

II. Multi electron Atoms

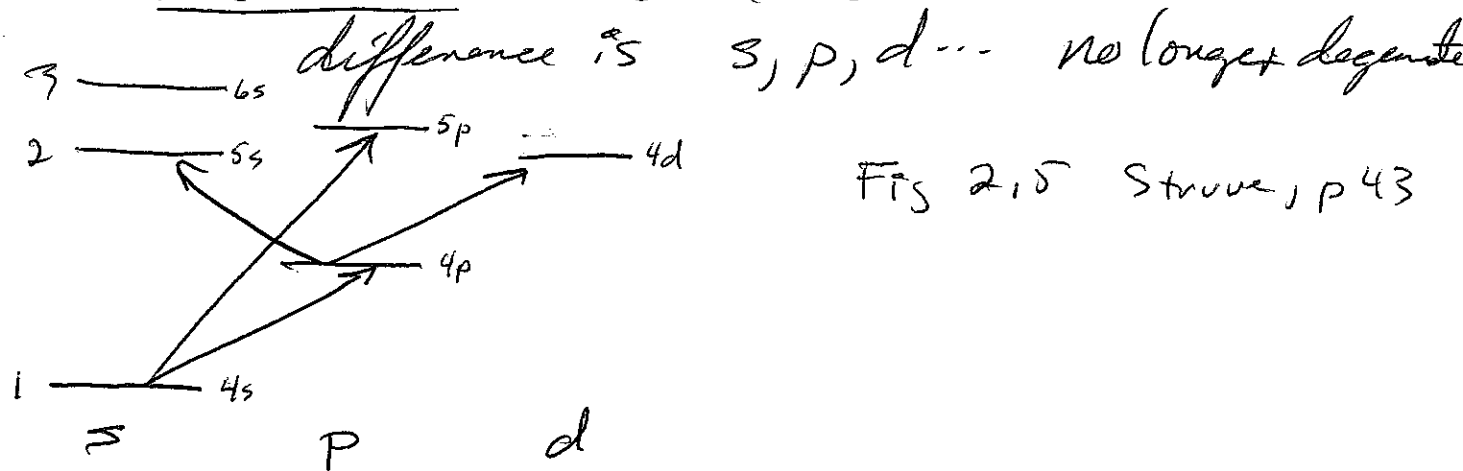
Strove Ch. 2
Levine Ch. 10, 11

Last semester did H-atom and He atom

E1 Spectra for H: $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$, $\Delta s = 0$
but for H, all l for given n are near degenerate
(except for "fine structure" constant α)

Aside Note: $2s$ state can go up to np state
but cannot go down (i.e. no $n=1, p$ state)
therefore meta stable

Alkali's - Li, Na, K, Rb, Cs are
somewhat "like" H-atom -
one elect outside core



Spin-Orbit coupling -

If look at K spectra - see splitting of lines
due to electron spin - intrinsic mag. mom,
which (if elect view as in orbit & charged) experience
magnetic field due to diamag rotation (current)

approx: $H_{so} = \frac{1}{2\mu^2 c^2 r} \frac{dV}{dr} (L \cdot S)$
 \uparrow
 $\propto m_e^2$

Note: $-V \sim -\frac{Ze^2}{r} \rightarrow$ inc atomic #, inc, H_{so}

So most important, heavy atoms
 - In general represent as a parameter

consider
now

$H = H_0 + H_{so}$

$H_{so} = A n_e (L \cdot S)$ often $L_n k$ used

where: $H_0 |nlm\rangle = E_n |nlm\rangle$

$|nlm\rangle$ eigen states of $\hat{L} \begin{cases} L_z |nlm\rangle = m\hbar |nlm\rangle \\ L^2 |nlm\rangle = l(l+1)\hbar^2 |nlm\rangle \end{cases}$

1/22/92

since electron has spin and $[L, S] = 0$
 if $H = H_0$ then $|nlm\rangle$ must be eigen state of S or - must extend descrip

