Read CTDL, pp. 1156-1178

LAST TIME: $\mathbf{H}^{SO} = \sum_i a(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \quad \rightarrow \zeta(N,L,S)\mathbf{L}\cdot\mathbf{S}$ (one ζ for each L - S term)

$\rightarrow \sum_i \zeta_{n\ell}\boldsymbol{\ell}_i \cdot \mathbf{s}_i$ (one ζ for entire configuration)

Landé interval rule (assignment!)

$\zeta(N,L,S) \leftrightarrow \zeta_{n\ell}$ examples

evaluate matrix elements in Slater determinantal basis and in many-e^- $|NJLSM_J\rangle$ or $|NLM_LSM_S\rangle$ basis

$\left[\begin{array}{l}\text{off - diagonal } (\Delta J = 0) \text{ intraconfigurational } \mathbf{H}^{SO} \text{ matrix elements:}\\ e.g. \ \left\langle {}^1I_6 \middle| \mathbf{H}^{SO} \middle| {}^3H_6 \right\rangle = ? \ \text{ See notes [page 35 - 9]!}\end{array}\right.$

TODAY:

1. electrons vs. holes—a shortcut: e^2/r_{ij} vs. $\mathbf{H}^{SO}$ (holes are a convenience in spectra of isolated atoms and molecules, but they are an essential part of the interpretive picture for solids)
2. Hund's 3rd rule
3. Zeeman effect: Landé g-factor formula via W-E Theorem (done previously by projection theorem)
4. Matrix elements of $\mathbf{H}^{\text{Zeeman}}$ in Slater determinantal basis set. No difference between electron and hole as far as Zeeman effect is concerned.

NEXT TIME: e^- in solids
(CTDL, pages 1156-1168)

1. relationship between configurations with N e^- vs. N "holes"

subshell	$(n\ell)^N$			
1/2 full subshell	s	p	d	f
# e^-	1	3	5	7

for p^5 is it necessary to consider all 5 e^-?

e.g. $\|1\alpha 1\beta 0\alpha 0\beta -1\alpha\| = |np^5\ {}^2P\ \ M_L = 1, M_S = 1/2\rangle$
($\pm 1\beta$ is the unoccupied spin-orbital. It is the "hole")

$$\mathbf{H}^{SO}|np^5\ {}^2P\ \ M_L = 1, M_S = 1/2\rangle = \zeta_{np}\sum_i \boldsymbol{\ell}_{iz}\mathbf{s}_{iz}\|1\alpha 1\beta 0\alpha 0\beta -1\alpha\|$$

$$= \hbar^2\zeta_{np}\left[\left(\frac{1}{2}-\frac{1}{2}\right)+(0-0)-\frac{1}{2}\right]\|5e^-\|$$

so expectation value of $\mathbf{H}^{SO}$: $\langle\|5e^-\|\rangle = -\frac{1}{2}\zeta_{np}\hbar^2$

but for single e^- (with the *same* M_L, M_S as the five e^-)

$$\mathbf{H}^{SO}|np^1\ {}^2P\ \ M_L = 1, M_S = 1/2\rangle = \zeta_{np}\boldsymbol{\ell}_z\mathbf{s}_z\|1\alpha\|$$

$$\langle\|1e^-\|\rangle = +\frac{1}{2}\zeta_{np}\hbar^2$$

is the sign flip just a coincidence? NO!

TRICK: Hole is exactly equivalent to e^- (for identical LM_LSM_S or $JLSM_J$) except that the sign of its charge is reversed.

* no effect on e^2/r_{ij} because 2 interacting particles have charge of the same sign (either both e^- or both hole), so e^2/r_{ij} is always a <u>repulsive interaction</u>. [What happens for $f^{13}p$? Certainly different from fp!]

