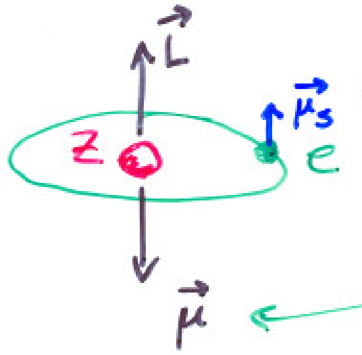
Optical Spectra involve the spin structure in an intimate way...

A variety of effects...

SPIN-ORBIT INTERACTION

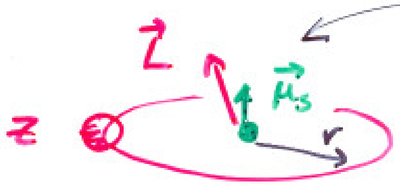


electron has spin ⇒ μ_e

electron orbits nucleus

FROM THE ELECTRON'S REST FRAME..

the proton/nucleus is orbiting it



these 2 angular momentum vectors interact.

Like an internal Zeeman Effect

In terms of Ampere's Law...

$$\vec{B} = \frac{\mu_0}{4\pi}(-Ze)\frac{\vec{v}\times\vec{r}}{r^3}$$

← magnetic field "seen" by electron $\vec{B}_{internal}$

got a moment.. $\vec{\mu}_e$

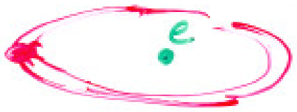
got a magnetic field.. $\vec{B}_{internal}$

⇒ got a potential energy and a precession.

$$\Delta E_{\mu B} = -\vec{\mu}_e \cdot \vec{B}_{internal}$$

How big is this? estimate using Bohr model.. H.

2p state. (s states have no L so no S.O.)



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

$$I = +\frac{e}{T} = fe$$

$$B = \frac{\mu_0 f e}{2r} \qquad f = \frac{v}{2\pi r} = 8.4 \times 10^{14}\,s^{-1}$$

$$r = n^2 a_0 = 4a_0 = 2.1 \times 10^{-10}\,m.$$

$$B = \frac{(4\pi \times 10^{-7}\,T\cdot m/A)(8.4 \times 10^{14}\,s^{-1})(1.6 \times 10^{-19}\,C)}{2(2.1 \times 10^{-10}\,m)} = 0.4\,T$$

pretty big field!

$$|\Delta E_{\mu B}| = \mu B = \frac{e\hbar}{2m}(0.4) = 3.7 \times 10^{-24}\,J$$

$$= 2.3 \times 10^{-5}\,eV$$

So, SPIN-ORBIT interaction splits every l state into 2. → "Fine structure" in the optical spectrum.

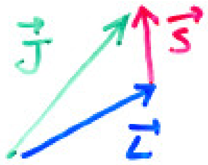
NO SPIN-ORBIT coupling of $\vec{S}$ and $\vec{L}$?

– they would be independent.

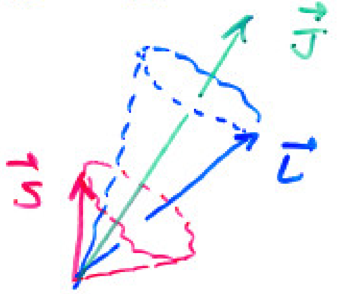
BUT... there is spin-orbit coupling.

a strong internal magnetic field acting on e.

They precess... about their SUM.



$\vec{J}$ is the TOTAL ANGULAR MOMENTUM



now instead of

(n, l, m_l, m_s)

the better set of quantum numbers is

(n, l, j, m_j)

TOTAL ANGULAR MOMENTUM

concentrate on alkali's ... one electron.

$$\vec{J} = \vec{L} + \vec{S}$$

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

j is the total angular momentum quantum number

$$J_3 = m_j \hbar$$

$$m_j = \underbrace{-j, \ldots +j}_{2j+1 \text{ of them.}}$$

Combining angular momenta is a standard task in Quantum Mechanics.

can draw pictures ...

or with out the Algebra. ✓

Addition of Quantum Mechanical Angular Momenta.

$\vec{D} = \vec{A} + \vec{B}$

$|\vec{A}| = \hbar\sqrt{a(a+1)}$ a is the quantum number

$A_3 = m_a \hbar$ $m_a = \underbrace{-a, -a+1, \ldots, a-1}_{2a+1 \text{ of them}}, a$

$|\vec{B}| = \hbar\sqrt{b(b+1)}$

$B_3 = m_b \hbar$ $m_b = -b, \underbrace{-b+1, \ldots b-1}_{2b+1 \text{ of them}}, +b$

$|\vec{D}| = \hbar\sqrt{d(d+1)}$

$D_3 = m_d \hbar$ $m_d = -d, \ldots, +d$

d's can be calculated from a & b_

special "addition"

$d = a \oplus b$

$a \oplus b = |a-b|, |a-b|+1, \ldots, a+b-1, a+b$

→ a SET of possible values for d

EACH of which has its own family of m_d's

Examples

$\vec{C} = \vec{A} + \vec{B}$ where A and B are electron spins

$a = 1/2 \qquad m_a = -1/2, +1/2$

$b = 1/2 \qquad m_b = -1/2, +1/2$

$c = a \oplus b$

$= |a-b|, \ldots (a+b)$

$c = 0, 1$ two values for c.

For $c = 0 \qquad m_c = 0$

For $c = 1 \qquad m_c = -c \ldots +c = -1, 0, 1$

GENERAL RULES

$$\vec{Y} = \vec{X}_1 + \vec{X}_2$$

$\boxed{1/2 + 1/2}$

X_1	m_{x_1}
$1/2$	$1/2, -1/2$

X_2	m_{x_2}
$1/2$	$1/2, -1/2$

Y	m_Y
0	0
1	$-1, 0, 1$

$\boxed{1/2 + 1}$

X_1	m_{x_1}
$1/2$	$1/2, -1/2$

X_2	m_{x_2}
1	$-1, 0, 1$

Y	m_Y
$1/2$	$-1/2, 1/2$
$3/2$	$-3/2, -1/2, 1/2, 3/2$

$$Y = |1 - 1/2| \ldots (1 + 1/2)$$
$$= 1/2, 3/2 \nearrow$$

$\boxed{1 + 1}$

X_1	m_{x_1}
1	$-1, 0, 1$

X_2	m_{x_2}
1	$-1, 0, 1$

Y	m_Y
0	0
1	$-1, 0, 1$
2	$-2, -1, 0, 1, 2$

$$Y = |1 - 1| \ldots (1 + 1)$$
$$Y = 0, 1, 2 \nearrow$$

Selection rules for single photon transitions --

$\Delta n =$ anything.

$\Delta j = 0$ or ± 1 (no $0 \to 0$)

$\Delta m_j = 0$ or ± 1

$\Delta \ell = \pm 1$

States are called by:

orbital angular momentum, capital S, P, D...

$$n L_j$$

principle quantum number

total angular momentum.

So.. back to hydrogen

the $S \cdot L$ coupling only affects $\geq P$ states.. why?