$S_z |s m_s\rangle = m_s \hbar |s m_s\rangle$
 $S^2 |s m_s\rangle = s(s+1)\hbar^2 |s m_s\rangle$
 or $S_z |nlm s m_s\rangle = m_s \hbar |nlm s m_s\rangle$
 $S^2 |nlm s m_s\rangle = s(s+1)\hbar^2 |nlm s m_s\rangle$

→ These eigen states represent the uncoupled arg. mon. state eigen set of L^2, L_z, S^2, S_z - commuting op

→ But could couple arg mon $\boxed{\vec{L} + \vec{S} = \vec{J}}$ to form $|nl s j m\rangle$ states that are eigen set of:

$L^2 |nl s j m\rangle = l(l+1)\hbar^2 |nl s j m\rangle$
 $S^2 |nl s j m\rangle = s(s+1)\hbar^2 |nl s j m\rangle$
 $J^2 |nl s j m\rangle = j(j+1)\hbar^2 |nl s j m\rangle$
 $J_z |nl s j m\rangle = m\hbar |nl s j m\rangle$

so $\boxed{L^2, S^2, J^2, J_z}$ - commuting set for coupled states

Note $[H_0, J^2] = [H_0, J_z] = [H_0, L^2] = [H_0, S^2] = 0$ but $[H_0, L_z] \neq 0$
 $[H_0, S_z] \neq 0$

under these conditions $\hat{J} = \hat{L} + \hat{S}$ is a vector sum
 $J = l+s, l+s-1, \dots, |l-s|$

Expanding: $\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$
 $\hat{L} \cdot \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$ ← operator

So how does this affect energies?

Example

consider $K: 4s \rightarrow 4p$ transition
 $L=0, S=1/2, J=1/2, M=\pm 1/2$

4s:

$|40 \pm 1/2\rangle$ only states are $\pm m_J$
 but E_{nlsj} is independent of m_j
 so both same energy:

$\langle 40 \pm 1/2 | H_0 + H_{so} | 40 \pm 1/2 \rangle =$
 $E_{4s} + A_{4s} (\frac{3}{4} - 0 - \frac{3}{4})/2 = E_{4s}$

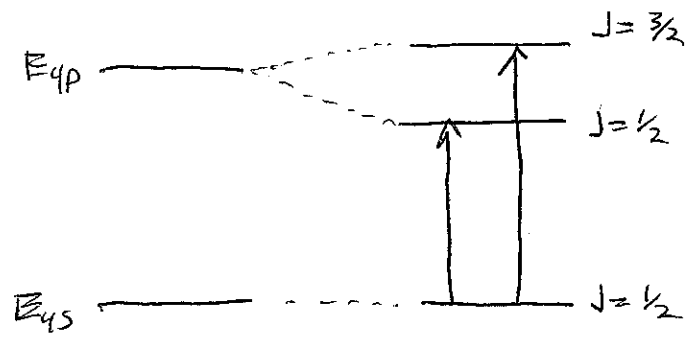
4p:

$L=1, S=1/2, J=3/2$ or $1/2$, no m dep
 of energy so clean cut

$J=3/2 \langle 41 \frac{3}{2} m | H_0 + H_{so} | 41 \frac{3}{2} m \rangle =$
 $E_{4p} + A_{4p} (\frac{15}{4} - 2 - \frac{3}{4})/2 = E_{4p} + A_{4p}/2$

$J=1/2 \langle 41 \frac{1}{2} m | H_0 + H_{so} | 41 \frac{1}{2} m \rangle =$
 $E_{4p} + A_{4p} (\frac{3}{4} - 2 - \frac{3}{4})/2 = E_{4p} - 2A_{4p}/2$

$E_{4p} - A_{4p}$



$\Delta E = 3A_{4p}/2 \rightarrow$ splitting of 4s \rightarrow 4p transition

note: degeneracy $J=3/2 = 4$
 $J=1/2 = 2$
 if add up all $E_{so} = 0$

In general see (Lande interval rule):

$$\underline{\Delta E_{J, J-1} = E_J - E_{J-1} = J A_{nl}}$$

These give rise to what are termed spin-orbit multiplets

These clusters of split transitions can be used to identify angular momentum character of state

$\Delta l = \pm 1$
 $\Delta s = 0$
select

(E) Selection rule $\Delta J = 0, \pm 1$ (except $j=0 \leftrightarrow j=0$), $\Delta m = 0, \pm 1$