* reverse sign for $\mathbf{H}^{SO}$ because $\mathbf{H}^{SO}$ is a relativistic electrostatic interaction between e^- and nucleus (+ charge). Replacing e^- by h^+ and leaving the sign on the nucleus the same reverses the sign of $\mathbf{H}^{SO}$!

$$
\begin{array}{lll}
p^1 \leftrightarrow p^5 & d^1 \leftrightarrow d^9 & \text{etc.} \\
p^2 \leftrightarrow p^4 & d^2 \leftrightarrow d^8 & \\
 & d^3 \leftrightarrow d^7 & \\
 & d^4 \leftrightarrow d^6 &
\end{array}
$$

pretend that holes are e^-, Slater determinants describe spin-orbitals occupied by holes.

* all F_k, G_k, $\zeta_{n\ell}$ remain positive (repulsions)

* all e^2/r_{ij} energy level patterns are unaffected

* <u>all</u> $\zeta(N,L,S)$ reverse sign

Look at Tinkham 6-2, page 187 figure.

ζ_{nd} vs. $\zeta(N,L,S)$ for lowest L-S term of $(3d)^N$ configuration

sign change, too rapid evolution with Z

$\propto Z_{eff}^3$ – periodicity, isoelectronic series, aufbau too

INSIGHT — regularization of trends
EXTRAPOLATION
ASSIGNMENT
LABOR SAVING!

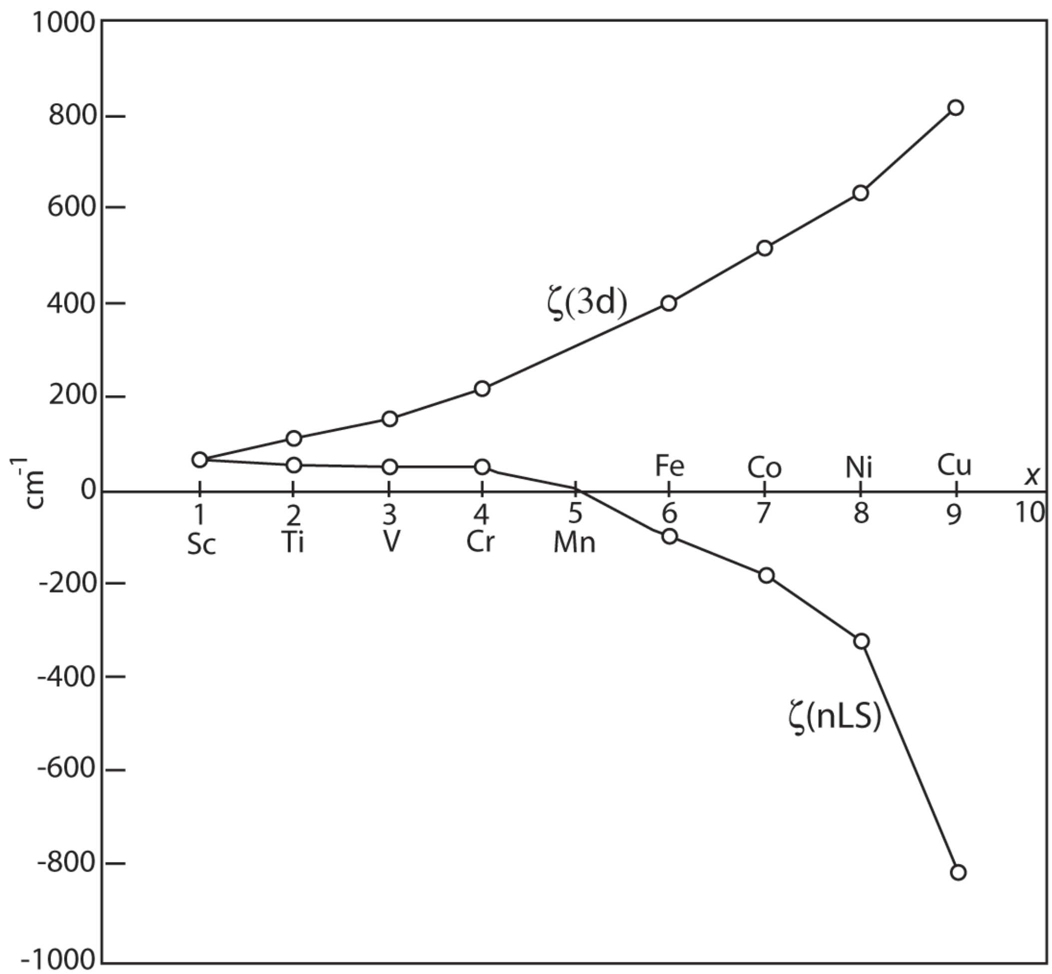
Shielding systematics: $Z \varnothing Z + 1$

