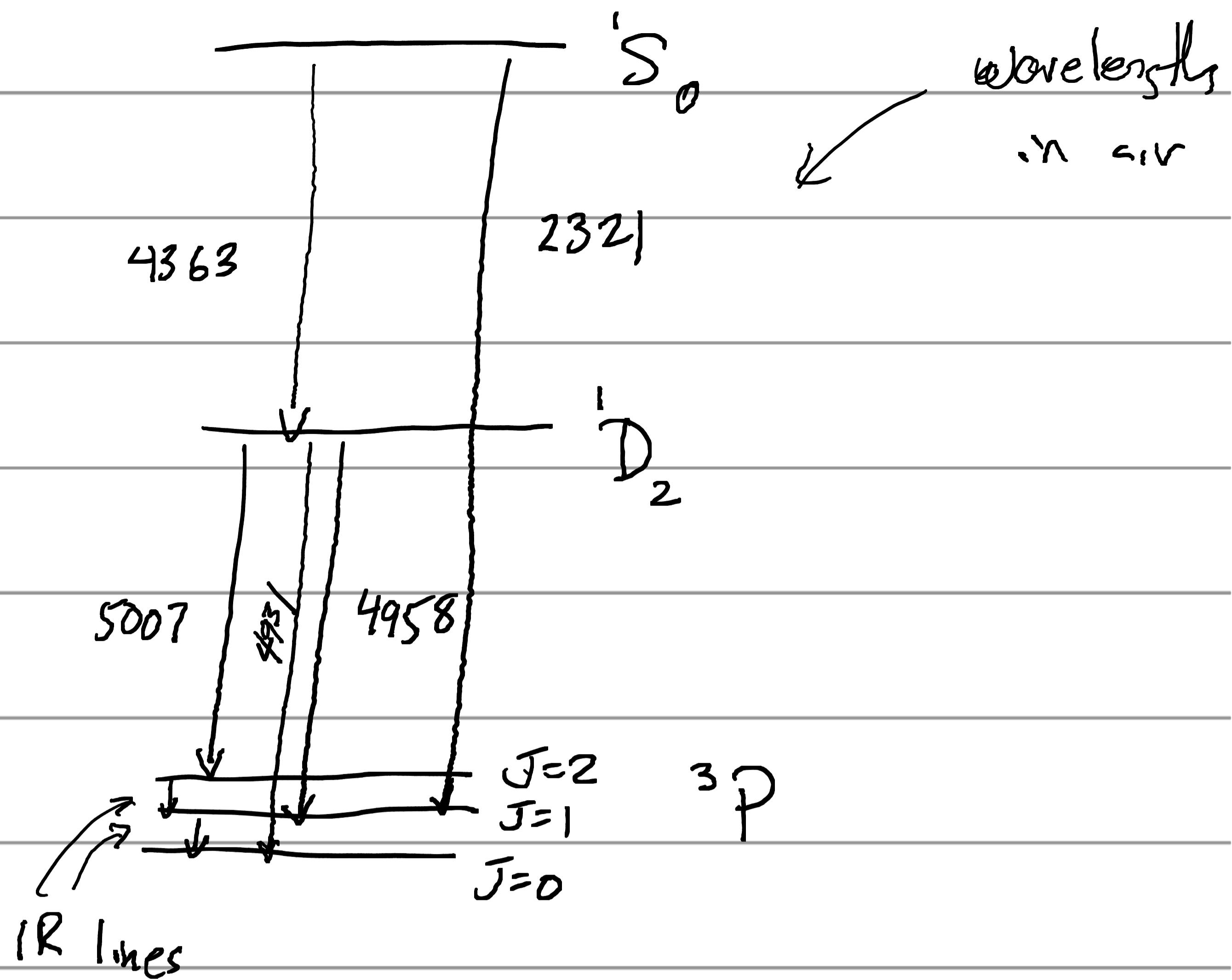
but that state is indistinguishable from the same state in 3P_0 ; similar argument rules out 1P ,

All transitions

forbidden because

$\sum \ell = 2$ doesn't change:

all even parity!



N II is similar because it also has $N=6$

$'S_0 - ^3P_0$ not allowed $J \neq \Delta$ not allowed

Note $'D_2 - ^3P_0$ (493 \AA) happens to be
much fainter

What a zoo! Luckily the good people at NIST
have made an online Atomic Spectra Database; see
<http://physics.nist.gov>

Population of energy levels

The population of the energy levels, and thus the radiative transitions that emerge from gas, depend on the balance of collisional excitation, deexcitation, radiative absorption & emission.

If the density is high enough then the electron temperature and the levels will be in thermodynamic equilibrium, so that for level i :

$$n_i \propto g_i e^{-E_i/kT_e}$$

Note that formally this doesn't make sense because when $E_i \sim E_{\text{ionization}}$, $n_i \propto (2J_i + 1) e^{-E_{\text{ionization}}/kT_e}$

and i increases forever and J_i keeps increasing.