From my table

$S = X_1 = 1/2$ Spin

$L = X_2 = 1$ P state L

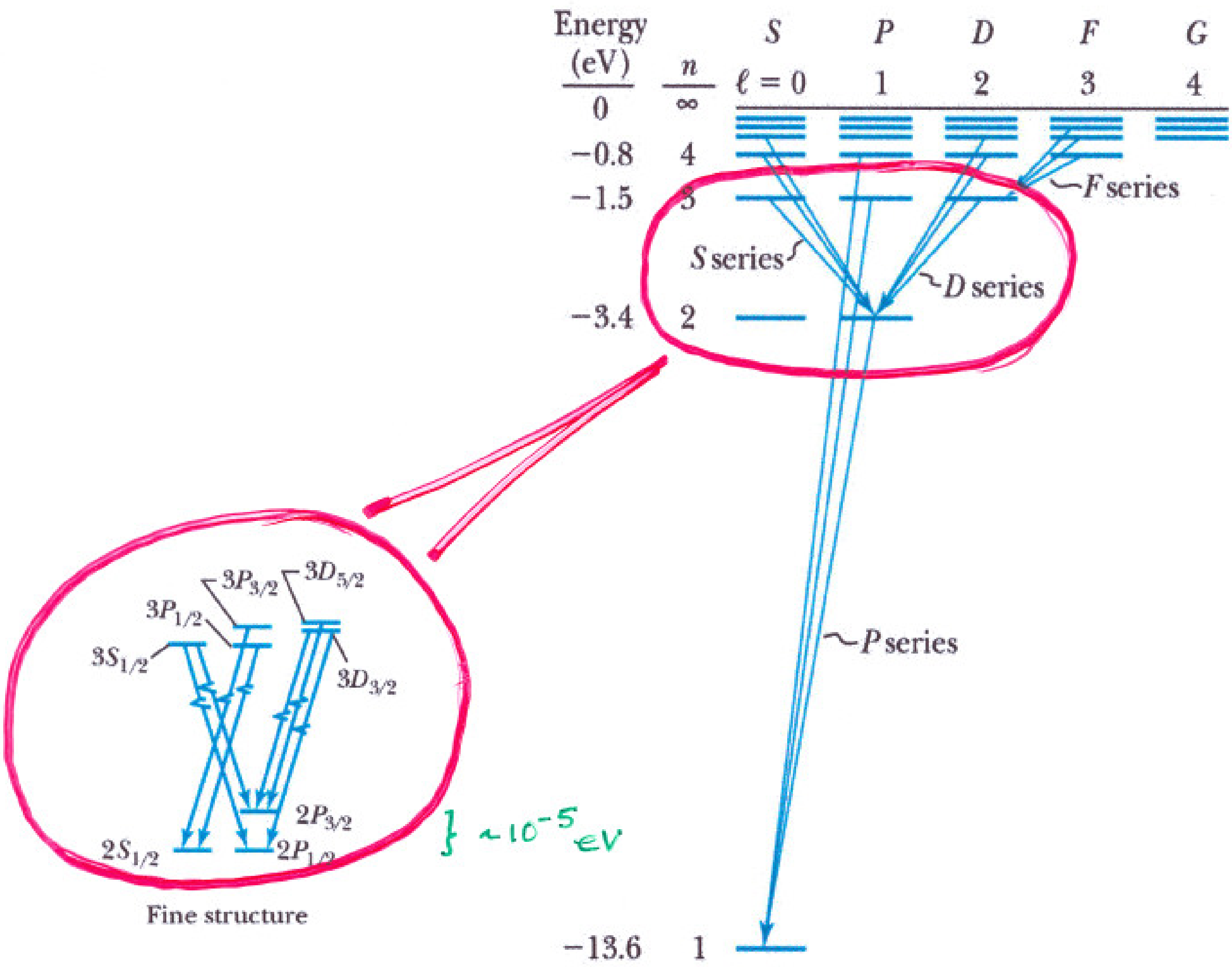
$J = 1/2$ and $3/2$

$\Rightarrow$ each P state becomes a doublet.. just like Zeeman effect.. an internal Zeeman Effect

2P levels: $2P_{1/2}$

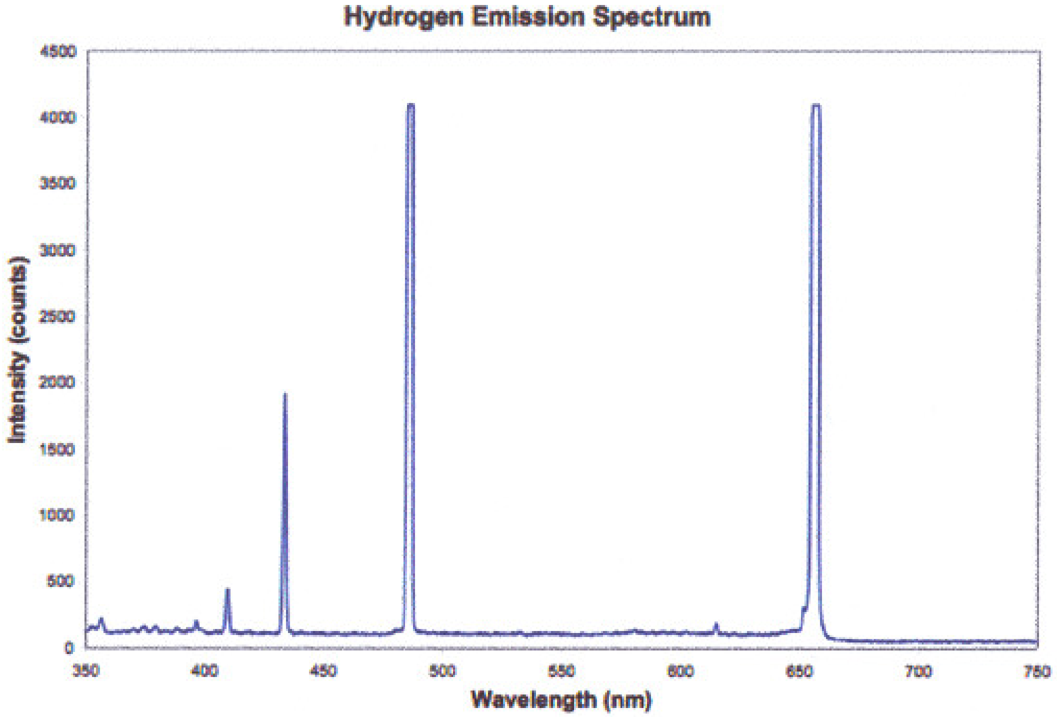
$2P_{3/2}$

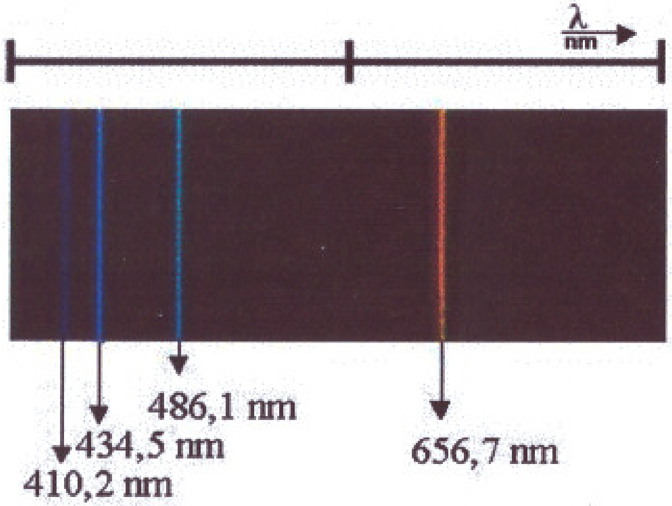
called "fine structure"