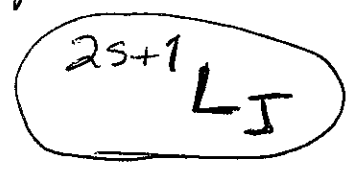
Same idea holds for multi-electron atoms where use total angular momenta:

$$\begin{aligned} \hat{L} &= \sum \hat{l}_i \\ \hat{S} &= \sum \hat{s}_i \end{aligned} \quad \left. \begin{array}{l} \text{vector sum over} \\ \text{all electrons} \end{array} \right\}$$

Note that for closed shells $\sum l_i = \sum s_i = 0$ only consider the open shells

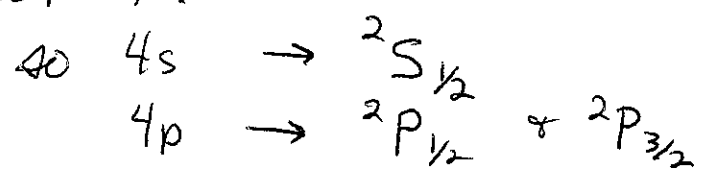
Shorthand use term symbols

$$\hat{J} = \hat{L} + \hat{S} = \sum_i \hat{J}_i$$

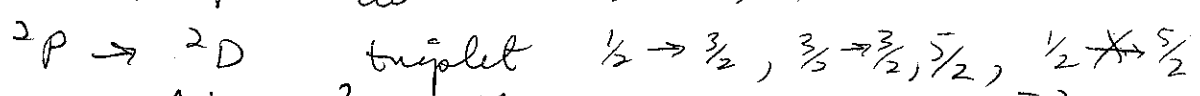
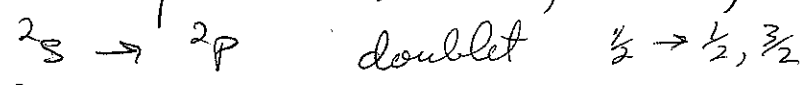


note 2S+1 - number of J values hence # lines in multiplet

eg. K ex:



Alkali spectra: $\Delta L = \pm 1, \Delta S = 0, \Delta J = 0, \pm 1, \Delta m = 0, \pm 1$



Size: Na - ³P split ~ 17 cm⁻¹; I - ⁵2P ~ 8000 cm⁻¹

Multi electron atoms

2.3 - Strove
 Chap 10.5-4 } Levine SI units?
 11.1

$$H_{\text{el}} = \sum_{i=1}^P \left(\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \underbrace{\sum_{i < j}^P \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{V_{ij}}$$

$h\phi_i = \epsilon_i \phi_i$ — soln to 1 elect
 H-like problem — know

if could ignore V_{ij}
 soln to $H_0 \psi^0 = E^0 \psi^0$

$$\psi^0 = \prod_{i=1}^P \phi_i(r_i) \quad \text{product set of H-like sets}$$

Note these soln span the space
 no real soln to $H_0 + V_{ij}$
 $\psi = \sum c_j \psi_j^0$

Problem — last semester learned that wave functions must be antisymmetric with respect to exchange of electrons

Normal method let — Slater determinant

$$\psi^0 = \frac{1}{\sqrt{P!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) & \dots & \phi_1(p)\alpha(p) \\ \phi_1(1)\beta(1) & \phi_1(2)\beta(2) & \dots & \phi_1(p)\beta(p) \\ \phi_2(1)\alpha(1) & & & \\ \vdots & & & \\ \phi_{p/2}(1)\beta(1) & & & \phi_{p/2}(p)\beta(p) \end{vmatrix}$$

P elect
 closed shell
 p-even
 all spins pair

Using $W = \langle H \rangle$ and $H = H_0 + V_{ij}$ above

$$W = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$= \sum_{i=1}^{P/2} \left[2H_{ii} + \sum_{j=1}^{P/2} (2\langle ij | ij \rangle - \langle ij | ji \rangle) \right]$$

where a) $H_{ii} = \langle \phi_i | H_i | \phi_i \rangle$ one electron core integral

b) $\langle ij | ij \rangle = \langle \phi_i(1) \phi_j(2) | V_{12} | \phi_i(1) \phi_j(2) \rangle$
2-e⁻ Coulomb Integral

c) $\langle ij | ji \rangle = \langle \phi_i(1) \phi_j(2) | V_{12} | \phi_j(1) \phi_i(2) \rangle$
2-e⁻ Exchange Integral

