SPIN - ORBIT: Many-Electron $\zeta(N, L, S) \leftrightarrow$ Single-Orbital $\zeta_{n\ell}$ Coupling Constants

LAST TIME: $\sum_{i \geq j} e^2/r_{ij}$

death of orbital picture
expansion of $1/r_{ij}$: multipoles, integrals over AOs in nucleus-centered coordinates
SELECTION RULES: orbital and many-e^- basis sets
Gaunt Coefficients: a^k, b^k, c^k [products of 3-j]
Slater-Condon $(F^k, G^k) \rightarrow (F_k, G_k)$
Sum Rule Method - avoid necessity to derive:
 *eigenvectors
 * off diagonal elements in Slater basis
Hund's 1st and 2nd Rules

TODAY:

A. General Importance of spin - orbit term

$$\mathbf{H}^{SO} = \sum_i a(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \qquad 1 - e^- \text{ operator}$$

B. Trick: replace 1 - e^- operator by more convenient $\zeta(N, L, S)\mathbf{L} \cdot \mathbf{S}$ for $\Delta S = 0$, $\Delta L = 0$ special case

C. Pattern: Landé Interval Rule (Patterns are for breaking! Information about "dark" states)

D. $\mathbf{H}^{SO}$ matrix elements in Slater Determinantal Basis Set
 * another operator replacement
 * Fundamental control parameter: n, ℓ - scaling of ζ_{nl}
 * $\zeta_{nl} \leftrightarrow \zeta(N, L, S)$
 * off - diagonal spin - orbit matrix elements: $\Delta L \neq 0$, $\Delta S \neq 0$, $\Delta J = 0$.

next time → Hund's 3rd Rule and Lande g_J–factors

A. Importance of spin-orbit

1. $\mathbf{H}^{SO}$ produces diagnostically significant "fine structure"
   CONFIGURATIONAL ASSIGNMENTS
   L,S term assignments
   PATTERNS:* # components
   * sign of pattern (largest splitting on top or bottom)
   * statistical weight (2J + 1) of lowest vs. highest energy component
   * overall magnitude of splitting

2. for heavy atoms, $\mathbf{H}^{SO}$ responsible for such large splittings and off-diagonal interactions that L-S terms "vanish", ΔS selection rules are violated. "Inter-System Crossing (ISC)".

   Need to "deperturb" to recover F_k, G_k parameters which should vary smoothly from atom to atom (isoelectronic series) (shielding rules)

3. spin-forbidden transitions provide energy linkages between manifolds of states with different values of S. "InterSystem Crossing (ISC)"

4. non-textbook Zeeman tuning coefficients (clues about unobserved "dark" states)

Atoms, Molecules, Quantum Dots, solids: in an electronic transition, light acts on single e^- and operates exclusively on spatial part of $\psi \rightarrow$ spin-flips are forbidden except when H^{SO} mixes states of different S — forbidden transitions "borrow" intensity from allowed transitions. In time-domain: a short pulse prepares, at t = 0, a non-eigenstate that is a pure $\Delta S = 0$ excitation (and $\Delta\ell = \pm 1$) basis state. The "pluck"!

Language: the name of each eigenstate is based on dominant (i.e., "nominal") character. It is the name of the dominant basis states. Use of same name for both eigenstate and basis state is a source of confusion.

B. Operator Replacement for $\mathbf{H}^{SO}$

$$\mathbf{H}^{SO} = \sum_i a(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \qquad \text{a one - } e^- \text{ operator}$$

Wigner-Eckart Theorem for vector operator — operator replacement for special case of ΔJ = 0 matrix elements.

$$\underbrace{\left\langle JM_J \middle| \hat{\mathbf{A}} \middle| JM'_J \right\rangle}_{\Delta J = 0} = \underbrace{\left\langle J \| \mathbf{A} \| J \right\rangle}_{\substack{\text{proportionality} \\ \text{constant}}} \underbrace{\left\langle JM_J \middle| \hat{\mathbf{J}} \middle| JM'_J \right\rangle}_{\substack{\text{matrix element of} \\ \text{corresponding component of } \hat{\mathbf{J}}}}$$

CTDL p. 1054 use projection theorem: $\mathbf{V} = \dfrac{\langle \mathbf{J}\Sigma\mathbf{V}\rangle}{\langle \mathbf{J}^2 \rangle}\mathbf{J}.$

Especially useful when **V** is an angular momentum that is included in **J**.