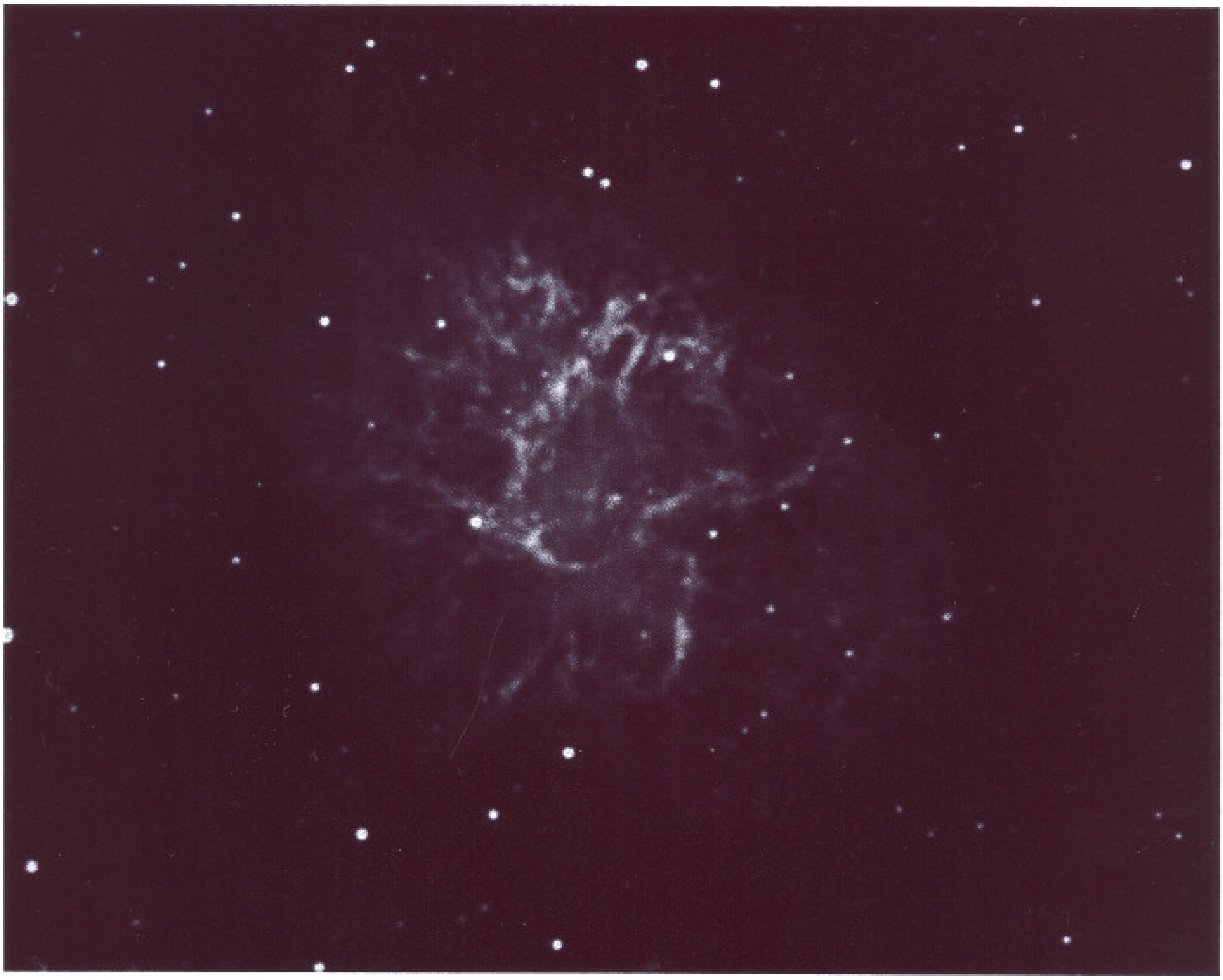

Energy (eV)
n
0
∞
−0.8
4
−1.5
3
−3.4
2
−13.6
1
S
P
D
F
G
ℓ = 0
1
2
3
4
F series
S series
D series
P series
3P3/2
3D5/2
3P1/2
3S1/2
3D3/2
2P3/2
2S1/2
2P1/2
Fine structure
} ~10^-5 eV