Note (a) — like H-like energy → shifts with n, l (from state type orb $e^{-\xi_i r_i}$, ξ_i dep on l)
→ leads to configurations $(nl)^p \dots$

(b) — like coulomb interaction of charge density
 $\phi_i(1)^* \phi_i(1) \sim$ charge density 1, same for 2

(c) — here electron charges labels — exchange
no simple classical picture

Now recall variational principle — if vary Ψ to get minimum value $\langle H \rangle$ (keep ϕ_i orthog)

$$\left\{ H_{ii} + \sum_{j=1}^{P/2} [2\langle \phi_j(2) | V_{12} | \phi_j(2) \rangle - \langle \phi_j(2) | V_{12} | \phi_i(2) \rangle] \right\} \phi_i(1) =$$

$$\left\{ H_{ii} + \sum_{j=1}^{P/2} [2J_j(1) - K_j(1)] \right\} \phi_i(1) = \sum_{j=1}^{P/2} \phi_j(1) \epsilon_{ji}$$

1/24/97
 This is central field \rightarrow equ. look like Sch. Eq. (of $E_j = E_i S_j$) and has potential of $-\frac{Ze^2}{r} + \sum_{j \neq i} \frac{e^2}{r_{ij}} - K_j$

Goal - one det & central $V(r)$: $\mathcal{H} = \sum_{i=1}^{p/2} (\frac{p^2}{2m} - Ze^2/r + V_{eff}(r))$

$$\{ H_{ii} \} \rightarrow \sum_{j=1}^{p/2} [2J_j(1) - K_j(1)] \phi_i^0(1) = \sum_{j=1}^{p/2} \phi_j^0(1) E_{ji} \quad \text{II-7}$$

Note: 1e equation \rightarrow answer deals w/ orbitals (ie w/p) but J, K for integration on all other elect

This is the Hartree-Fock equation
 *note - it is actually a 1 elect eqn (1) but the terms on left side (J - coulomb) & K - exchange integrals) are dependent on the other electrons
 E_{ji} matrix ($p/2 \times p/2$) with energy unit

Simplify $F \phi_i = \sum_j \phi_j E_{ji}$

see' has form to lead to a new linear comb of states

Note - this makes an integral eqn w/ft to get E_{ji} done (self-consistent)

Solution \rightarrow F-Fock operators depend on ϕ_i !
 initially let $E_{ji} = S_{ji} E_i$ and assume set $\{\phi_i\}$ starting set
 use these to calculate $J_j + K_j$ integrals and thereby evaluate new E_{ji} and thereby a new set $\{\phi_i\}$
 Continue until ϕ_i do not change or conversely $J_j + K_j$ constant
Self consistent Field

At the end: $E_i = H_{ii} + \sum_j (2 \langle j^0 | j^0 \rangle - \langle j^0 | i^0 \rangle)$
 and $W = \sum_{i=1}^{p/2} (H_{ii} + E_i)$
 when E_i represents the orbital energies

Result - best method of form Slater detm - norm use for radial part / Hydrogenic ϕ

Problem → What does this do? (Leone II, 1)

Central Field Approx

Assume that any electron repelled by average electron density of other electrons.

