5.73 Lecture #36

Read CTDL, pp. 1156-1178

LAST TIME: \[ H^{SO} = \sum_i a(r_i)\ell_i \cdot s_i \rightarrow \zeta(N, L, S) L \cdot S \] (one \(\zeta\) for each L - S term)

\[ \rightarrow \sum_i \zeta_{nl} \ell_i \cdot s_i \] (one \(\zeta\) for entire configuration)

Landé interval rule (assignment!)

\[ \zeta(N, L, S) \leftrightarrow \zeta_{nl} \] examples

evaluate matrix elements in Slater determinantal basis and in many-e- |NJLSM\rangle or |NLMLSMS\rangle basis

\[ \begin{bmatrix} \text{off - diagonal (}\Delta J = 0)\text{ intraconfigurational } H^{SO}\text{ matrix elements:} \\
\end{bmatrix} \]

\[ \text{e.g. } \langle 1 I_0 | H^{SO} | H_0 \rangle = ? \text{ See notes [page 35 - 9]!} \]

TODAY: 1. electrons vs. holes—a shortcut: \( e^2/r_{ij} \) vs. \( H^{SO} \)
(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 \( H^{Zeeman} \) 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\textsuperscript{−} vs. N “holes"

<table>
<thead>
<tr>
<th>subshell</th>
<th>((n\ell)^N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 full subshell</td>
<td>s   p   d   f</td>
</tr>
<tr>
<td># e\textsuperscript{−}</td>
<td>1   3   5   7</td>
</tr>
</tbody>
</table>

for \(p^5\) is it necessary to consider all 5 e\textsuperscript{−}? 

e.g. \(\lVert l\alpha l\beta 0\alpha 0\beta - 1\alpha \rVert = \lvert np^5 2P M_L = 1, M_S = 1/2 \rvert(\pm 1\beta \text{ is the unoccupied spin-orbital. It is the "hole"})

\[
H^{SO}\lvert np^5 2P M_L = 1, M_S = 1/2 \rangle = \zeta_{np} \sum_i \ell_{iz-iz} \lVert l\alpha l\beta 0\alpha 0\beta - 1\alpha \rVert 
\]

\[
= \hbar^2 \zeta_{np} \left[ \frac{1}{2} + \frac{1}{2} \right] = \frac{1}{2} \zeta_{np} \hbar^2 
\]

so expectation value of \(H^{SO}\): 

\[
\langle 5e^- \rangle = -\frac{1}{2} \zeta_{np} \hbar^2 
\]

but for single e\textsuperscript{−} (with the same \(M_L, M_S\) as the five e\textsuperscript{−}) 

\[
H^{SO}\lvert np^1 2P M_L = 1, M_S = 1/2 \rangle = \zeta_{np} \ell_{z-\ell} \lVert l\alpha \rVert 
\]

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

is the sign flip just a coincidence? NO!

TRICK: Hole is exactly equivalent to e\textsuperscript{−} (for identical \(LM_L, SM_S\) or \(JLJ_m\)) 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\textsuperscript{−} or both hole), so \(e^2/r_{ij}\) is always a repulsive interaction. [What happens for \(f^{13}p^\)? Certainly different from fp!]

* reverse sign for \(H^{SO}\) because \(H^{SO}\) is a relativistic electrostatic interaction between e\textsuperscript{−} and nucleus (+ charge). Replacing e\textsuperscript{−} by h\textsuperscript{+} and leaving the sign on the nucleus the same reverses the sign of \(H^{SO}\)!
pretend that holes are e⁻, Slater determinants describe spin-orbitals occupied by holes.

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

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

* all $\zeta(N,L,S)$ reverse sign

Look at Tinkham 6-2, page 187 figure.

\[ \zeta_{nd} \text{ vs. } \zeta(N,L,S) \text{ for lowest L-S term of (3d)^N configuration} \]

\[ \propto Z_{\text{eff}}^3 \quad \text{— periodicity, isoelectronic series, aufbau too} \]

INSIGHT — regularization of trends
EXTRAPOLATION
ASSIGNMENT
LABOR SAVING!

