## SPIN - ORBIT: Many-Electron ς(N, L, S) ↔ Single-Orbital $\varsigma_{n\ell}$ 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 coefficients]
- Slater-Condon ($F^k$, $G^k$)⟶($F_k$, $G_k$)Parameters
- Sum Rule Method - avoid necessity to derive:
  - *eigenvectors
  - * off-diagonal elements in Slater basis
- Hund's 1st and 2nd Rules → predict lowest L-S term of configuration based on rapid decrease in size of $F_k$ as k increases

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A single-configuration pattern of assigned L-S terms.

For $nf^2$ there are 91 Slater determinants. To use the sum rule method to get the relative energies of all 7 L-S terms ($^1$I, $^3$H, $^1$G, $^3$F, $^1$D, $^3$P, $^1$S), it turns out it is necessary to compute 28 *diagonal* matrix elements in the $f^2$ Slater determinantal basis set. This is wonderful because it is unnecessary to compute any off-diagonal matrix elements (see page 34-8). These L-S term energies are expressed in terms of $F_0$, $F_2$, $F_4$, and $F_6$ (and $G_k$) Slater-Condon parameters.

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TODAY:

A. General Importance of spin-orbit term

$\mathbf{H}^{SO} = \sum_i a(r_i)\hat{\ell}_1\hat{\mathbf{s}}_1$ $\quad 1-e^-$ operator

B. *Trick*: replace 1–e⁻ operator by more convenient $\zeta(N,L,S)\mathbf{L}\cdot\mathbf{S}$ for ΔS = 0, ΔL = 0 special case matrix elements

C. *Pattern*: Landé Interval Rule (Patterns are for breaking! Broken patterns provide information about "dark" states)

D. $\mathbf{H}^{SO}$ matrix elements in Slater Determinantal Basis Set

* another operator replacement

* A single-orbital integral is the most fundamental control parameter: $n,\ell$-scaling of $\zeta_{n\ell}$

* $\zeta_{n\ell} \leftrightarrow \zeta(N, L, S)$ relationship between a single-orbital coupling constant and that for a specific $L$-$S$ state

* off-diagonal spin-orbit matrix elements: $\Delta L \neq 0$, $\Delta S \neq 0$, $\Delta J = 0$.

PATTERN BREAKING

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 (based on which L-S terms are present and the ± signs of spin-orbit splittings)
   L,S term assignments are based on
   PATTERNS:* # components
   * sign of pattern (largest splitting on top or on bottom)
   * statistical weight (2J + 1) of lowest vs. highest energy component
   * overall magnitude of splitting

2. for heavy atoms, $\mathbf{H}^{SO}$ is 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 $F_k$, $G_k$ inter-electronic $(1/r_{ij})$parameters which should vary smoothly from atom to atom (isoelectronic series) (shielding rules). Periodicity! The PERIODIC TABLE

3. Spin-forbidden transitions provide energy linkages between manifolds of states with different values of S. "InterSystem Crossing (ISC)", e.g. Hg $^3P_1 \leftarrow {}^1S_0$ 254nm

4. Non-textbook Zeeman tuning coefficients (clues about unobserved "dark" states) finer detail to be used after S-O patterns reduce the possibilities that must be considered.

**Atoms, Molecules, Quantum Dots, solids: in an electronic transition, light acts on a single $e^-$ and operates exclusively on the 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 the 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 its dominant (i.e., "nominal") character. It is the name of the dominant basis state. Use of the same name for both *eigenstate* and *basis state* is a source of confusion.

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

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

Wigner-Eckart Theorem for a vector operator — operator replacement for special cases where only $\Delta J = 0$ matrix elements are considered.

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

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

Especially useful when $\mathbf{V}$ is an angular momentum that is included in $\mathbf{J}$.