useful trick for $\mathbf{H}^{SO}$

$a(r_i)\boldsymbol{\ell}_i$ vector with respect to **L**

$\mathbf{s}_i$ vector with respect to **S**

Special case of $\Delta L = 0, \Delta S = 0$ matrix elements in $\left|NLM_L SM_S\right\rangle$ basis set

configuration label

$$\mathbf{H}^{SO} = \sum_i a(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \rightarrow \underbrace{\zeta(N,L,S)\mathbf{L}\cdot\mathbf{S}}_{\substack{\text{operator} \\ \text{replacement!}}}$$

* $\zeta(N,L,S) \equiv \sum_i \left\langle L \middle\| a(r_i)\boldsymbol{\ell}_i \middle\| L \right\rangle \left\langle S \middle\| \mathbf{s}_i \middle\| S \right\rangle$

* a different spin-orbit coupling constant for EACH L-S term of the N configuration

* convenient because it is easy to evaluate matrix elements of **L·S** without having to resort to Slater determinatal basis set

[ASIDE: $a(r_i)\boldsymbol{\ell}_i$ and $\mathbf{s}_i$ are both vectors with respect to **J**, thus $\mathbf{H}^{SO}$ is scalar with respect to **J**, hence matrix elements in $\left|\mathrm{NJLSM_J}\right\rangle$ basis set are ΔJ = 0, $\Delta M_J = 0$, and independent of M_J.]

CAUTION: **L·S** seems to imply ΔS = 0 selection rule, but we assumed ΔS = 0 in deriving the simplified form of H^{SO}: ζ**L·S**

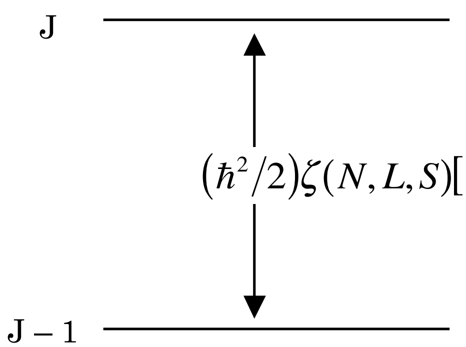
C. Landé Interval Rule (useful for recognizing and assigning an isolated L-S term)

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

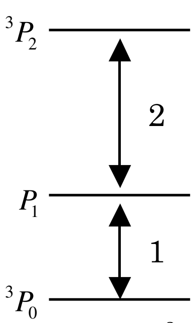
$$\mathbf{L}\cdot\mathbf{S} = \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2}{2}$$

$$\left\langle NJLSM_J \middle| \mathbf{H}^{\mathbf{SO}} \middle| NJLSM_J \right\rangle = \frac{\hbar^2}{2}\underbrace{\zeta(N,L,S)}_{\substack{\text{can be positive,}\\ \text{zero, or negative}}}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

So, <u>within</u> an L-S term, $\mathbf{H}^{\mathrm{SO}}$ causes splitting into 2S+1 (or 2L+1 if S > L) components.



$$\left(\hbar^2/2\right)\zeta(N,L,S)\left[J(J+1) - (J-1)J\right] = \underbrace{\hbar\zeta(N,L,S)J}_{\substack{\text{Landé interval}\\ \text{rule}}}$$



regular ^{3}P [2 intervals: 2:1]

* spacing is ∝ to larger of 2 J's
* largest spacing locates largest J
* large spacing on top: "regular" L-S term
  bottom: "inverted" L-S term

[Convince yourself that you should be able to tell ^{3}D from ^{3}P…]

Easy to show that degeneracy–weighted average spin-orbit energy of a multiplet = 0 (easiest to show from trace of $\mathbf{H}^{\mathrm{SO}}$ in LM_LSM_S basis, followed by trace invariance).

$$\sum_{J=|L-S|}^{L+S} (2J+1)E_J = 0$$

The interval rule plus the number of J-components of a multiplet determine the values of L and S.
[^{4}P 5:3, 2 intervals; ^{2}P 1 interval, ^{4}D 7:5:3, 3 intervals]

D. Matrix Elements of $\mathbf{H}^{SO}$ in Slater Determinantal Basis Set

<u>GOALS</u>:

* $\Delta S \neq 0$ matrix elements, $\Delta L \neq 0$ matrix elements
* relationships between $\underbrace{\zeta(N,L,S)}_{\text{L-S term}}$ and $\underbrace{\zeta_{n\ell}}_{\text{orbital}}$
* no interconfigurational $\mathbf{H}^{SO}$ matrix elements $\left[\text{except } n'\ell \sim n\ell \propto (n'n)^{-3/2}\right]$ (Rydberg scaling rule.)