Potential $V = V(r_i)$ for each electron

But sometimes close (r_{ij} high), sometimes far → system will choose to be far → correlation electrostatic

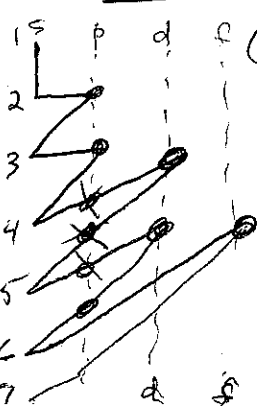
Correlation error - small fraction of total atomic energy but big compared to spectral energies

CI - configuration interaction used to correct for this —

$\Psi_{CI} = \sum c_k \Psi_k$ Ψ_k - state detn each diff basis set represent excited electron config

The coef c_k can be optimized in variational approx

Result standard Aufbau:



$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2 (3d)^{10} (4p)^6$
 $(5s)^2 (4d)^{10} (5p)^2 (6s)^2 (4f)^{14} (5d)^{10} (6p)^6$
 $(7s)^2 \dots$

- consequence of s penetrates more p etc
 - $n = l - 1 + k$ ($k = \#$ nodes)

This is neutral atom sequence (exp detn) and for ions shift a bit on d & f stab

Angular Momentum in Atoms: Struven 2.4
Lecture 11.4

for multi electron atoms, $L = \sum l_i = \sum_{\text{shells}} l_i$
 $S = \sum s_i = \sum s_j$
 some $\sum = 0$

Possible values: 2 electrons
 $|L| = l_1 + l_2, \dots, |l_1 - l_2|$
 $|S| = s_1 + s_2, \dots, |s_1 - s_2| = 1, 0$

so if 2 electrons are independent - i.e. diff l or diff n

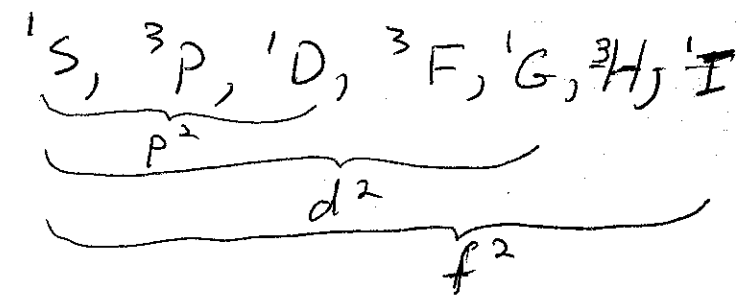
$p+p \rightarrow \begin{matrix} 1S & 1P & 1D \\ 3S & 3P & 3D \end{matrix}$
 $p+d \rightarrow \begin{matrix} 1^3P & 1^3D & 1^3F \\ \# & & \end{matrix} \quad \underline{\text{etc}}$

but if two electrons indistinguishable must account for Pauli principle

$(P)^2 = \begin{matrix} \uparrow & \uparrow & \uparrow \\ m_l & +1 & 0 & -1 \end{matrix}$ if $L=D$ then $M_L = \pm 2, \pm 1, 0$
 together ± 2 both elect must be $m_l = +1$ forbidden unless $m_{s_1} = +1/2, m_{s_2} = -1/2$
 so Max $M_S = +1/2 - 1/2 = 0$ if Max $M = 0, S = 0$

∴ longest $L \Rightarrow 1D$
 $\uparrow \quad \uparrow \quad _$
 Same: longest $S = 1$, requires $M_S = \pm 1, 0$
 Max L this way
3P

In general for 2 electrons
 $L = 2l, 2l-1, \dots, 0$ } alternate, max $L \rightarrow S=0$
 $S = 1, 0$



Slater diagram — count # ways these can result:

$M_L \backslash M_S$	+1	0	-1
+2		1	
+1	1	2	1
0	2	3	1
-1	1	2	1
-2		1	

$(1^+ 0^-), (0^+ 1^-) \Rightarrow M_L=0, M_S=0$
 $(0^+ 0^-), (1^+ -1^-), (1^- -1^+) = 0, 0$

note right half & bottom half must be same - sym

Now count:
 $^1D \rightarrow 5 \text{ states } M_S=0$
 $^3P \rightarrow 3 \text{ states } M_S = \pm 1, 0$
 $^1S \rightarrow 1 \text{ state } M_S=0$ (1) \rightarrow balance!