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

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

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

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

* $\zeta(N,L,S) \equiv \sum_i \left\langle L \left\| a(r_i)\boldsymbol{\ell}_i \right\| L \right\rangle \left\langle S \left\| \mathbf{s}_i \right\| S \right\rangle$
* a different spin-orbit coupling constant for EACH L-S term of the N configuration (loss of simplicity)
* convenient because it is easy to evaluate matrix elements of $\mathbf{L}\cdot\mathbf{S}$ without having to resort to use of the Slater determinantal basis set

[ASIDE: $a(r_i)\boldsymbol{\ell}_i$ and $\mathbf{s}_i$ are both vectors with respect to $\mathbf{J}$, thus $\mathbf{H}^{SO}$ is scalar with respect to $\mathbf{J}$, hence matrix elements in the $\left| NJLSM_J \right\rangle$ basis set have 3 special characteristics: $\Delta J = 0, \Delta M_J = 0$, and independent of $M_J$.]

CAUTION: the $\mathbf{L}\cdot\mathbf{S}$ operator seems to imply a $\Delta S = 0$ selection rule, but we *assumed* $\Delta S = 0$ in deriving the simplified form of $\mathbf{H}^{SO}$: $\zeta\mathbf{L}\cdot\mathbf{S}$

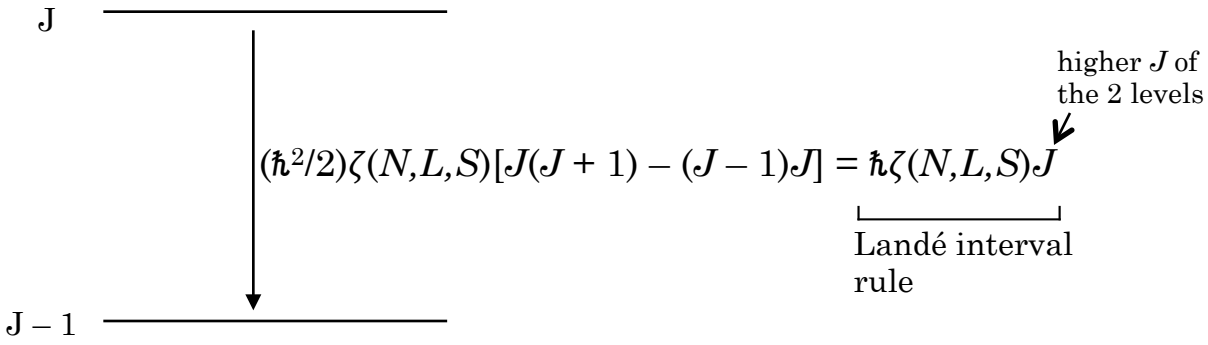
C. Landé Interval Rule (useful for recognizing and assigning an isolated L-S term)

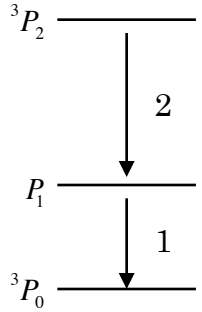
$$\mathbf{J} = \mathbf{L} + \mathbf{S} \qquad \mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$$

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

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

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




* 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 are able to tell $^3$D from $^3$P…]

regular $^3$P [2 intervals: 2:1]

$^3$D 3:2 $^3$F 4:3
$^4$P 5/2:3/2 $^4$D 7/2:5/2:3/2 (4 components)
(3 components)

Easy to show that the degeneracy–weighted average (each $J$-component has degeneracy $2J + 1$) spin-orbit energy of a multiplet = 0 (easiest to show from the trace of the $\mathbf{H}^{SO}$ in $|LM_LSM_S\rangle$basis). Off-diagonal elements (between same-J components of different L-S states) do not affect the trace of $\mathbf{H}^{SO}$.