$Z_{eff} \varnothing Z_{eff} + 1 - 0.5$

:

shielding

Burns' Rules. G. Burns, J. C. P. **41**, 1561 (1964).



Spin-orbit parameters in $3d^x$ transition elements. The splitting parameters z(LS) are averaged over the various splittings. The data used are for the $3d^x4s^2$ configurations of the neutral atoms. (Adapted from Charlotte E. Moore, "Atomic Energy Levels," Natl. Bur. Standards, Circ. 467, vols. I and II, 1949 and 1952. A very similar figure appears in Condon and Shortley.)

2. Hund's Third Rule

Consider only MAX-S, MAX-L L-S term, which Hund's 1st and 2nd rules identify as the lowest lying within the $(n\ell)^N$ configuration

This L-S term will always be a single Slater determinant for the $M_L = L_{MAX}$, $M_S = S_{MAX}$ component

$$\left|L_{MAX},\ M_L = L_{MAX},\ S_{MAX},\ M_S = S_{MAX}\right\rangle = \left\|\ell\alpha(\ell-1)\alpha\ldots\right\|$$

(as many α spins as possible)

diagonal element of $\mathbf{H}^{SO}$

$$\zeta\left((n\ell)^N, L_{MAX},\ S_{MAX}\right)\overset{M_L}{L_{MAX}}\overset{M_S}{S_{MAX}} = \zeta_{n\ell}\sum_i m_{\ell_i} m_{s_i}$$

$$\zeta\left((n\ell)^N, L_{MAX},\ S_{MAX}\right) = \zeta_{n\ell}\frac{\Sigma m_{\ell_i} m_{s_i}}{L_{MAX}S_{MAX}}$$

S_{MAX}? shell less than 1/2 full, $N < 2\ell+1$, all spins are α

$\therefore S = N/2$

L_{MAX}? if all spins are α, maximize M_L by putting $1e^-$ into each m_ℓ starting at $m_\ell = \ell$ and working downward.

$$M_{L_{MAX}} = \underbrace{\ell + (\ell-1) + \ldots(\ell - N + 1)}_{\substack{\text{N terms in sum} \\ \text{get } \ell \text{ from each term in sum}}} = N\left[\ell - (N-1)/2\right]$$

$$\zeta\left(n\ell^N\ \ L_{MAX},\ S_{MAX}\right) = \zeta_{n\ell}\frac{\overbrace{\tfrac{1}{2}}^{\text{all spins }\alpha}\Sigma m_{\ell_i}}{L_{MAX}\underbrace{(N/2)}_{S_{MAX}}} = \zeta_{n\ell}\frac{\tfrac{1}{2}\overbrace{M_L}^{L_{MAX}}}{L_{MAX}(N/2)}$$

$$\boxed{= \zeta_{n\ell}/N \quad \text{WHICH IMPLIES} \quad \zeta_{n\ell}/2S_{MAX}}\ !$$