Method can now be expanded, ~~these must~~ keep track of # of states "micro states" $(m_{l_1}^{\pm}, m_{l_2}^{\pm}, \dots, m_{l_n}^{\pm})$ # = $\frac{[2(2l+1)][2(2l+1-1)] \dots [2(2l+1-n)]}{n!}$
 $2 = 2 \cdot 5/2 = 15$

L,S states $\sum_{L,S} (2L+1)(2S+1) = ^1D + ^3P + ^1S = 5 + 9 + 1 = 15$
 $\sum_J (2J+1) = ^1D_2 + ^3P_0 + ^3P_1 + ^3P_2 + ^1S_0 = 5 + 1 + 3 + 5 + 1$

Note - next simplest are almost full config holes behave like electrons:

$$p^4 \sim p^2 \rightarrow {}^1D_2, {}^3P_{0,1,2}, {}^1S_0$$

$$p^5, d^1 \rightarrow {}^1D_2, {}^3P_{0,1,2}, {}^1S_0$$

$$d^8 \rightarrow {}^1G_4, {}^3F_{2,3,4}, {}^1D_2, {}^3P_{0,1,2}, {}^1S_0$$

Now how about 3 electrons \rightarrow
 f^3 example:

Max M_L	$\uparrow\downarrow$	\uparrow	—	M_L	+3	0	0
					+2	0	1
Max M_S	\uparrow	\uparrow	\uparrow		+1	0	1+1
					0	1	2+1

$2D$	$\left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array} \right)$	$2P$	$\left(\begin{array}{c} \\ \\ \end{array} \right)$
$4S$	$\left(\begin{array}{c} \\ \\ \end{array} \right)$	$2S$	$\left(\begin{array}{c} \\ \end{array} \right)$

$(1+1-0+)$
 $(1+0-0+)$
 $(1+0-1+)(1+0+1-)$
 $(1-0+1+)$

must explore all combinations

Test:

$$\sum (2L+1)(2S+1) = 2(5) + 2(3) + 4(1) = 20$$

$$6 \cdot 5 \cdot 4 / 3 \cdot 2 \cdot 1 = 20 \quad \text{agrees}$$

$$\sum (2J+1) = \left(\frac{5}{2} + 4 \right) + \left(\frac{4}{2} + 2 \right) + \frac{4}{2} = 20$$

1/27/92 - Have now developed picture of possible terms \rightarrow how do these fit with observed spectra? E -levels?

How about spectra?

Selection $\rightarrow \Delta L = \pm 1$ for $(1e^-)$ change state
 $\Delta L = 0, \pm 1; \Delta S = 0; \Delta J = 0, \pm 1$
 $\Delta L = 0 \rightarrow L=0$ $\Delta S = 0 \rightarrow S=0$

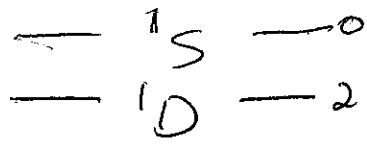
Hand's rules - max S - lowest

Simple rules of avoidance of change

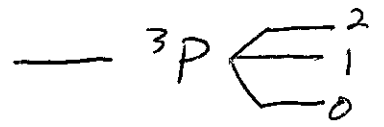
$2S_{max} + 1$ L: Max L among those w/ max S - lowest

< half filled - then $2S_{max} + 1$ L_{max} small J lowest
 > half filled - " " " high J lowest

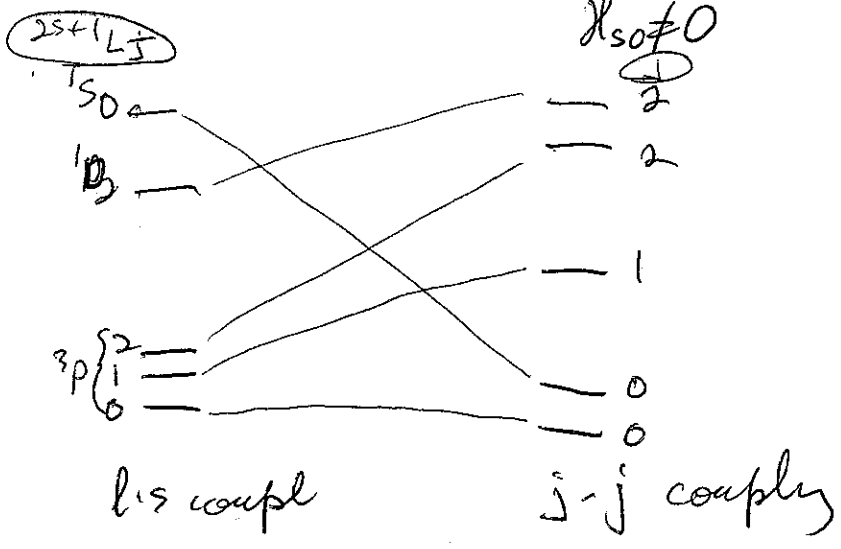
for p^2 :