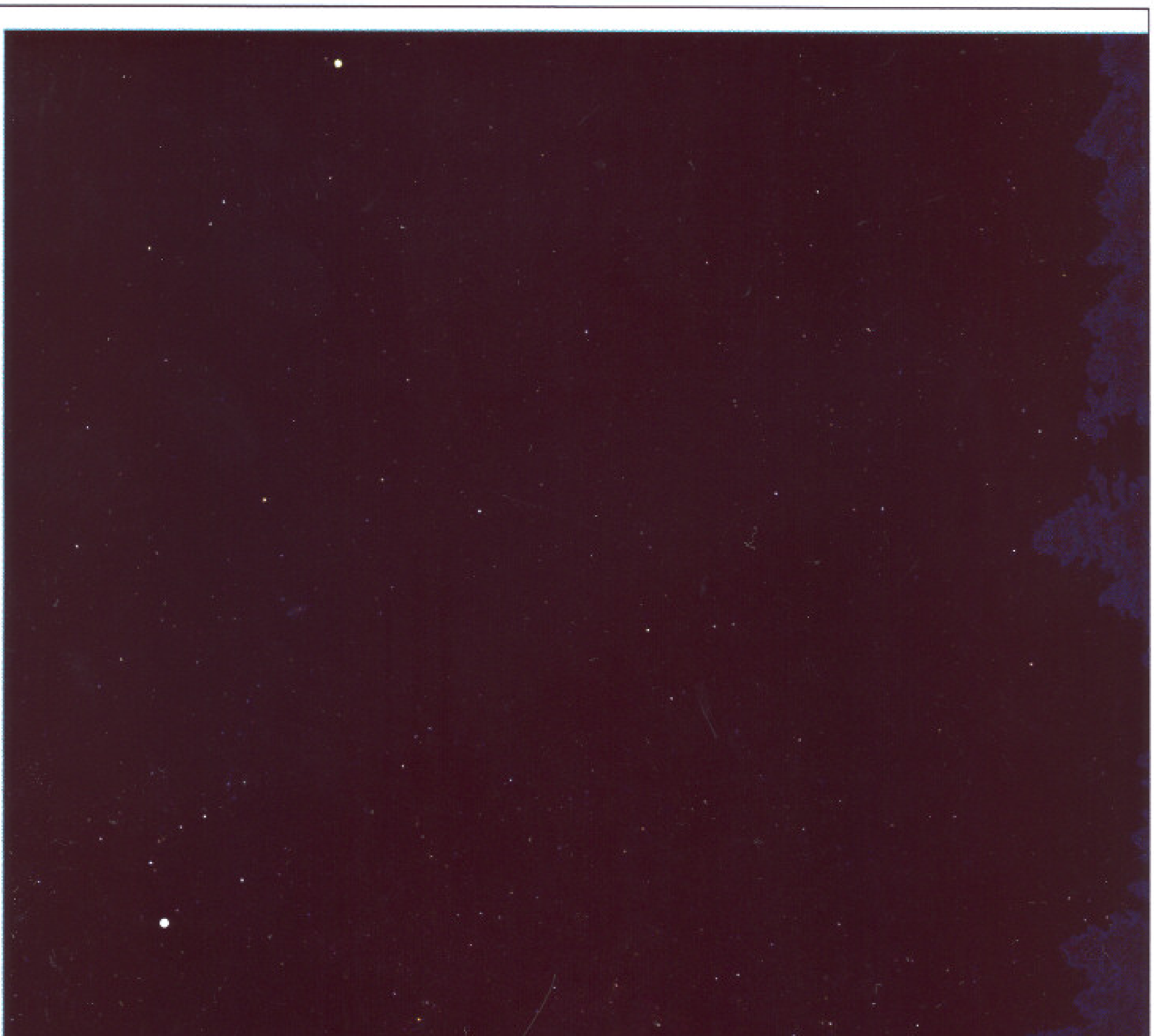
↑ 121.6 nm
2P-1S

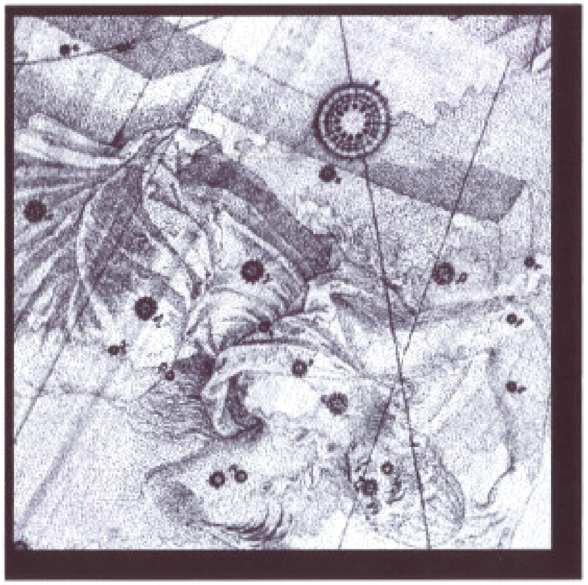
...


Hydrogen Emission Spectrum
Intensity (counts)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
350
400
450
500
550
600
650
700
750
Wavelength (nm)

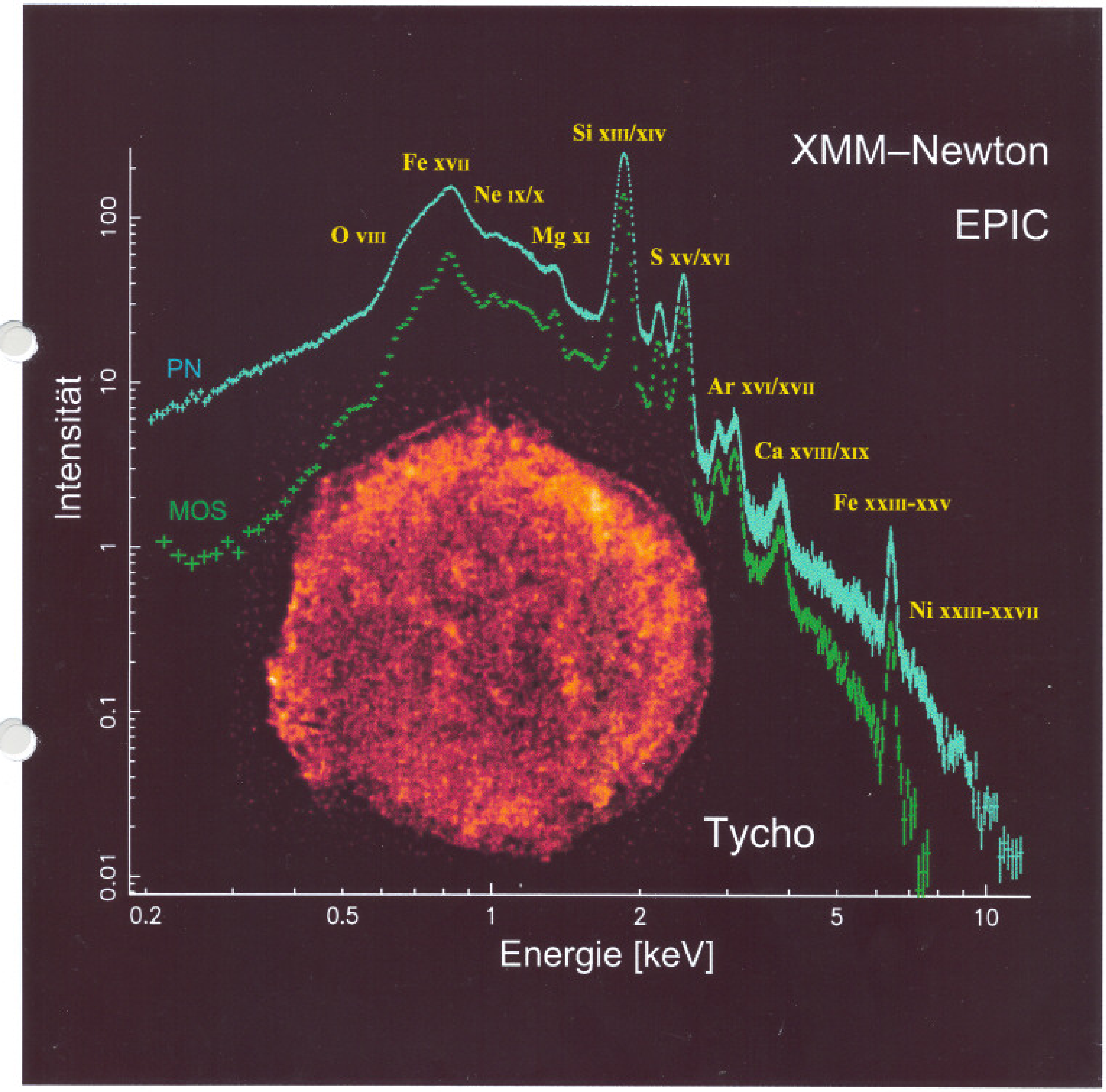

λ
nm
486,1 nm
434,5 nm
410,2 nm
656,7 nm







A caput Caßiopeæ
B pectus Schedir.
C Cingulum
D flexura ad Ilia
E Genu
F Pes
G ſuprema Cathedræ
H media Cathedræ
I Noua ſtella.
I
H
G
D
F
E
C
B
A

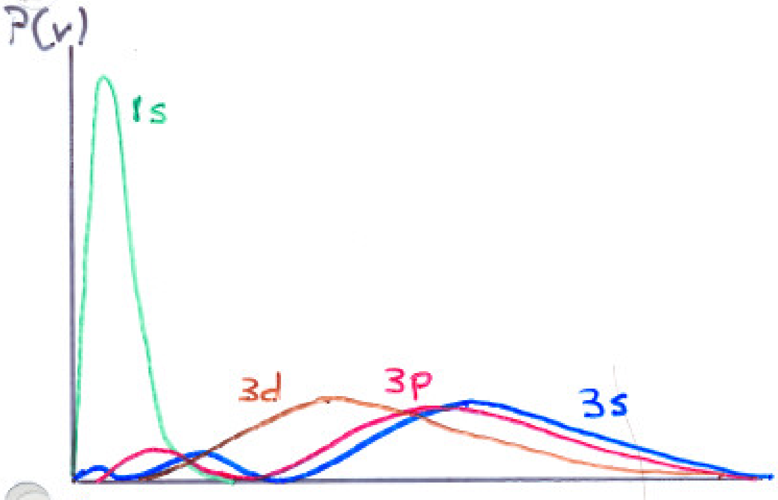

XMM–Newton
EPIC
Si XIII/XIV
Fe XVII
Ne IX/X
O VIII
Mg XI
S XV/XVI
Ar XVI/XVII
Ca XVIII/XIX
Fe XXIII-XXV
Ni XXIII-XXVII
PN
MOS
Tycho
Intensität
100
10
1
0.1
0.01
0.2
0.5
1
2
5
10
Energie [keV]