But in fact perturbations cut off the series so the divergence does not occur. In many cases, $n_i \ll n_0$ for $i > 0$.

In these cases we use:

$$n = \sum_i n_i = \text{total number (or number density)}$$

$$= \sum_i A g_i e^{-E_i/kT_e} \approx A g_0$$

and so
$$n_i = n \frac{g_i}{g_0} e^{-E_i/kT_e}$$

If we consider optical transitions, these require $T_e \sim eV \sim 10^4 \text{ K}$, that is a lot of gas in a universe can excite the appropriate levels.

Note however that at low density the electron temperature is decoupled from the level temperature. It is interesting to ask what the density has to be for this to happen.

Take a simplified two-level state. The equilibrium is given by:

$$n_e n_1 q_{f12} = n_e n_2 q_{f21} + n_2 A_{21}$$

(collisional
excitation) de-excit.

(assumes very low $I_{\nu_{21}}$) distribution of v , not \vec{v}

Where $q_{f12} = \int d\nu \left(v \sigma_{12} \right) f(v)$

$$f(v) \propto \frac{v^2}{(kT)^{3/2}} e^{-mv^2/2kT}$$

x-section $\propto \frac{1}{v^2}$

$$\propto T^{-1/2}$$

$$q_{f12} = \int d\nu \left(v \sigma_{12} \right) f(v)$$

If only collisions matter then in thermodynamic eqm detailed balance has:

$$\sigma_{12}(v) n_e n_1 v_1 f(v_1) dv_1 = n_e n_2 v_2 \sigma_{21}(v_2) f(v_2) dv_2$$

Where $\frac{1}{2} m v_1^2 = \frac{1}{2} m v_2^2 + \gamma$

And $\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\chi/kT}$ in thermodynamic equilibrium

So: $\int v_1 \sigma_{12}(v_1) f(v_1) dv_1 = \frac{g_2}{g_1} \int v_2 \sigma_{21}(v_2) f(v_2) dv_2 e^{-\chi/kT}$

$$f(v_1) \propto v_1^2 e^{-mv_1^2/2kT} \quad f(v_2) \propto v_2^2 e^{-mv_2^2/2kT} \propto v_2^2 e^{-mv_1^2/2kT + \chi/kT}$$

$$v_1 dv_1 = v_2 dv_2$$

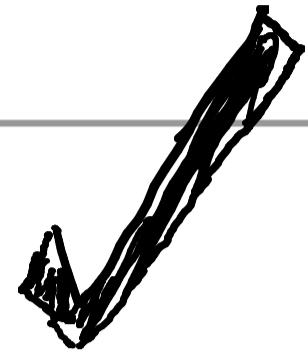
$\therefore g_1 v_1^2 \sigma_{12}(v_1) = g_2 v_2^2 \sigma_{21}(v_2)$

So: $\frac{g_{12}}{g_{21}} = \frac{\int dv_1 \sigma_{12} f(v_1) v_1}{\int dv_2 \sigma_{21} f(v_2) v_2} = \frac{g_2}{g_1} e^{-\chi/kT}$

Then we solve:

$$\frac{n_2}{n_1} = \frac{n_e g_{12}}{A_{21}} \left[\frac{1}{1 + \frac{n_e g_{21}}{A_{21}}} \right]$$

$$\frac{n_2}{n_1} = \frac{n_e g_{f12}}{A_{21}} \left[\frac{1}{1 + \frac{n_e g_{f21}}{A_{21}}} \right]$$



As required, as $n_e \rightarrow \infty$ $\frac{n_2}{n_1} = \frac{g_{f12}}{g_{f21}} = \frac{g_2}{g_1} e^{-\chi/kT}$

and as $n_e \rightarrow 0$ $\frac{n_2}{n_1} = \frac{n_e g_{f12}}{A_{21}}$

Define "critical density for collisional deexcitation":

$$n_c = \frac{A_{21}}{g_{f21}} \rightarrow \text{density above which thermodynamic equilibrium can be maintained}$$

(or $n_c = \sum_{j < i} A_{ij} / \sum_{i \neq j} g_{fij}$)

These critical densities range from $10 - 10^6 \text{ cm}^{-3}$ for many ions with detectable lines. Eg. 1D_2 level of OIII has $n_c \sim 7 \times 10^5 \text{ cm}^{-3}$, OII ${}^2D_{5/2}^0$ (3729 \AA) has $n_c \sim 3 \times 10^3 \text{ cm}^{-3}$.

