Zeeman Effect

Read CTDL, pp. 1156-1178, preparation for 1-D solids

LAST TIME:

- * computational tricks and inter-relationships among atomic and molecular constants
- * $\mathbf{H}^{\mathrm{SO}} = \zeta(\mathrm{N,L,S})\mathrm{L}\cdot\mathrm{S} \rightarrow$ a different $\zeta(\mathrm{N,L,S})$ constant for each L–S state in configuration N

or, from $\mathbf{H}^{\mathrm{SO}} = \sum_i a(r_i)\boldsymbol{\ell}_i\mathbf{s}_i \rightarrow$ one $\zeta_{n\ell}$ parameter valid for all diagonal and off-diagonal intra-configurational matrix elements

$\zeta(\mathrm{N,L,S})$ a fit parameter
$\zeta_{n\ell}$ an orbital integral

micro→macro forms of operators

TODAY:

1. electrons↔holes
   shortcuts for e^2/r_{ij} and $\mathbf{H}^{\mathrm{SO}}$
2. Hund's 3rd Rule: the lowest L–S–J level of an electronic configuration
3. Zeeman effect. Landé g-factor via Wigner-Eckart Theorem. Another way to evaluate reduced matrix elements.
4. $\mathbf{H}^{\mathrm{Zeeman}}$ in Slater determinantal basis set.

1. electrons (e^-)⟷holes (h^+) shortcuts

subshell		$n\ell^N$		
½ full	s	p	d	f
#e^-	1	3	5	7

for p^5 do we need to consider $5e^-$ or one h^+?

p^5 ^2P $M_L = 1, M_S = 1/2$ $\|1\alpha 1\beta 0\alpha 0\beta {-1}\alpha\|$

$(ph^+)^1$ ^2P $M_L = 1, M_S = 1/2$ $\|1\alpha\|$

Get same energy order of L-S states via $5e^-$ or $1h^+$ Slater determinant

Why? e^2/r_{ij} expresses $e^- - e^-$ repulsion
$h^+ - h^+$ is also repulsion

so we get the same result for e^2/r_{ij} by e^- or h^+ algebra. All F_k, G_k Slater-Condon parameters are > 0.

What about p^5d^1 vs. p^1d^1? Is the energy level order inverted? Hund's 1st and 2nd rules predict the same lowest state in p^5d as in $(ph^+)^1\ d^1$.

What about e^- vs. h^+ for $\mathbf{H}^{SO}$?

$$\mathbf{H}^{SO} = \zeta(N,L,S)\mathbf{L}\cdot\mathbf{S} = \sum_i a(r_i)\ell_i \cdot \mathbf{s}_i$$

Take $\Delta M_J = 0$, $M_J = J = L + S$ matrix element of both sides of the $\mathbf{H}^{SO}$ equation.

This is an extreme state from the M_L, M_S box diagram. There is only one Slater determinant in this box.

$p^{5}\ {}^{2}P$ vs. $p^{1}\ {}^{2}P$

$$\hbar^{2}\zeta\left(p^{5\ 2}P, M_{L}=1, M_{s}=1/2\right)\left(1\cdot\frac{1}{2}\right)=\hbar^{2}\zeta_{np}\left[1\cdot\frac{1}{2}+1\cdot\left(-\frac{1}{2}\right)+0+0+-1\cdot\frac{1}{2}\right]$$