Shell 1/2 full $\quad N = 2\ell + 1$, all spins α, $\sum_i m_{\ell_i} = 0$

$S = N/2,\ L = 0$

lowest L-S term is ${}^{2S+1}L_J = {}^{N+1}S_{N/2}$

(single J for all L = 0 terms) - no fine structure

Shell more than 1/2 full

S_{MAX}? $\quad 2\ell + 1\ \alpha$ spins

$N - (2\ell + 1)\ \beta$ spins

$$M_S = \frac{1}{2}\left[(2\ell+1) - \left[N - (2\ell+1)\right]\right] = 2\ell + 1 - N/2$$

$$S_{MAX} = 2\ell + 1 - N/2$$

L_{MAX}? $\quad$ for the $2\ell + 1\ \alpha$ spins $\sum m_{\ell_i} = 0$

for the $N - (2\ell+1)\ \beta$ spins,

$$\sum m_{\ell_i} = \ell + (\ell - 1) + \ldots = M_L = L_{MAX}$$

$$\zeta(n\ell^N L_{MAX},\ S_{MAX}) = \frac{\zeta_{n\ell}\left[\frac{1}{2}\overbrace{\left(\sum_{(\alpha)} m_{\ell_i}\right)}^{0\ \alpha\text{ spins}} - \frac{1}{2}\overbrace{\left(\sum_{(\beta)} m_{\ell_i}\right)}^{L_{MAX}\ \beta\text{ spins}}\right]}{L_{MAX} S_{MAX}}$$

$$= \frac{\zeta_{n\ell}(-1/2)L_{MAX}}{L_{MAX}\left[(2\ell+1) - N/2\right]} = \frac{-\zeta_{n\ell}}{\underbrace{2(2\ell+1) - N}_{\#\text{ of holes}}}$$

$$= \boxed{-\frac{\zeta_{n\ell}}{2\ S_{MAX}}}\ !$$

Summary for lowest energy L-S term:

** $\quad \zeta(n\ell^N, L_{MAX}, S_{MAX})$ > 0 for less than 1/2 full, $= 0$ for 1/2 full, < 0 for more than 1/2 full

** $\quad \zeta(n\ell^N, L_{MAX}, S_{MAX}) = \pm \dfrac{\zeta_{n\ell}}{\left\{\begin{matrix}\#\ \text{of } e^-\\ \#\ \text{of } h^+\end{matrix}\right\}}$

Hund's third rule: ONLY FOR LOWEST ENERGY L-S term, lowest J component is

$$
\begin{array}{lll}
J = |L-S| \ \text{for} & N < 2\ell+1 & \text{“regular”} \\
\text{J} = \text{S} & \text{N} = 2\ell+1 & \text{no fine structure} \\
\text{J} = \text{L}+\text{S} & \text{N} > 2\ell+1 & \text{“inverted”}
\end{array}
$$

Assignments:
- sign of ζ(NLS)
- # of J components
- extreme J values (recognize via interval rule)
- magnitude of $\zeta_{n\ell}$
- # of M_J components
- Zeeman tuning rates

---

3. Zeeman effect in many-e⁻ atoms

$$\mathbf{H}^{\text{Zeeman}} = -(\mu_0/\hbar)(\mathbf{L}_z + 2\mathbf{S}_z)B_z$$

1.399613 MHz/Gauss
Bohr magneton
(Used γ previously)

remember that $\mathbf{H}^{\text{Zeeman}}$ is awkward in $|\text{JM}_\text{J}\text{LS}\rangle$ basis set

W–E Theorem trick to simplify $\mathbf{H}^{\text{Zeeman}}$:
consider only matrix elements diagonal in J [There are also nonzero matrix elements of H^{Zeeman} off-diagonal in J.]

[$\mathbf{H}^{\text{SO}}$ and e^2/r_{ij} are strictly diagonal in J. Since $\mathbf{H}^{\text{Zeeman}}$ has sum of 2 vectors with respect to $\mathbf{J}$, W - E Theorem says it can have $\Delta J = 0, \pm 1$ matrix elements. When we evaluated matrix elements of $\mathbf{L}_z$ and $\mathbf{S}_z$ in $|\text{JM}_\text{J}\text{LS}\rangle$ the hard way, we saw that there were nonzero $\Delta J = \pm 1$ matrix elements.]