The transition allows good determinations of n_e within $\sim \times 10$ of n_c

Ionization

In hot & dense enough gas, there will also be ionized species. In thermodynamic equilibrium, the ionized fraction can be derived from the Boltzmann distribution:

Define $dN_0^+(v) \rightarrow$ number of ions in volume $dx dy dz$ density associated with a free electron in the range $(v, v + dv)$

$$\frac{dN_0^+(v)}{N_0} = \frac{g}{g_0} \exp \left[-\frac{\frac{2}{I} + \frac{1}{2} m v^2}{kT} \right]$$

\uparrow degeneracy in ground state
number in ground state density

$$g = g_0^+ g_e = g_0^+ \cdot \left(\frac{2 dx dy dz dp_x dp_y dp_z}{h^3} \right)$$

multiplicity of ground state

$N_e =$ electron number density
 \uparrow i.e. this defines volume we consider

$$\frac{dN_o^+(v)}{N_o} = \frac{8\pi m_e^3}{h^3} \frac{g_0^+}{N_e g_0} \exp\left[-\frac{K_I + \frac{1}{2}mv^2}{kT}\right] v^2 dv$$

$$\int dv \rightarrow \frac{N_o^+ N_e}{N_o} = \frac{8\pi m_e^3}{h^3} \frac{g_0^+}{g_0} e^{-K_I/kT} \int dv v^2 e^{-\frac{mv^2}{2kT}}$$

$$= \left(\frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} \frac{2g_0^+}{g_0} e^{-K_I/kT}$$

It is extremely revealing to define the "thermal de Broglie wavelength":

$$\lambda_{Te} = \frac{h}{p_T} = \frac{h}{\sqrt{2\pi mkT}}$$

$$\text{Then: } \frac{N_o^+}{N_o} = \frac{1}{N_e \lambda_{Te}^3} \frac{2g_0^+}{g_0} e^{-K_I/kT}$$

$\underbrace{g_e}$ \overbrace{m} $\underbrace{k}_{\sim "mv"}$

In most situations (eg in stars) g_e is relatively high — ie the gas is far from degenerate.

If we define :

$$\xi = \ln \left(\frac{2}{nX_{Te}^S} \right)$$

$$-\mu_e = kT\xi$$

Then: $\frac{N_e^+}{N_e} = \frac{g_0^+}{g_0^-} e^{-(\mu_e + \chi_T)/kT}$

in stellar atmospheres is 10^{-30} .

$$n_e \sim \text{cm}^{-3}$$

$$T_e \sim 10,000 \text{ K} \rightarrow X_{Te} = \frac{h}{\sqrt{2\pi m_e kT}} = \frac{6.6 \times 10^{-27} \frac{\text{g cm}^2}{\text{s}}}{(6.67 \times 9 \times 10^{-28} \text{ g})} \times (1.38 \times 10^{-16} \frac{\text{J cm}^2}{\text{K s}^2}) \times (10^4 \text{ K})^{1/2}$$

$$h = 6.62 \times 10^{-27} \frac{\text{g cm}^2}{\text{s}}$$

$$m_e = 9 \times 10^{-28} \text{ g}$$

$$= \frac{6.6 \times 10^{-27} \text{ cm}}{(10^{-38})^{1/2}}$$

$$T = 10^4 \text{ K}$$

$$k = 1.38 \times 10^{-16} \frac{\text{J cm}^2}{\text{K s}^2} \text{ K}^{-1} = 10^{-7} \text{ cm}$$

$$\xi = \ln(10^{21}) \sim 50$$

This is important because for $\frac{N_e^+}{N_e}$ to be large requires $-\mu_e \approx \psi_I$ or

$$-\beta kT \approx \psi_I \rightarrow T \approx \frac{\psi_I}{k\beta}$$

Since β is large, because $N_e \lambda_{Te}^3$ is small, this is very low. So you get substantial ionization at $T \gtrsim 10^4 K$ even though $\frac{\psi_I}{k} \approx 10^5 K$.

This is because there is lots of available multiplicity for an ionized electron in a nondegenerate gas.

Note that Saha holds in thermodynamic equilibrium, typically maintained by collisional effects.

Photoionization

In many situations the gas is photoionized by UV radiation. The cross section for ionization out of n for H:

$$\sigma_{bf} = \frac{512\pi^7 m e^4 Z^4}{3\sqrt{3} c h^6 n^5} g(\omega, n, l, Z) \frac{1}{\omega^3}$$

Giant factor very typical
 ↳ highest σ
 right above threshold

(for $\omega > \frac{\chi_I}{h}$)

Recombination

Detailed balance arguments yield

$$\frac{\sigma_{bf}}{\sigma_{fb}} = \frac{m^2 c^2 v^2}{v^2 h^2} \frac{g_e g_+}{2 g_n}$$

Along these lines one calculates ionization equilibria given an ionizing flux. Subject of Osterbrock & Ferland

Ionized regions can be modeled by being in photoionization equilibrium.