$$=\hbar^{2}\zeta_{np}(-1)\left(\frac{1}{2}\right)$$

$\zeta(p^{5}\ {}^{2}P) = -\zeta_{np}$

Now $p^{1}\ {}^{2}P$

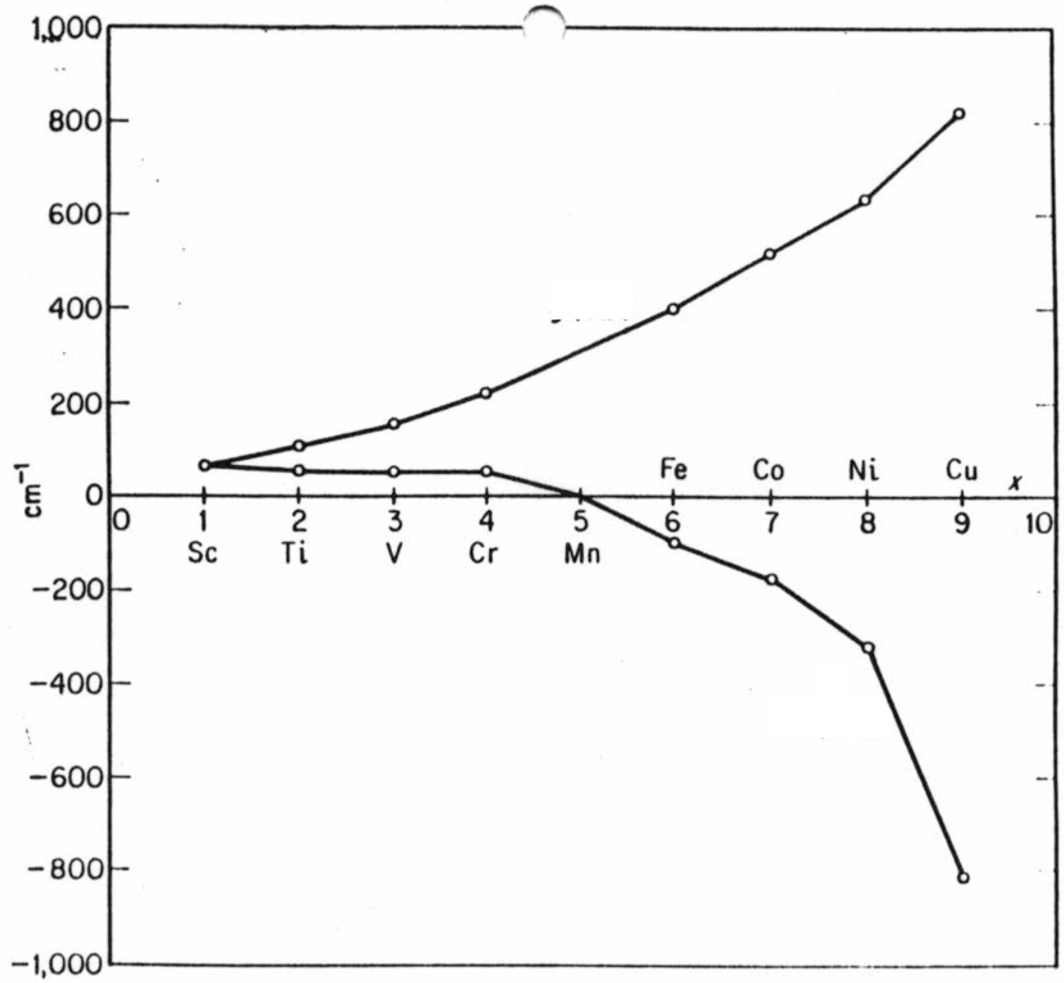
$$\hbar^{2}\zeta\left(p^{1\ 2}P, M_{L}=1, M_{s}=1/2\right)\underbrace{L\cdot S}_{1\cdot\frac{1}{2}}=\hbar^{2}\zeta_{np}\left[1\cdot\frac{1}{2}\right]$$

$\zeta(p^{1}\ {}^{2}P) = \zeta_{np}$

So we get a sign reversal in $\zeta(N\ {}^{2}P)$ for p^{5} vs. p^{1}.

So $e^{-}\leftrightarrow h^{+}$ gives no change in e^{2}/r_{ij} expressed by an always positive F_{k} and G_{k}. However, get sign reversed in $\mathbf{H}^{SO}$ for $\zeta(N,L,S)$ but not for $\zeta_{n\ell}$.

Figure 6-2 from Tinkham (page 187) for L_{MAX}, S_{MAX} state of $3d^N\,4s^2$ configuration



This figure is in the public domain.

Fig. 6-2. *Spin-orbit parameters in $3d^x$ transition elements. The splitting parameters $\zeta(LS)$ are computed as indicated in Table 6-2 and averaged over the various splittings. The data used are for the $3d^x4s^2$ configurations of the neutral atoms. (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.)*

Note that $\zeta_{n\ell}$ is a one-e$^-$ orbital integral and is expected to exhibit "periodic" variation. It increases with atomic number and this is expected for increasing Z^{eff}:

$$Z \longrightarrow Z + 1,\ Z^{eff} \longrightarrow Z^{eff} + 1 - 1/2$$

See Burns' rule paper on shielding included here: *J. Chem. Phys.* **41**, 1521 (1964).