Our special case $\Delta J = 0$ is useful as long as

$$\underbrace{\left\langle J'\middle|\mathbf{H}^{\text{Zeeman}}\middle|J\right\rangle}_{\propto \text{B}_z} << \left|E_{J'}^{(0)} - E_J^{(0)}\right|$$

(This fails at high B_z when ζ(nLS) is small.)

for $\Delta J = 0$ matrix elements, replace both $\mathbf{L}_z$ and $\mathbf{S}_z$ by $\mathbf{J}_z$

$$\langle JM'LS|\mathbf{L}|JMLS\rangle = \langle JLS\|\mathbf{L}\|JLS\rangle\langle JM'LS|\mathbf{J}|JMLS\rangle$$

$$\langle JM'LS|\mathbf{S}|JMLS\rangle = \langle JLS\|\mathbf{S}\|JLS\rangle\langle JM'LS|\mathbf{J}|JMLS\rangle$$

but $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Add the 2 equations

$$\langle\ |\mathbf{J}|\ \rangle = \underbrace{\Big(\underset{(1-\alpha)}{\langle\ \|\mathbf{L}\|\ \rangle} + \underset{(\alpha)}{\langle\ \|\mathbf{S}\|\ \rangle}\Big)}_{=1}\langle\ |\mathbf{J}|\ \rangle$$

[This trick is equivalent to, but not as elegant as, the projection Theorem.]

$$\mathbf{H}^{\text{Zeeman}} = \frac{-\mu_0}{\hbar}\Bigg[\underbrace{(1-\alpha)\mathbf{J}_z}_{\substack{L_z\\ \text{part}}} + \underbrace{2\alpha\mathbf{J}_z}_{\substack{2S_z\\ \text{part}}}\Bigg]B_z = \frac{-\mu_0}{\hbar}B_z(1+\alpha)\mathbf{J}_z!$$

Trick to evaluate α:

$\mathbf{L}^2 = (\mathbf{J}-\mathbf{S})^2 = \mathbf{J}^2 + \mathbf{S}^2 - 2\mathbf{J}\cdot\mathbf{S}$

diagonal $|\mathrm{JM_J LS}\rangle$ matrix element of both sides

$$\hbar^2\mathrm{L(L+1)} = \hbar^2\mathrm{J(J+1)} + \hbar^2\mathrm{S(S+1)} - 2\langle\mathrm{JMLS}|\mathbf{J}\cdot\mathbf{S}|\mathrm{JMLS}\rangle \quad **$$

$$\Downarrow$$

completeness: $\mathbf{J}$ has $\Delta\mathrm{J} = 0$ selection rule, $\mathbf{L}$ has $\Delta\mathrm{L} = 0$, $\mathbf{S}$ has $\Delta\mathrm{S} = 0$, $\mathbf{J}\cdot\mathbf{S}$ is scalar with respect to $\mathbf{J}$, $\Delta\mathrm{M} = 0$

$$\begin{aligned}\langle JMLS|\mathbf{J}\cdot\mathbf{S}|JMLS\rangle &= \sum_{J'M'L'S'}\langle JMLS|\mathbf{J}|J'M'L'S'\rangle\langle J'M'L'S'|\mathbf{S}|JMLS\rangle\\ &= \langle JMLS|\mathbf{J}|JMLS\rangle\underbrace{\langle JMLS|\mathbf{S}|JMLS\rangle}_{\alpha\mathbf{J}}\\ &= \alpha\langle JMLS|\mathbf{J}^2|JMLS\rangle = \alpha J(J+1)\hbar^2\end{aligned}$$

Plug this into the $**$ equation above and rearrange:

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

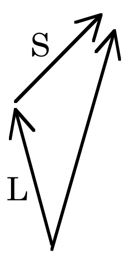
$$\langle \mathbf{H}^{\text{Zeeman}} \rangle = -\mu_0 B_z M_J \left[\overbrace{(1-\alpha)}^{\substack{\text{from} \\ \mathbf{L}_z}} + \overbrace{2\alpha}^{\substack{\text{from} \\ 2\mathbf{S}_z}} \right]$$

$$= -\mu_0 B_z M_J \underbrace{[1+\alpha]}_{g_J}$$

Landé g-value

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

* g_J is Zeeman tuning coefficient $= -\frac{1}{\mu_0}\frac{dE}{dB_z}\frac{1}{M_J} = g_J$
* equally spaced M_J components
* excellent diagnostic for different L,S of same J