Shielding systematics:

\[ Z \quad \varnothing Z + 1 \]
\[ Z_{\text{eff}} \quad \varnothing Z_{\text{eff}} + 1 - 0.5 \]

: shielding

Spin-orbit parameters in $3d^x$ transition elements. The splitting parameters $\zeta(\text{LS})$ 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.)
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 \(M_L = L_{\text{MAX}}, M_S = S_{\text{MAX}}\) component

\[
\left| L_{\text{MAX}}, M_L = L_{\text{MAX}}, S_{\text{MAX}}, M_S = S_{\text{MAX}} \right> = \| \ell \alpha (\ell - 1) \alpha \ldots \|
\]

(as many \(\alpha\) spins as possible)

diagonal element of \(H^{SO}\)

\[
\zeta\left((n\ell)^N, L_{\text{MAX}}, S_{\text{MAX}}\right) L_{\text{MAX}} S_{\text{MAX}} = \zeta_{n\ell} \sum_i m_{\ell i} m_{s i}
\]

\[
\zeta\left((n\ell)^N, L_{\text{MAX}}, S_{\text{MAX}}\right) = \zeta_{n\ell} \frac{\Sigma m_{\ell i} m_{s i}}{L_{\text{MAX}} S_{\text{MAX}}}
\]

\(S_{\text{MAX}}\)?

shell less than 1/2 full, \(N < 2\ell + 1\), all spins are \(\alpha\)

\[ \therefore S = \frac{N}{2} \]

\(L_{\text{MAX}}\)?

if all spins are \(\alpha\), maximize \(M_L\) by putting 1e\(^-\) into each \(m_i\) starting at \(m_i = \ell\) and working downward.

\[ M_{L_{\text{MAX}}} = \ell + (\ell - 1) + \ldots (\ell - N + 1) = N[\ell - (N - 1)/2] \]

\(N\) terms in sum

\(\ell\) from each term in sum

\[
\zeta\left(n\ell^N, L_{\text{MAX}}, S_{\text{MAX}}\right) = \zeta_{n\ell} \frac{1}{2} \frac{\Sigma m_{\ell i}}{L_{\text{MAX}} (N/2)} = \zeta_{n\ell} \frac{1}{2} \frac{M_L}{L_{\text{MAX}} (N/2)}
\]

\[
= \zeta_{n\ell} / N \quad \text{WHICH IMPLIES} \quad \zeta_{n\ell} / 2S_{\text{MAX}}
\]

updated September 19.
Shell 1/2 full

$N = 2\ell + 1$, all spins $\alpha$, $\sum_i m_{\ell i} = 0$

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

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

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

Shell more than 1/2 full

$S_{\text{MAX}}$?

$2\ell + 1$ $\alpha$ spins

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

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

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

$L_{\text{MAX}}$?

for the $2\ell + 1$ $\alpha$ spins $\sum \ m_{\ell i} = 0$

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

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

$\zeta(n\ell^N, L_{\text{MAX}}, S_{\text{MAX}}) = \frac{L_{\text{MAX}}S_{\text{MAX}}}{L_{\text{MAX}} \left(2\ell + 1 - \frac{N}{2}\right)}$

$= \frac{-\zeta_{n\ell} \left(-\frac{1}{2}\right) L_{\text{MAX}}}{L_{\text{MAX}} \left(2\ell + 1 - \frac{N}{2}\right)} = \frac{-\zeta_{n\ell}}{2 \left(N - \frac{1}{2}\right)}$

Summary for lowest energy L-S term:

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

** $\zeta(n\ell^N, L_{\text{MAX}}, S_{\text{MAX}}) = \pm \frac{\zeta_{n\ell}}{\# \text{ of } e^-}$

updated September 19,
Hund’s third rule: ONLY FOR LOWEST ENERGY L-S term, lowest J component is

\[ J = |L - S| \quad \text{for} \quad N < 2\ell + 1 \quad \text{“regular”} \]
\[ J = S \quad \text{N} = 2\ell + 1 \quad \text{no fine structure} \]
\[ J = L + S \quad \text{N} > 2\ell + 1 \quad \text{“inverted”} \]

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

3. Zeeman effect in many-e\(^-\) atoms

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

1.399613 MHz/Gauss
Bohr magneton
(Used \(\gamma\) previously)

remember that \(\mathbf{H}^{\text{Zeeman}}\) is awkward in \(|JM_JLS\rangle\) 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 \(\mathbf{H}^{\text{Zeeman}}\) off-diagonal in J.]