Sodium is everyone's favorite

$Z = 11$ Na $1s^2 2s^2 2p^6 \underline{3s^1}$

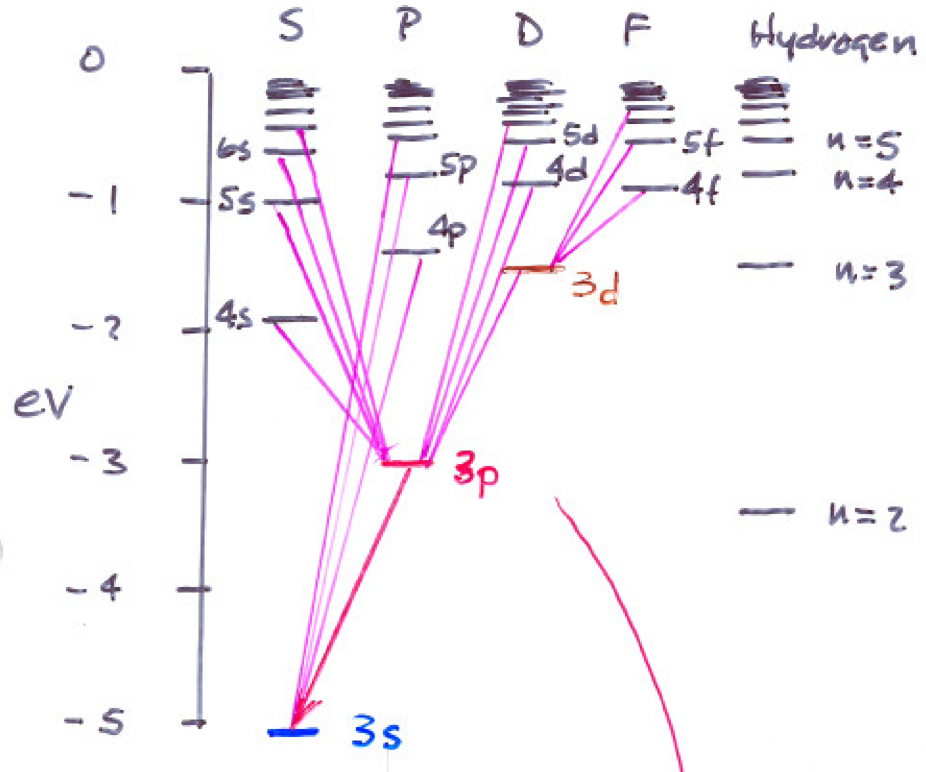
one electron outside closed shells.

an interesting feature involving the 3s wavefunction

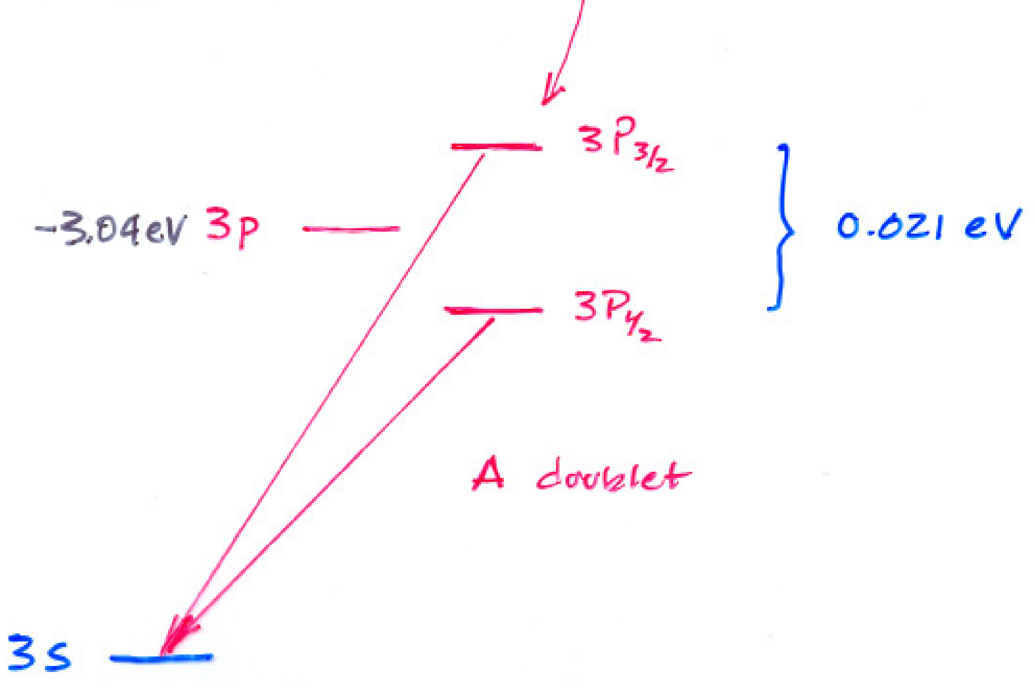


that little penetration of 3s with 1s → greatly increases its binding relative to 3p