NONLECTURE: alternative operator replacement for $\mathbf{H}^{SO}$ that is appropriate for orbital matrix elements

$$\mathbf{H}^{SO} = \sum_i a(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i$$

replace $a(r_i)\hat{\boldsymbol{\ell}}_i$ by $\zeta_{n\ell}\hat{\boldsymbol{\ell}}_i$ using completeness:

$$\left\langle n'\ell'm_\ell'sm_s'\middle|\mathbf{H}^{SO}\middle|n\ell m_\ell sm_s\right\rangle =$$

$$\sum_i \sum_{''} \left\langle n'\ell'm_\ell'sm_s'\middle|a(r_i)\middle|n''\ell''m_\ell''sm_s''\right\rangle\left\langle n''\ell''m_\ell''sm_s''\middle|\boldsymbol{\ell}_i \cdot \mathbf{s}_i\middle|n\ell m_\ell sm_s\right\rangle$$

$a(r_i)$ is scalar with respect to $s_i \rightarrow m_s' = m_s''$ and m_s' independent

$a(r_i)$ is scalar with respect to $\boldsymbol{\ell}_i \rightarrow \ell' = \ell'', m_\ell' = m_\ell'', m_\ell'$ independent

$\hat{\boldsymbol{\ell}}_i$ can't change ℓ in $\left|\ell m_\ell\right\rangle \rightarrow \ell'' = \ell$

$\boldsymbol{\ell}_i \cdot \mathbf{s}_i$ does not operate on radial part of $\psi \rightarrow n'' = n$

thus $\left\langle n'\ell'm_\ell'sm_s'\middle|\mathbf{H}^{SO}\middle|n\ell m_\ell sm_s\right\rangle = \delta_{\ell'\ell}\left\langle n'\ell\middle\|a(r_i)\middle\|n\ell\right\rangle\left\langle \ell m_\ell'sm_\ell'\middle|\boldsymbol{\ell}\cdot\mathbf{s}\middle|\ell m_\ell sm_s\right\rangle$

$$\left\langle n'\ell\middle\|a(r_i)\middle\|n\ell\right\rangle = \underbrace{(n'n)^{-3/2}}_{\text{Rydberg scaling for inner part of orbital}}\zeta_\ell^\circ = \left(\frac{n'}{n}\right)^{-3/2}\underbrace{\zeta_{n\ell}}_{\propto n^{-3}}$$

so, for $n' = n$, $\left\langle n\ell\middle\|a(r_i)\middle\|n\ell\right\rangle = \zeta_{n\ell} = n^{-3}\zeta_\ell^\circ$

This reduction of $\mathbf{H}^{SO}$ shows that, for atoms, $\mathbf{H}^{SO}$ acts exclusively within a configuration except for interconfigurational matrix elements where the two configurations differ by a single spin-orbital of the same value of ℓ: $\underbrace{n\ell \leftrightarrow n'\ell}_{\text{same } \ell}$

Examples

A is a single Slater determinant

$$\left\langle A \middle| \mathbf{H}^{SO} \middle| A \right\rangle = \sum_{\substack{k \\ \text{spin-orbitals}}} \left\langle u_k \middle| a(r_k) \boldsymbol{\ell}_k \mathbf{s}_{\leftarrow k} \middle| u_k \right\rangle$$

$$= \sum_{k} \zeta_{n_k l_k} \left\langle \ell_k m_{\ell_k} s_k m_{s_k} \middle| \underbrace{\boldsymbol{\ell} \cdot \mathbf{s}}_{\text{diagonal element picks out } \ell_z s_z} \middle| \ell_k m_{\ell_k} s_k m_{s_k} \right\rangle$$

$$= \hbar^2 \sum_{\substack{k \\ \text{spin-orbitals}}} \zeta_{n_k \ell_k} m_{\ell_k} m_{s_k}$$

if $|A\rangle$ is also an eigenfunction of $\mathbf{L}^2$, $\mathbf{L}_z$, $\mathbf{S}^2$, and $\mathbf{S}_z$ then

$$\left\langle NLM_L SM_S \middle| \mathbf{H}^{SO} \middle| NLM_L SM_S \right\rangle = \zeta(N,L,S)\hbar^2 M_L M_S$$

$$\zeta(N,L,S) = \frac{\sum_k \zeta_{n_k \ell_k} m_{\ell_k} m_{s_k}}{M_L M_S}.$$

The matrix element is evaluated 2 ways in order to reduce a many-e$^-$ spin-orbit coupling constant ($\zeta(N,L,S)$) to a sum of one-e$^-$ orbital coupling constants ($\zeta_{n\ell}$)!