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

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

\[
\left\langle J' | \mathbf{H}^{\text{Zeeman}} | J \right\rangle \ll \left| E_{J'}^{(0)} - E_J^{(0)} \right|
\]

(This fails at high \(B_z\) when \(\zeta(nLS)\) is small.)
for $\Delta J = 0$ matrix elements, replace both $L_z$ and $S_z$ by $J_z$

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

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

but $J = L + S$. Add the 2 equations

$$\langle |J| \rangle = \left( \frac{\langle |L| \rangle}{1 - \alpha} + \frac{\langle |S| \rangle}{\alpha} \right) \langle |J| \rangle$$

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

$$H_{\text{Zeeman}} = \frac{-\mu_0}{\hbar} \left[ (1 - \alpha)J_z + 2\alpha J_z \right] B_z = \frac{-\mu_0}{\hbar} B_z (1 + \alpha) J_z!$$

Trick to evaluate $\alpha$:

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

diagonal $|JM_LS\rangle$ matrix element of both sides

$$\hbar^2 L(L + 1) = \hbar^2 J(J + 1) + \hbar^2 S(S + 1) - 2\langle JMLS|J \cdot S|JMLS \rangle$$

completeness: $J$ has $\Delta J = 0$

selection rule, $L$ has $\Delta L = 0$,$S$ has $\Delta S = 0$, $J \cdot S$ is scalar with respect to $J$, $\Delta M = 0$

$$\langle JMLS|J \cdot S|JMLS \rangle = \sum_{J'M'L'S'} \langle JMLS|J|J'M'L'S' \rangle \langle J'M'L'S'|S|JMLS \rangle$$

$$= \langle JMLS|J|JMLS \rangle \langle JMLS|S|JMLS \rangle$$

$$= \alpha \langle JMLS|J^2|JMLS \rangle = \alpha J(J + 1) \hbar^2$$

Plug this into the ** equation above and rearrange:

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

updated September 19.
Landé g-value

\[ g_j = 1 + \alpha = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \]

* \( g_j \) is Zeeman tuning coefficient = \( -\frac{1}{\mu_0} \frac{1}{dB_z M_j} \)
* equally spaced \( M_j \) components
* excellent diagnostic for different \( L, S \) of same \( J \)

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

\( g_j \) small when \( \bar{L}, \bar{S} \) are antiparallel

e.g. \( J = 3 : \)

\[
\begin{array}{cccc}
L = 0, S = 3 & L = 1, S = 2 & L = 2, S = 1 & L = 3, S = 0 \\
g_j & 2.000 & 1.667 & 1.333 & 1.000 \\
\end{array}
\]

\[
\begin{array}{ccccc}
L = 3, S = 1 : & J = 4 & J = 3 & J = 2 \\
(\text{parallel}) & (\text{antiparallel}) & \\
1.250 & 1.1667 & 0.667 \\
\end{array}
\]

* \( g_j \) 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
Matrix Elements of $H_{\text{Zeeman}}$ in Slater determinantal basis set?

\[ H_{\text{Zeeman}} = -\left(\mu_0/\hbar\right)B_z \sum_i \left(\ell_{iz} + 2s_{iz}\right) \]

\[ \langle 3\alpha 2\alpha \vert H_{\text{Zeeman}} \vert 3\alpha 2\alpha \rangle = -\left(\mu_0 B_z\right)[(3 + 1) + (2 + 1)] \]
\[ = -7\mu_0 B_z \]

Now compare with $g_J$ equation:

\[ \langle 3H_6 6 \vert H_{\text{Zeeman}} \vert 3H_6 6 \rangle = -\left(\mu_0 B_z\right)g_J M_J \]

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

\[ \langle \rangle = -\left(\mu_0 B_z\right)\frac{7}{6} = -7\mu_0 B_0 \quad \text{agrees!} \]
Hole vs. $e^-$ for Zeeman effect.

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

\[
\begin{align*}
|f^{13} \ ^2F_{7/2} \ 7/2\rangle &= \|3\alpha \ldots - 3\alpha 3\beta \ldots - 2\beta\| \\
|f^1 \ ^2F_{7/2} \ 7/2\rangle &= \|3\alpha\|
\end{align*}
\]

\[
\begin{align*}
E^{\text{Zeeman}}(f^{13} \ ^2F_{7/2} \ 7/2) &= -(\mu_0 B_z)_{\alpha\text{-spins}} \left[(0 + 7) + (3 - 6)\right] \\
&= -4\mu_0 B_z \\
E^{\text{Zeeman}}(f^1 \ ^2F_{7/2} \ 7/2) &= -(\mu_0 B_z)_{\beta\text{-spins}} \left[3 + 1\right] = -4\mu_0 B_z
\end{align*}
\]

Same as $f^{13}$

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