General result for ζ (N,L,S):

$$\zeta(N,L,S) = \pm\frac{1}{2S_{\text{MAX}}}\zeta_{n\ell}$$

$+$ for $n < 2\ell + 1$

$-$ for $n > 2\ell + 1$

$\zeta(N,L,S) = 0$ for $n = 2\ell + 1$

Burn's paper on Pages 5 and 6 has been removed due to copyright restrictions. See Burn, Gerald. "Atomic Shielding Parameters." *J. Chem. Phys*. **41** (1964): 1521–1522.

Isoelectronic species (5 valence electrons):

C^- N O^+

large and diffuse ← C⁻ O⁺ → compact

poorly shielded strongly shielded

$$\begin{array}{ccc} C & N & O \\ Si & P & S \end{array} \xrightarrow{\quad} \downarrow$$

Z^{eff} increases by much smaller amount than $Z(n\ell) \rightarrow Z((n+1)\ell)$

[e.g. O Z(2p) = 8, S Z(3p) = 16]

Z^{eff} increases more slowly than Z

Hund’s 3rd Rule

1st and 2nd Hund's rules (for most stable *L-S* term) specify S_{MAX} and then L_{MAX} among all of the *L-S* states of a configuration.

$L_{\text{MAX}} M_{L_{\text{MAX}}} S_{\text{MAX}} M_{S_{\text{MAX}}}$ is a single Slater determinant. It is also equal to

$$J = L_{\text{MAX}} + S_{\text{MAX}} M_{J_{\text{MAX}}} = L_{\text{MAX}} + S_{\text{MAX}}$$

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

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

$\text{Shell} < \frac{1}{2}$ full $\qquad N < 2\ell + 1$

All spins are α

$S_{\text{MAX}} = N/2$

$M_{L_{\text{MAX}}} = \ell + (\ell - 1) + \ldots (\ell - N + 1)$

Sum includes sum of one ℓ for each of N terms, each additive term decreased by 0, 1, … $N - 1$.

$$M_{L_{\text{MAX}}} = N\left(\ell - (N-1)/2\right)$$

$$\zeta\left(n\ell^N, L_{\mathrm{MAX}}, S_{\mathrm{MAX}}\right) = \zeta_{n\ell} \frac{\overset{m_s = \alpha \text{ for all occupied spin-orbitals}}{\frac{1}{2}\sum_i} \underbrace{m_{\ell_i}}_{M_L = L_{\mathrm{MAX}}}}{L_{\mathrm{MAX}} S_{\mathrm{MAX}}}$$

$$= \zeta_{n\ell} \frac{\frac{1}{2} L_{\mathrm{MAX}}}{L_{\mathrm{MAX}}(N/2)} = \zeta_{n\ell}/N = \zeta_{n\ell}/2S_{\mathrm{MAX}}$$

Similarly for shell that is more than half-full.

$$\begin{aligned} S_{\mathrm{MAX}} &= \frac{1}{2}\left\{(2\ell+1)\alpha \text{ spins} - [N-(2\ell+1)]\beta \text{ spins}\right\} \\ &= (2\ell+1) - N/2 \\ M_S = S_{\mathrm{MAX}} &= (2\ell+1) - N/2 \end{aligned}$$

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

$$= -\frac{\zeta_{n\ell}}{2S_{\mathrm{MAX}}} = -\frac{\zeta_{n\ell}}{(2\ell+1) - N/2}$$

So we have

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

$$S_{\text{MAX}} = N/2 = \frac{1}{2}\ \#\ \text{of}\ e^{-} \qquad N = 2\ell+1$$

$$= -\frac{\zeta_{n\ell}}{2S_{\text{MAX}}} \qquad N > 2\ell+1$$

$$S_{\text{MAX}} = \left[(2\ell+1) - N/2\right] = \frac{1}{2}\ \left(\#\ \text{of}\ h^{+}\right)$$

Shell half full

$$\left.\begin{aligned} L_{\text{MAX}} &= 0 \\ S_{\text{MAX}} &= N/2 \end{aligned}\right]{}^{N+1}S_{N/2}$$

No fine structure. Only a single J-Level, J = N/2.