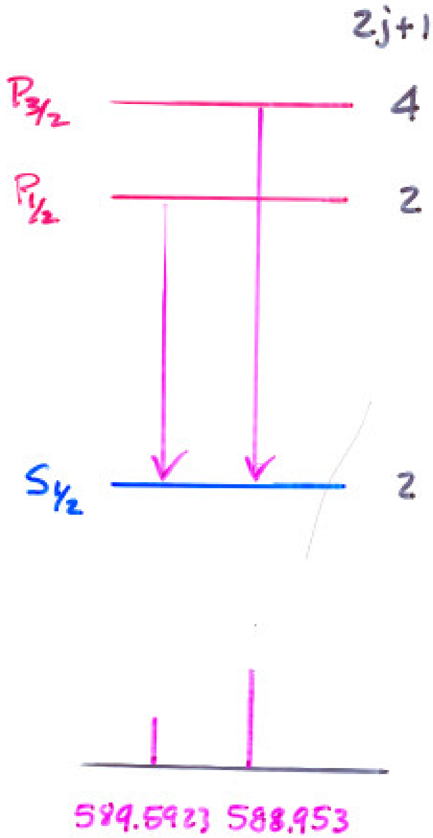
Sodium

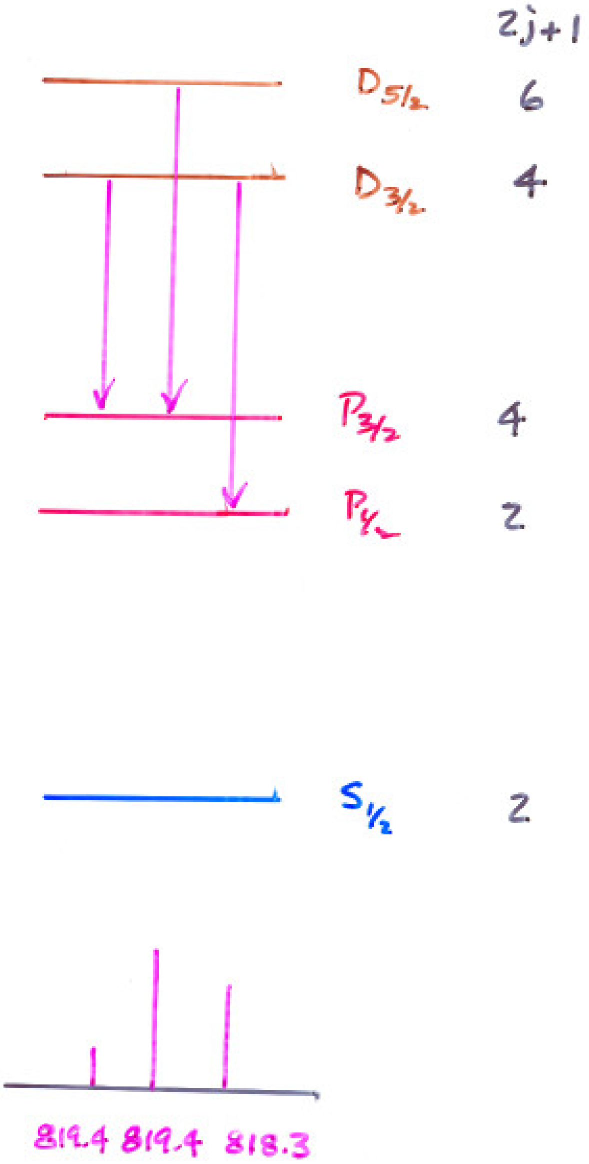


But, again the spin-orbit coupling modifies the P states.. in particular



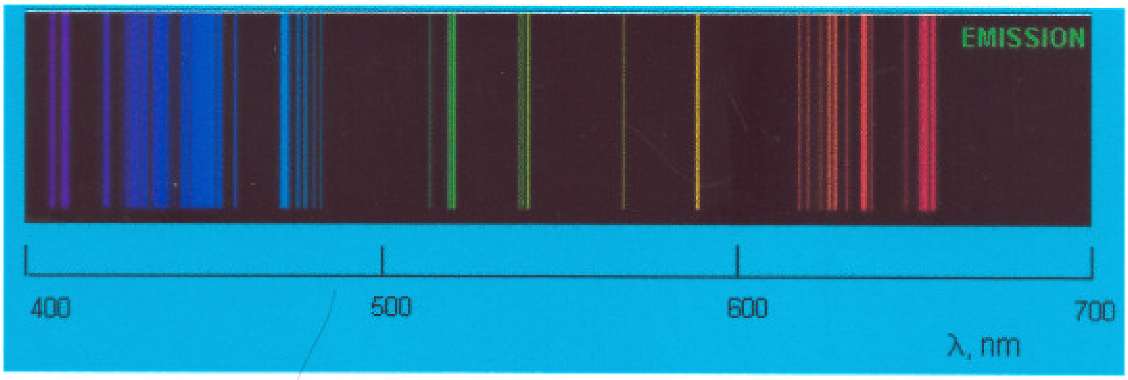
We can learn more

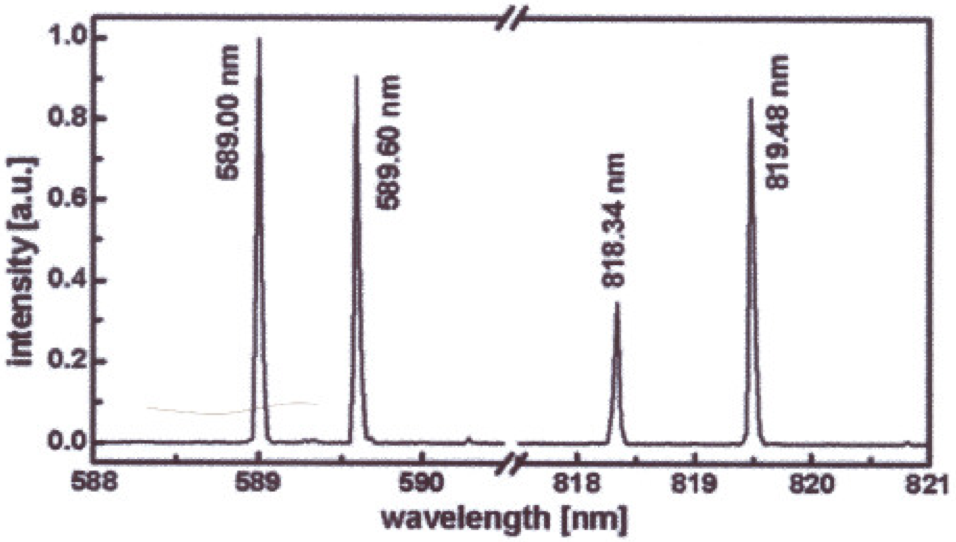




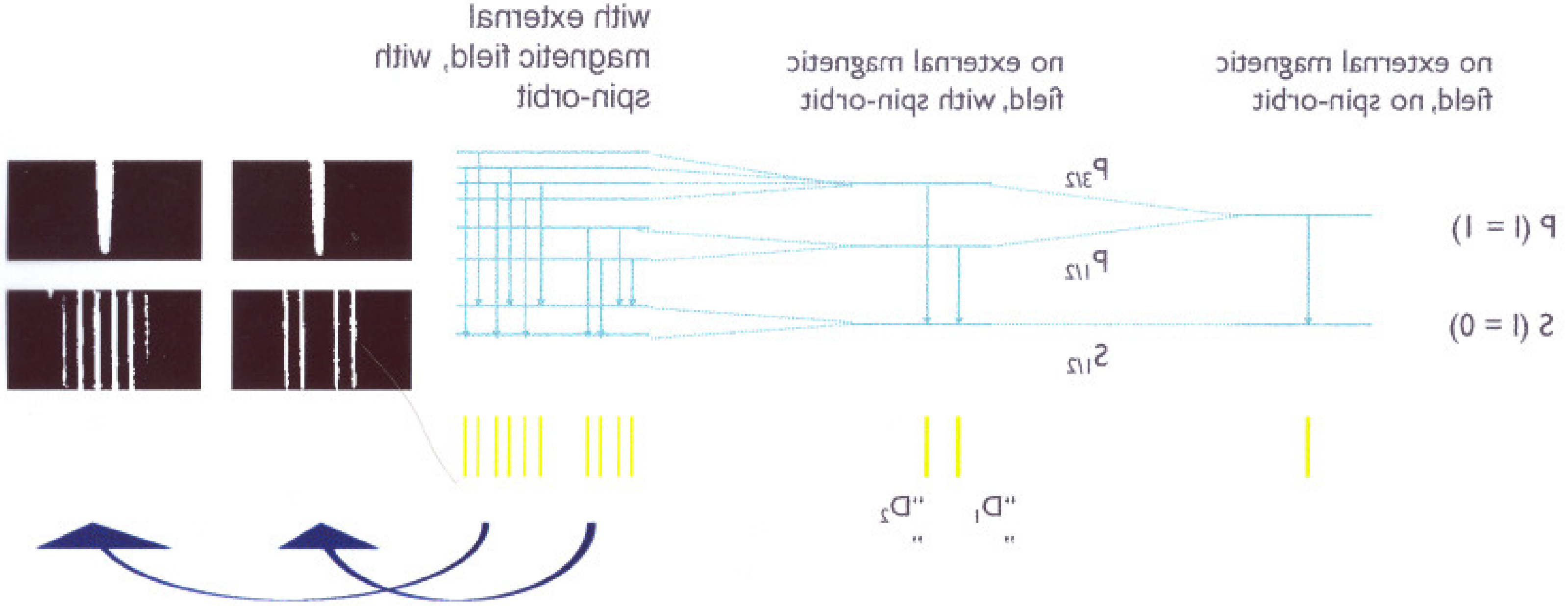
relative
intensities
according to
relative
degeneracy of
states

notice no $D_{5/2} \to P_{1/2}$
which would be
$\Delta J = 2$
which is forbidden.