Transitions Note $\Delta S = 0$ } all forbidden
 $\Delta L = \pm 1$



if S.O. large then $\Delta S = 0$ relaxes
 $\Delta S = 0, \pm 1$ operates



Caradon correlation diagram between 2 coupling regimes
 $l_1 + s_1 = j_1$
 $l_2 + s_2 = j_2$
 $J = j_1 + j_2$

Note - J values # terms + levels must be the same in both

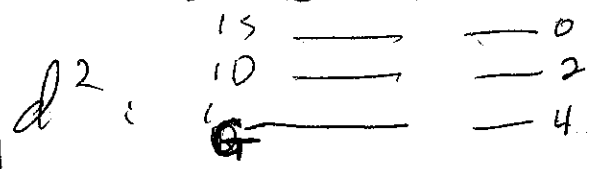
- Identity of L, S is varying w/ A.L.S (i.e. L, S not always good q.n., although L, S)

- must account for Pauli again i.e. $J = 1/2, 3/2$ for p-electron

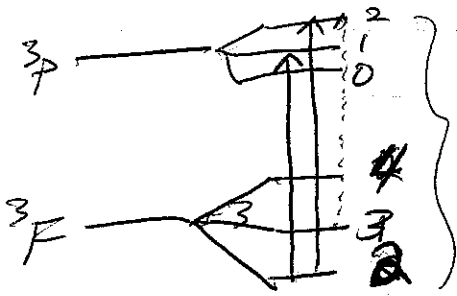
2p elect $3/2 + 3/2 = 3 \leftrightarrow 3/2 - 3/2 = 0$ but $J = 3 \Rightarrow$ best pos $J_1 + J_2 = 3/2$

In general - light atoms →
Russel Saunders LS coupling best

Then also $\Delta S = 0$ pretty good selection rule



drop

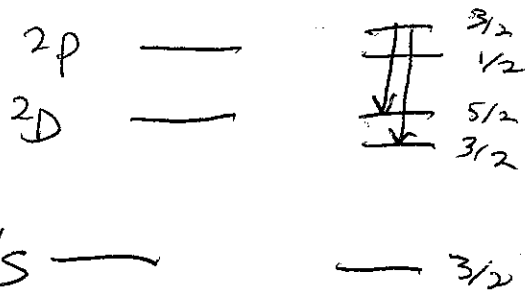


here $\Delta L \neq \pm 1$
 ${}^3F_2 \rightarrow {}^3P_1, {}^3P_2$

only if
 S.L. big

and in excited
 ${}^1S_0 \rightarrow {}^1D_2, {}^1G_4$
 ${}^1S_0 \rightarrow {}^3P_{0,1}$ if high S.L.

but P³



$\Delta S \neq 0$
 $4s \rightarrow 2p, 2D$

$2P_{3/2} \rightarrow 2D_{5/2, 3/2}$
oh

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

Zeeman Effect

Placing an atom in a magnetic field lowers the degeneracy by imparting a perturbation:

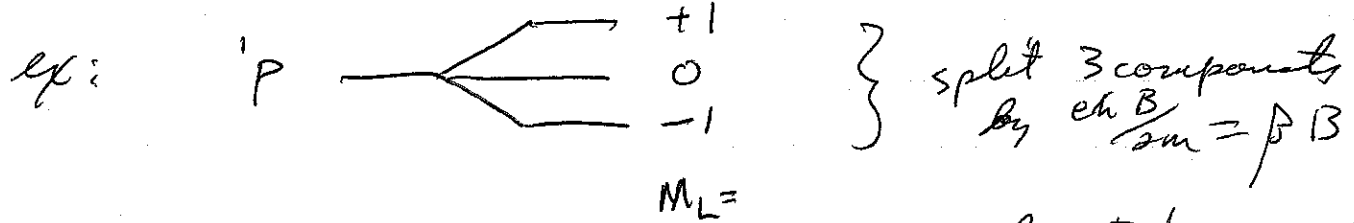
$$W = -\mu_m \cdot B = \frac{e}{2me} (L + gS) B$$