3. Zeeman Effect.

Provides additional information for assignment of an L–S–J state.

$$\mathbf{H}^{\text{Zeeman}} = -\underbrace{\left(\mu_0/\hbar\right)}_{\downarrow}\left(L_Z + 2S_Z\right)\underbrace{B_Z}_{\downarrow}$$

Bohr Magneton
1.399613 MHz/Gauss
1 cm^{-1} = 29979 MHz

magnetic field
(entirely along Z
laboratory axis)

In the coupled representation, $|JM_J L_S\rangle$ matrix elements of $\mathbf{H}^{\text{Zeeman}}$ are awkward because it is necessary to transform from coupled to uncoupled $|LM_L SM_S\rangle$ basis set in order to evaluate matrix elements of $\mathbf{H}^{\text{Zeeman}}$.

This is a fast way to get a closed-form expression for matrix elements of $\mathbf{H}^{\text{Zeeman}}$ in the coupled basis set. It involves a clever way to evaluate reduced matrix elements using the Wigner-Eckart Theorem.

$\mathbf{H}^{\text{SO}}$ and e^2/r_{ij} are rigorously diagonal in J (WHY?) but $\mathbf{H}^{\text{Zeeman}}$ is not (WHY?). [Answers depend on how you classify an operator relative to $\vec{\mathbf{J}}$.]

We have a battle between [$\mathbf{H}^{\text{SO}}$ and e^2/r_{ij}], which is diagonal in J, thus it tries to *defend* the coupled representation against $\mathbf{H}^{\text{Zeeman}}$, which is non-diagonal in J and tries to *destroy* the coupled representation.

We are interested in the weak field limit where

$$\left\langle J'\middle|\mathbf{H}^{\text{Zeeman}}\middle|J\right\rangle \ll \left|E_{J'}^{(0)} - E_J^{(0)}\right| \text{ due to the operators } \mathbf{H}^{\text{SO}} \text{ and } e^2/r_{ij}$$

Our special case, limited to ΔJ = 0 matrix elements, fails when ζ(NLS) is small and B_Z is large.

Wigner Eckart Theorem tells us

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

Similarly for **S**

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

but $J = L + S$

$$\langle|\mathbf{J}|\rangle = \underbrace{\left(\underset{(1-\alpha)}{\langle||\mathbf{L}||\rangle} + \underset{\alpha}{\langle||\mathbf{S}||\rangle}\right)}_{=1}\left\langle JM'LS\right|\mathbf{J}\left|JMLS\right\rangle$$

Thus $\langle|\mathbf{S}|\rangle = \alpha\langle|\mathbf{J}|\rangle$ or $\boxed{\mathbf{S} = \alpha\mathbf{J}}$! An operator replacement!

Now for the cleverness:

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

$$\mathbf{J} - \mathbf{S} = \mathbf{L}$$

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

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

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

Matrix elements of $\mathbf{J}^2$, $\mathbf{S}^2$, and $\mathbf{L}^2$ are explicitly evaluable in the coupled representation, $|JLSM_J\rangle$.

Thus:

$$\langle JM'LS|\mathbf{J}\cdot\mathbf{S}|JMLS\rangle = \delta_{M'M}\hbar^2\left[\frac{J(J+1)+S(S+1)-L(L+1)}{2}\right]$$

but $\mathbf{J}\cdot\mathbf{S} = \alpha\mathbf{J}^2$

$$\langle JM'LS|\alpha\mathbf{J}^2|JMLS\rangle = \delta_{m'm}\left[\hbar^2\alpha J(J+1)\right]$$

we can solve for α

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

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

$$\mathbf{H}^{\text{Zeeman}} - \mu_0 B_z\Big(\underset{\underset{(1-\alpha)\mathbf{J}_z}{\Big\downarrow}}{\mathbf{L}_z} + 2\underset{\underset{\alpha\mathbf{J}_z}{\Big\downarrow}}{\mathbf{S}_z}\Big) = -\mu_0 B_z(1+\alpha)\mathbf{J}_z$$

$$\langle JMLS|\mathbf{H}^{\text{Zeeman}}|JMLS\rangle = -\mu_0 B_z\hbar M_J\underbrace{(1+\alpha)}_{g_J}$$