EMISSION
400
500
600
700
λ, nm


intensity [a.u.]
1.0
0.8
0.6
0.4
0.2
0.0
589.00 nm
589.60 nm
818.34 nm
819.48 nm
588
589
590
818
819
820
821
wavelength [nm]

Zeeman is happy



with external magnetic field, with spin-orbit

no external magnetic field, with spin-orbit

no external magnetic field, no spin-orbit

Multi electron Atoms are even more complicated!

- spin-orbit couplings.
- spin-spin couplings.
- orbit-orbit couplings.

Rules of Thumb -- one of which is the set called

Hund's "Rules" → likelihood for quantum numbers ordered within a subshell

1. The total spin should be maximized.

2. Following rule #1, the total angular momentum should be maximized

why? -- plausibility.

For example .. Maximum spin ⇒ both (of 2) electrons would be ↑↑

→ but that can only happen in different L shells because of Pauli Exclusion.

→ remember Carbon?

Suppose we have 2 electrons.

Total orbital angular momentum of the system

$$\vec{L} = \vec{L}_1 + \vec{L}_2$$

$$L = |L_2 - L_1| \text{ -- } L_2 + L_1$$

so $L_{MAX} = L_1 + L_2$

$L_{MIN} = |L_1 - L_2|$

$$L_z = L_{1z} + L_{2z}$$

or $M_L = M_{L_1} \oplus M_{L_2} = |M_{L_1} - M_{L_2}| \ldots M_{L_1} + M_{L_2}$

Likewise for spin

$\vec{S} = \vec{S}_1 + \vec{S}_2$ $\quad s_1 = s_2 = 1/2$

$S_{MAX} = 1$

$S_{MIN} = 0$

$M_S = s_1 \oplus s_2 = \cancel{1 \oplus 0, 1}$ $0, 1$

So, in Hund's Rule language:

1. find arrangement so $S = M_{S,\max}$

2. then in addition, find arrangement so $L = M_{L,\max}$

Example, Carbon $1s^2 2s^2 2p^2$

$$(\uparrow,\downarrow) \,\vdots\, (\uparrow\downarrow);\ \underset{M_L=-1}{(\ ,\ )}\ \underset{0}{(\ ,\ )}\ \underset{+1}{(\ ,\ )}$$

$S = M_{S\,\max} \Rightarrow S = 1 \Rightarrow \uparrow \,\&\, \uparrow$

can't be in same M_L & ( )

so, which ones ~~do~~ they go into...

maximize $M_L = m_{\ell_1} + m_{\ell_2}$

$$\begin{array}{cccc} & (\ ,\ ) & (\uparrow,\ ) & (\uparrow,\ ) \\ m_\ell & -1 & 0 & +1 \end{array}$$

$\Rightarrow M_L = 1 + 0 = 1$

$\Rightarrow L = 1$

So, ground state is $S = 1$, $L = 1$

Example, Nitrogen $1s^2 2s^2 2p^3$

$(\uparrow,\downarrow) \;\vdots\; (\uparrow\,\downarrow);\; (\;,\;)\;\;(\;,\;)\;\;(\;,\;)$

$m_\ell = -1 \quad 0 \quad +1$

where do the 3 electrons go?

maximize S... M_S? $\uparrow, \uparrow, \uparrow$ $M_S = 3/2$

maximize L... M_L? $-1, 0, 1$

$(\uparrow,\;)\;(\uparrow,\;)\;(\uparrow,\;)$

$m_\ell = \quad -1 \quad 0 \quad 1$

so, $M_L = -1 + 0 + 1 = 0$

$\Rightarrow L = 0$

Ground state of Nitrogen is the $L=0$ $S = 3/2$ state

You do oxygen by tomorrow -- in class.

There are at least 2 standard ways of combining spins and angular momenta ...

"L-S Coupling" (Russell-Saunders Coupling)

- when spin-orbit is negligible ... relatively light elements

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_3 + \dots \vec{L}_n$$

$$\vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \dots \vec{S}_n$$

then the quantum numbers for the atom are

$$\vec{J} = \vec{L} + \vec{S}$$

"J-J Coupling"

- relatively heavy elements where spin-orbit can be high.

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1$$

$$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$$

$$\vdots$$

$$\vec{J}_n = \vec{L}_n + \vec{S}_n$$

then the quantum numbers for the atom are

$$\vec{J} = \vec{J}_1 + \vec{J}_2 + \vec{J}_3 + \dots \vec{J}_n$$

we'll ... say no more.

L-S coupling

Each individual electron has an L and an S

→ the whole state will have a combined L, S.

which will characterize the J

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \dots \vec{L}_n = \vec{L}_1 + \vec{L}_2 \quad \text{for } n=2$$

so, L = set of $|L_1 - L_2|$ to $(L_1 + L_2)$

S = set of $|S_1 - S_2|$ to $(S_1 + S_2)$

when $L \geq S$, then the number of J states is $2S+1$

leads to a notation: $n\,^{2S+1}L_J$

(quantum numbers for many-electron atoms are conventionally capitals -- sorry)

Bodi's example: 2 electrons, one in 4P & other 4D

$L_1 = 1$ & $L_2 = 2$

$S_1 = 1/2$ & $S_2 = 1/2$

$L = L_1 \oplus L_2 = |L_1 - L_2|, \dots, (L_1 + L_2)$

$L = |2-1| \dots 3 = 1, 2, \text{ or } 3$

$S = S_1 \oplus S_2 = |1/2 - 1/2| \dots (1/2 + 1/2) = 0, 1$

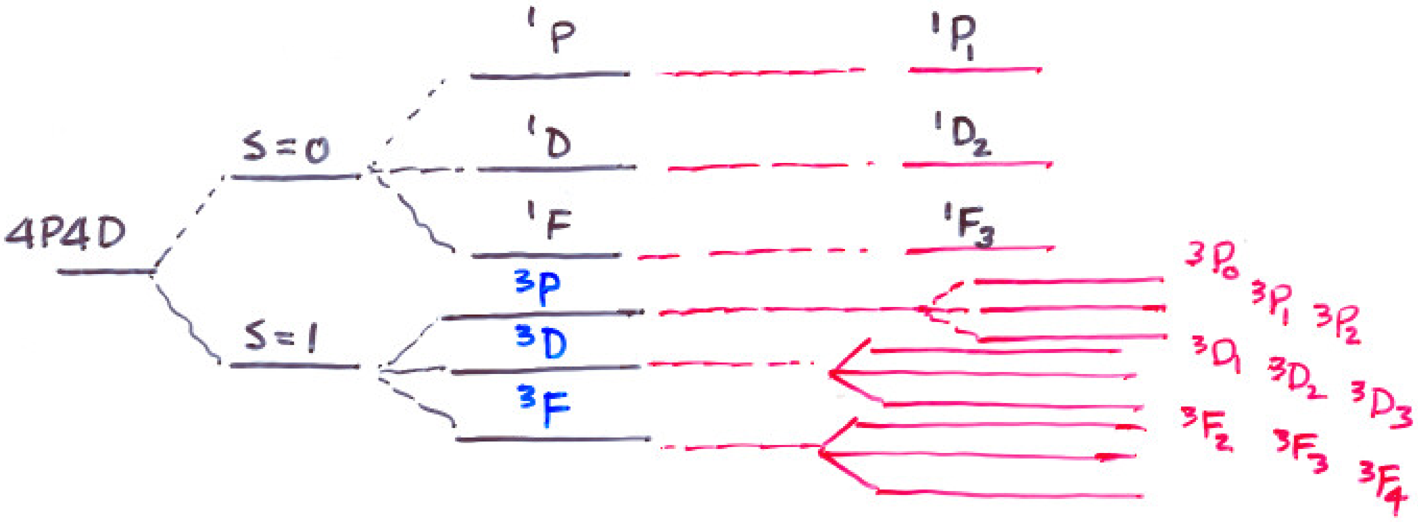
$J = L \oplus S$

$J = L \oplus 0$ and $J = L \oplus 1$

$J = L$

$J = |L-1| \dots (L+1)$

$J = L-1, L, L+1$



Back... to Helium.