so if $\vec{B} = B_z \hat{z}$

$$W = \frac{B_z e}{2me} \langle L M_L S M_S | L + gS | L M_L S M_S \rangle$$

if choose $S=0$ for ex: 1P

$W = \frac{Be\hbar}{2me} M_L$ Energy vary w/ M



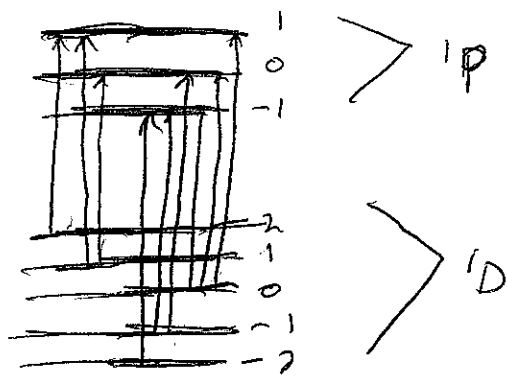
$\beta = \frac{e\hbar}{2m} \mu_B$
 $= \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T}$

$B=0$ $B \neq 0$

Now $\Delta M = 0, \pm 1$
 selection rule becomes operative

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 8000 \text{ cm}^{-1}$
 $J \approx 5 \times 10^{22} \text{ cm}^{-1}$
 $\beta \approx 0.46 \text{ cm}^{-1}/T$
 recall $1T = 10^4 G$

Struve p 67:
 "normal Zeeman"



no split

if have $S \neq 0$ a bit more complex

$W = -\mu_B B = \frac{e\hbar}{4m} (L_z + 2S_z) B_z$

now can show that for given J state

$W = -\mu_J \cdot B$

$\mu_J = \frac{e\hbar}{4m} (L + 2S) \cdot J / J^2$

simplify μ_J and using $g_s = 2$

$\mu_J = -\frac{\beta}{g} g_J \hat{J}$

can show in book

where

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

and

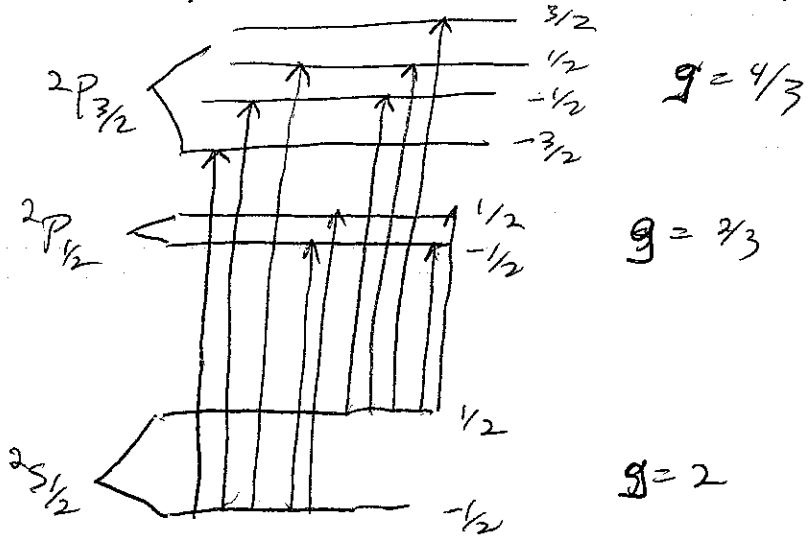
$$W = -\mu_B B$$

$$W = g_J \beta B_z M_J$$

see g_J dep on L, S

anomalous Zeeman effect because splitting modified by spin

Sturwe p 71



$$\Delta S = 0$$

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

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

See that pattern gives one a way of identifying the states - each term-level has a different g -value