Example 1. nf^2

uncoupled $\left|nf^2 \quad {}^3H \quad M_L = 5 \quad M_S = 1\right\rangle = \|3\alpha 2\alpha\|$ Single Slater determinant!

$$\zeta\left(nf^2, {}^3H\right) = \frac{\zeta_{nf}\left[3(1/2) + 2(1/2)\right]}{5 \cdot 1} = \zeta_{nf}/2$$

(fill in the steps!)

Example 2. nf^2

coupled $\left|nf^2 \quad {}^3H_6 \quad M_J = 6 \quad\right\rangle = \|3\alpha 2\alpha\|$

Landé : $\left\langle nf^2 \; {}^3H_6 \; M_J = 6\right|\mathbf{H}^{\mathrm{SO}}\left|nf^2 \; {}^3H_6 \; 6\right\rangle$

$$= \frac{\hbar^2}{2}[\underbrace{J(J+1)}_{6\cdot 7} - \underbrace{L(L+1)}_{5\cdot 6} - \underbrace{S(S+1)}_{1\cdot 2}]\zeta\left(nf^2, {}^3H\right)$$

$$= \hbar^2 5\zeta\left(nf^2, {}^3H\right) \text{ from many-e}^- \text{ form}$$

$$= \hbar^2\zeta_{nf}\left[3(1/2) + 2(1/2)\right] \text{ from orbital form}$$

$$\therefore \zeta\left(nf^2, {}^3H\right) = \zeta_{nf}/2$$

Example 3. $\zeta(nf^{2,3}F)$ $\quad$ ^3F is never a single Slater determinant for any value of (M_L, M_S)

Evaluate 2 ways:

a. Obtain explicit linear combination of Slater determinants using ladders and orthogonality or using $\mathbf{L}^2, \mathbf{S}^2$ to get $\left|\mathrm{nf}^2 \quad {}^3F \quad M_L = 3 \quad M_S = 1\right\rangle$ [laborious].

b. Slater sum rule method [simple].

$$M_L = 3, M_S = 1 \text{ box: } \|3\alpha 0\alpha\|, \|2\alpha 1\alpha\|$$

$$\langle\|3\alpha 0\alpha\|\rangle + \langle\|2\alpha 1\alpha\|\rangle = E\left({}^3H \;\; M_L = 3, M_S = 1\right) + E\left({}^3F \;\; M_L = 3, M_S = 1\right)$$

$$\langle\|3\alpha 0\alpha\|\rangle = \left\langle\|3\alpha 0\alpha\|\right|\mathbf{H}^{\mathrm{SO}}\left|\|3\alpha 0\alpha\|\right\rangle = \hbar^2\zeta_{nf}\left[\frac{3}{2} + 0\right]$$

$$\left\langle \|2\alpha 1\alpha\| \right\rangle = \left\langle \|2\alpha 1\alpha\| \mathbf{H}^{\mathrm{SO}} \|2\alpha 1\alpha\| \right\rangle = \hbar^2 \zeta_{nf}\left[1+\frac{1}{2}\right]$$

$$\boxed{\text{trace of } M_L = 3,\ M_S = 1 \text{ box is } 3\hbar^2\zeta_{nf}}$$

$$E\left({}^3H\ \ M_L = 3\ \ M_S = 1\right) = \left\langle {}^3H\ \ M_L = 3\ \ M_S = 1 \middle| \mathbf{H}^{\mathrm{SO}} \middle| {}^3H\ \ 3\ \ 1 \right\rangle = \zeta\left(nf^2, {}^3H\right)\hbar^2 3\cdot 1$$

but already showed $\zeta\left(nf^2, {}^3H\right) = \zeta_{nf}/2$

$$E\left({}^3H\ \ M_L = 3, M_S = 1\right) = \hbar^2\zeta_{nf}(3/2)$$

$$\therefore \mathrm{E}\left({}^3\mathrm{F}\ \ \mathrm{M_L} = 3, \mathrm{M_S} = 1\right) = 3\hbar^2\zeta_{\mathrm{nf}} - (3/2)\hbar^2\zeta_{\mathrm{nf}} = (3/2)\hbar^2\zeta_{\mathrm{nf}}$$