the ground state $1s^2$

$L_1 = 0$ $L_2 = 0$ $\Rightarrow$ $L = 0$

$S_1 = 1/2$ $S_2 = 1/2$ $\Rightarrow$ $S = 0, 1$

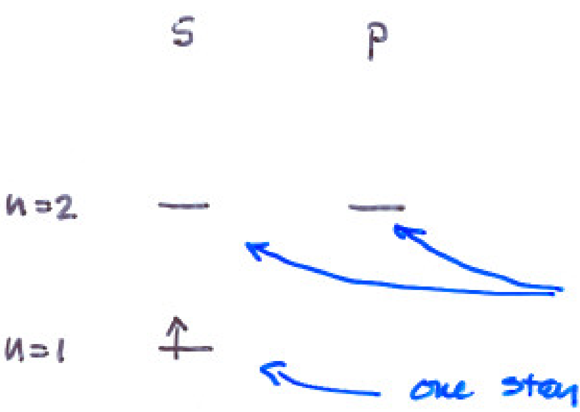
BUT! $S = 1$ $\Rightarrow$ $\uparrow\uparrow$ in same state

Forbidden by Pauli Exclusion

so: $S = 0$

$1\,{}^1S_0$ is the spectroscopic notation

Helium excited states...



the other can go to s or p

one stays home

$\boxed{1s^1 2s^1}$

$(\uparrow, \ ) \vdots (\uparrow, \ )$ or! $(\uparrow, \ ) \vdots (\downarrow, \ )$

$S = 1 \Rightarrow$ triplet
$L = 0$

$S = 0 \Rightarrow$ singlet
$L = 0$

$J = |L-S| \ldots |L+S|$
$J = 1$

$J = |L-S| \ldots |L+S|$
$J = 0$

overall state: $^3S_1$ $^1S_0$

$\boxed{1s^1 2p^1}$

$(\uparrow, \ ) \vdots (\ , \ ); (\uparrow, \ )(\ , \ )(\ , \ )$ $(\uparrow, \ ) \vdots (\ , \ ); (\downarrow, \ )(\ , \ )(\ , \ )$

$S = 1$
$L = 1$

$J = |L-S| \ldots |L+S|$
$J = 0, 1, 2$
$^3P_{0,1,2}$

$S = 0$
$L = 1$

$J = |L-S| \ldots |L+S|$
$= 1$
$^1P_1$

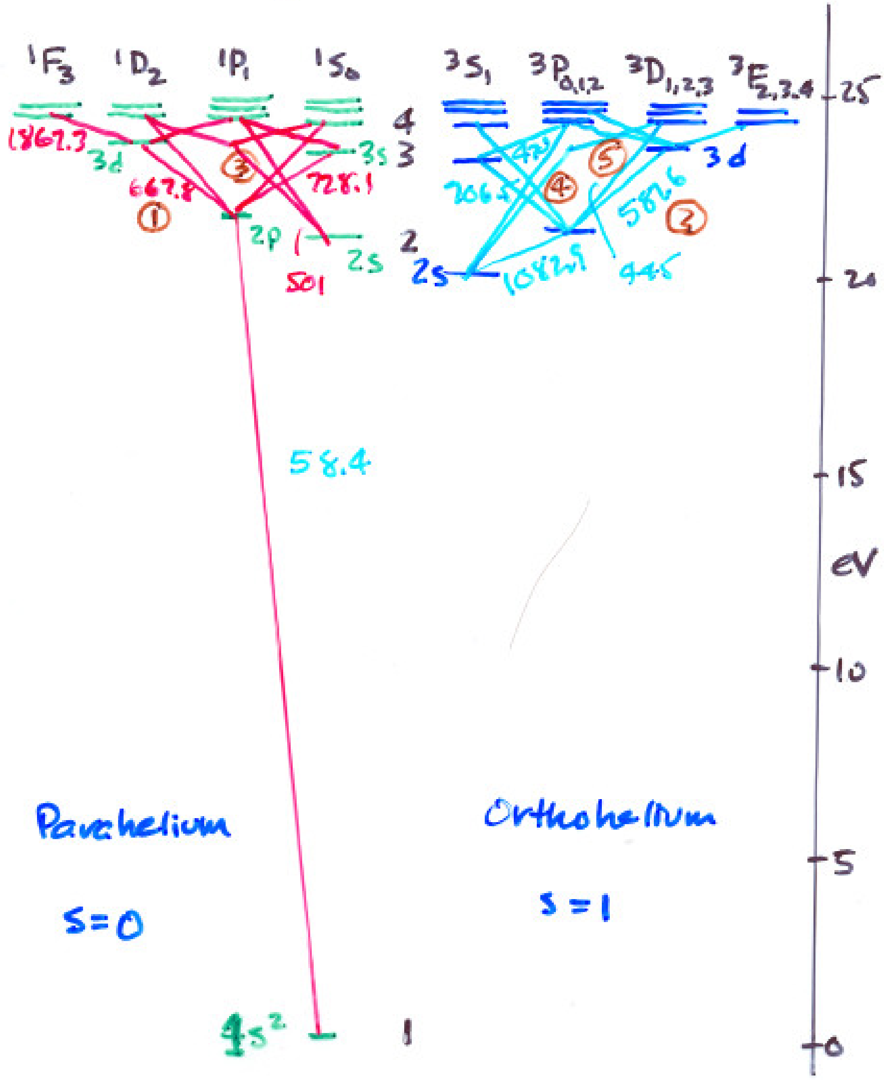
Helium was discovered in 1868 during solar eclipse --

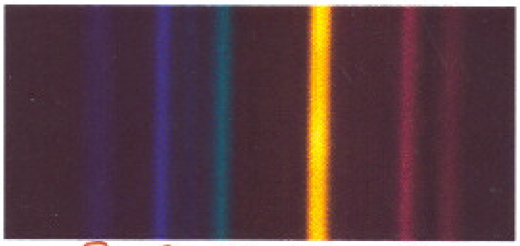
studying the spectral lines it was thought that there were 2 KINDS of helium --

orthohelium and parahelium

triplet lines singlet lines

(!)





⑤ ④ ③ ② ①

$4^3D \rightarrow 2^3P$ $3^1P \rightarrow 2^1S$ $^3D^1 \rightarrow 2^1P$,

$4^3P \rightarrow 2^3p$ $3^3D \rightarrow 2^3P$