g_J is large when $\vec{L}$ and $\vec{S}$ are parallel (i.e. since $J = L + S$, parallel $\vec{L},\vec{S}$ at constant J means smallest possible L in order to have largest possible S)

g_J small when $\vec{L},\vec{S}$ are antiparallel

e.g. $J = 3$:	$L = 0, S = 3$	$L = 1, S = 2$	$L = 2, S = 1$	$L = 3, S = 0$
g_J	2.000	1.667	1.333	1.000
$L = 3, S = 1$:	$J = 4$ (parallel)	J = 3	J = 2 (antiparallel)	
	1.250	1.1667	0.667	

* g_J decreases at constant J when S is replaced by L.
* g_J decreases at constant L and S as J decreases from L+S to |L–S|.

How to determine J:

* apply B-field and count M_J components
  (constant splittings in upper and in lower L-S term)

* measure g_J (Quantum Beats)

* polarization dependent Zeeman splitting pattern: $\Delta M_J = 0$ for z polarized, $\Delta M_J = \pm 1$ for x or y polarized, $\Delta M_J = +1$ or -1 for circularly polarized

Compare direct evaluation of Zeeman matrix element to g_J determined independently.

<u>Matrix Elements of $\mathbf{H}^{\text{Zeeman}}$ in Slater determinantal basis set</u>?

e.g. $\left|f^2\ {}^3H_6 \quad M_J = 6\right\rangle = \|3\alpha 2\alpha\|$

$$\mathbf{H}^{\text{Zeeman}} = -(\mu_0/\hbar)B_z \sum_i \left(\boldsymbol{\ell}_{iz} + 2\mathbf{s}_{iz}\right)$$

$$\left\langle \|3\alpha 2\alpha\| \middle| \mathbf{H}^{\text{Zeeman}} \middle| \|3\alpha 2\alpha\| \right\rangle = -(\mu_0 B_z)[(3+1)+(2+1)]$$

$$= -7\mu_0 B_z$$

Now compare with g_J equation:

$$\left\langle {}^3H_6\ 6 \middle| \mathbf{H}^{\text{Zeeman}} \middle| {}^3H_6\ 6 \right\rangle = -(\mu_0 B_z) g_J M_J$$

$$g_J = 1 + \frac{6\cdot 7 + 1\cdot 2 - 5\cdot 6}{2\cdot 6\cdot 7} = 1 + \frac{1}{6} = \frac{7}{6}$$

$$\langle \quad \rangle = -(\mu_0 B_z)\frac{7}{6}6 = -7\mu_0 B_0 \qquad \text{agrees!}$$

Hole vs. e^- for Zeeman effect.

What about a single hole state? Does Zeeman effect reverse sign?

$$\left.\begin{array}{l} \left|f^{13}\ {}^2F_{7/2}\ \ 7/2\right\rangle = \|3\alpha \ldots -3\alpha 3\beta \ldots -2\beta\| \\ \left|f^{1}\ {}^2F_{7/2}\ \ 7/2\right\rangle = \|3\alpha\| \end{array}\right\} \text{same } M_L, M_S$$

$$\mathbf{E}^{\text{Zeeman}}\left(f^{13}\ {}^2F_{7/2}\ \ 7/2\right) = -\left(\mu_0 B_z\right)\Big[\underset{\substack{\alpha\text{-spins} \\ 7e^-}}{(0+7)} + \underset{\substack{\beta\text{-spins} \\ 6e^-}}{(3-6)}\Big]$$

$$= -4\mu_0 B_z$$

$$\mathbf{E}^{\text{Zeeman}}\left(f^{1}\ {}^2F_{7/2}\ \ 7/2\right) = -\left(\mu_0 B_z\right)[3+1] = -4\mu_0 B_z$$

$$\text{same as } f^{13}$$

no sign change for Zeeman for e^- vs. h^+. WHY?