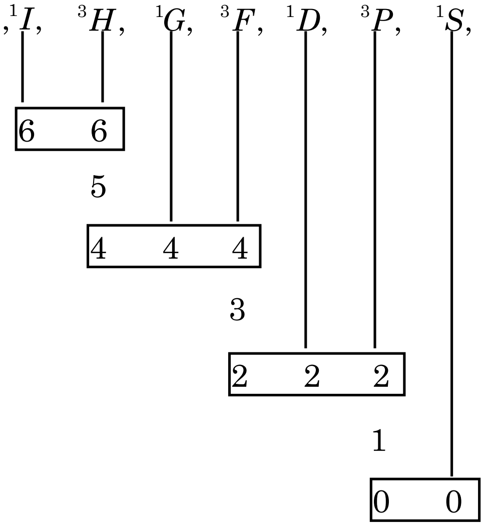
$$= \left\langle {}^3\mathrm{F}\ \ 3\ \ 1 \middle| \mathbf{H}^{\mathrm{SO}} \middle| {}^3\mathrm{F}\ \ 3\ \ 1 \right\rangle = \zeta\left(\mathrm{nf}^2, {}^3\mathrm{F}\right)(3\cdot 1)\hbar^2$$

$$\therefore \zeta\left(\mathrm{nf}^2, {}^3\mathrm{F}\right) = \frac{1}{2}\zeta_{\mathrm{nf}}$$

$\left(\text{actually would find, for } nf^2, \zeta\left(nf^2, {}^3L\right) = \frac{1}{2}\zeta_{nf} \text{ for all } L\right)$

[not true for all configurations]

We are not done. There are some *off-diagonal matrix elements* between the L-S-J terms of the same configuration. $nf^2, {}^1I,\ \ {}^3H,\ \ {}^1G,\ \ {}^3F,\ \ {}^1D,\ \ {}^3P,\ \ {}^1S,$



$\mathbf{H}^{\mathrm{SO}}$ is diagonal in J
must diagonalize 2 3×3
and 2 2×2 matrices.

set up J = 6 matrix because it is simplest

$$\left|{}^1I_6 \quad 6\right\rangle = \left\|3\alpha 3\beta\right\|$$

$$\left|{}^3H_6 \quad 6\right\rangle = \left\|3\alpha 2\alpha\right\|$$

$$\left\langle {}^1I_6 \quad 6\right|\mathbf{H}^{\text{SO}}\left|{}^3H_6 \quad 6\right\rangle = \left\langle \left\|3\alpha 3\beta\right\|\mathbf{H}^{\text{SO}}\left\|3\alpha 2\alpha\right\|\right\rangle$$

Mismatch is in 2nd spin-orbital.
Needs 1/2 $\ell_+ s_-$ operator to give nonzero spin-orbital matrix element.

$$= \left\langle 3\beta \left| \frac{1}{2}\boldsymbol{\ell}_+ \mathbf{s}_- \right| 2\alpha \right\rangle \zeta_{nf}$$

$$= \hbar^2 \zeta_{nf} \frac{1}{2}\left[3\cdot 4 - 2\cdot 3\right]^{1/2} = \hbar^2 \zeta_{nf}\left(3/2\right)^{1/2}$$

zero for all singlet states

$$\mathbf{H}^{\text{SO}}_{J=6} = \begin{array}{c} {}^1I_6 \\ {}^3H_6 \end{array}\begin{pmatrix} 0 & (3/2)^{1/2} \\ (3/2)^{1/2} & 5/2 \end{pmatrix}\hbar^2\zeta_{nf}$$

$$\left\langle {}^3H_6 \quad 6\right|\mathbf{H}^{\text{SO}}\left|{}^3H_6 \quad 6\right\rangle = \frac{\hbar^2}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\zeta\left(nf^2, {}^3H\right)$$

$$= \hbar^2 5\zeta\left(nf^2 \ {}^3H\right) = \hbar^2 \quad 5/2 \quad \zeta_{nf}$$

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for more complex configurations such as $(n\ell)^a(n'\ell')^b \rightarrow \zeta_{n\ell}$ and $\zeta_{n'\ell'}$: two ζ parameters needed for the two open subshell orbitals.
But can use the value of $\zeta_{n\ell}$ determined from some other configuration:
e.g. ζ_{3d} from $3d^6 4s^2$ can be used to predict the 3d part of $\mathbf{H}^{\text{SO}}$ in $3d^6\ 4s4p$. Unexpected inter-relationships between superficially unrelated observables. Small number of control parameters.

<u>Hund's 3rd Rule</u>: lowest energy J of lowest energy L-S term is $J = |L - S|$ if subshell is less than 1/2 full, is $J = L + S$ if subshell is more than 1/2 full, and $J = S$ because L = 0 for half filled subshell. Sign of $\zeta(N, L, S)$ as diagnostic!

NEXT TIME!