Zeeman energy level tuning rate:

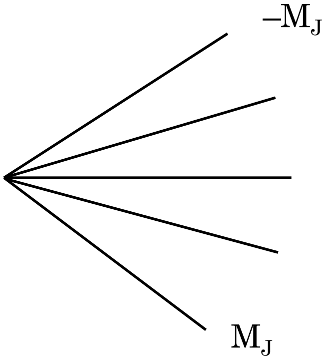
$$\frac{dE}{dB_z} = \frac{d}{dB_z}\left(-\mu_0 B_z M_J(1+\alpha)\right)$$

$$= -\mu_0 M_J g_J$$

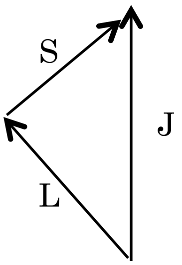
$$g_J = -\frac{1}{\mu_0}\frac{1}{M_J}\frac{dE}{dB_z} \quad\longleftarrow$$

Apply a magnetic field, each J level splits into 2J + 1 M_J components.

# of components tells us J, g_J tells us something about L and S



tuning is linear in B_z



$J_{\text{MAX}} = L + S$ L and S parallel (magnetic moments add)

$J_{\text{MIN}} = |L - S|$ L and S anti-parallel (magnetic moments partially cancel)

e.g.

for 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
or for L = 3, S = 1		J = 4	J = 3	J = 2
g_J		1.250 parallel	1.0833	0.667 anti-parallel

To determine J: apply B_Z field and count M_J components

light Z polarized, $\Delta M_J = 0$

$$\left.\begin{array}{ll} J' & \text{set of equal } M'_J, M'_J-1 \text{ splittings} \\ J'' & \text{another set of equal } M''_J, M''_J-1 \text{ splittings} \end{array}\right] g_{J'} \neq g_{J''}$$

($'$ for upper state, $''$ for lower state)

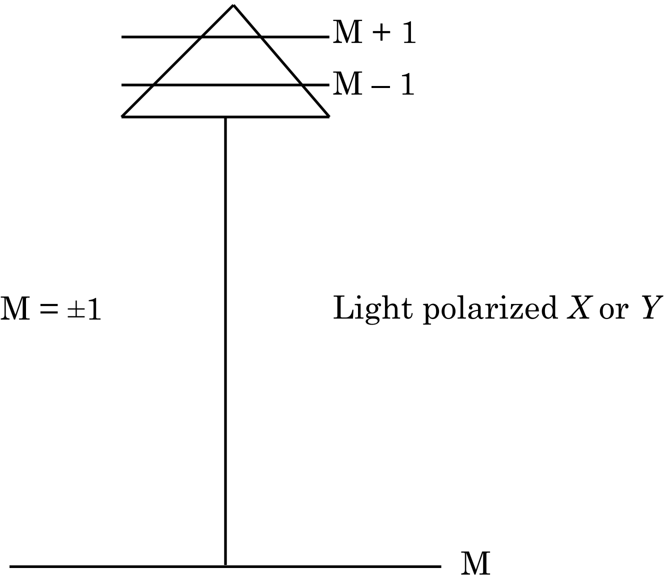
Alternatively, light polarized X or Y (perpendicular to B_Z)

get $M' - M'' = \pm 1$

If you know the upper and lower state patterns, you can disentangle the spectrum and get $g_{J'}$ and $g_{J''}$.

Use a pulsed laser

Excite



Get quantum beats ⟶ determine $g_{J'}$! For many M'' components, get a set of Zeeman Quantum Beats for J' upper levels, but all upper level quantum beats are at the same frequency!

You can show that g_J is the same for e^- and h^+.

You can use the hole Slater determinant representation to evaluate $\mathbf{H}^{\text{Zeeman}}$ for more than 1/2 filled shells.

5.73 Quantum Mechanics I
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