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

The interval rule plus the number of J-components of a multiplet determine the values of both 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

GOALS:
* $\Delta S \neq 0$ matrix elements, $\Delta L \neq 0$ matrix elements
* relationships between $\underbrace{\zeta(N,L,S)}_{\text{L-S term}}$ and $\underbrace{\zeta_{n\ell}}_{\text{orbital}}$
* excluding interconfigurational $\mathbf{H}^{SO}$ matrix elements

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

$$\left\langle n'\ell'm'_\ell sm'_s \middle| \mathbf{H}^{SO} \middle| n\ell m_\ell s m_s \right\rangle =$$

$$\sum_i \sum_{"} \left\langle n'\ell'm'_\ell sm'_s \middle| a(r_i) \middle| \underbrace{n''\ell''m''_\ell sm''_s \rangle\langle n''\ell''m''_\ell sm''_s}_{\text{completeness}} \middle| \boldsymbol{\ell}_i \bullet \mathbf{s}_i \middle| n\ell m_\ell s m_s \right\rangle$$

$a(r_i)$ is scalar with respect to $\mathbf{s}_i \rightarrow m'_s = m''_s$ and value is $m'_s$-independent

$a(r_i)$ *i*s scalar with respect to $\boldsymbol{\ell}_i \rightarrow \ell' = \ell'', m'_\ell = m''_\ell,$ and value is $m'_\ell$-independent

$\boldsymbol{\ell}_i$ can't change $\ell$ 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 $\left\langle n'\ell'm'_\ell sm'_s \middle| \mathbf{H}^{SO} \middle| n\ell m_\ell s m_s \right\rangle = \delta_{\ell'\ell} \left\langle n'\ell' \middle|\middle| a(r_i) \middle|\middle| n\ell \right\rangle \left\langle \ell m'_\ell sm'_s \middle| \boldsymbol{\ell} \cdot \mathbf{s} \middle| \ell m_\ell s m_s \right\rangle$

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

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

Spin-orbit scaling for all members of a Rydberg series.

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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 $\ell$: $\underbrace{n\ell \leftrightarrow n'\ell}_{\text{same } \ell}$

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Examples

A is a single Slater determinant

$$\left\langle A\left|\mathrm{H}^{\mathrm{SO}}\right|A\right\rangle = \sum_{\substack{k \\ \text{spin-orbitals}}} \left\langle u_k\left|a\left(r_k\right)\ell_k\cdot \mathrm{s}_k\right|u_k\right\rangle$$

$$= \sum_k \zeta_{n_k\ell_k}\left\langle \ell_k m_{\ell_k} s_k m_{s_k}\left|\underbrace{\ell\cdot \mathrm{s}}_{\substack{\text{diagonal element picks out } \ell_z\mathbf{s}_z}}\right|\ell_k m_{\ell_k} s_k m_{s_k}\right\rangle$$

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

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

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

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

The matrix element is evaluated 2 ways in order to reduce a many-e⁻ spin-orbit coupling constant ($\varsigma$(N,L,S)) to a sum of one-e⁻ orbital coupling constants ($\varsigma_{n\ell}$)! This reveals the "periodicity" for which the periodic table is famous.

Example 1. $nf^2$ $^3$H uncoupled representation

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

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

(fill in the steps!)

Example 2. $nf^2$ in coupled representation

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

Landé :

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

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

($J(J+1)$: $6\cdot 7$; $L(L+1)$: $5\cdot 6$; $S(S+1)$: $1\cdot 2$)

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

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

$$\therefore \underbrace{\zeta\left(nf^2, {}^3H\right)}_{\text{what you measure}} = \underbrace{\zeta_{nf}/2}_{\text{what you want to know}}$$

Example 3: $\zeta(nf^2, {}^3F)$

$^3$F is never expressed as a single Slater determinant for any value of ($M_L$,$M_S$)

Evaluate in either of 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].

$M_L = 3, M_S = 1$ box: contains only $||3\alpha 0\alpha||, ||2\alpha 1\alpha||$

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

1st Matrix Element $\left\langle ||3\alpha 0\alpha|| \right\rangle = \left\langle ||3\alpha 0\alpha|| \middle| \mathrm{H^{SO}} \middle| ||3\alpha 0\alpha|| \right\rangle = \hbar^2\zeta_{nf}\left[\frac{3}{2} + 0\right]$

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

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

exploit sum rule $E\left( {}^3H\ M_L = 3\ M_S = 1 \right) = \left\langle {}^3H\ M_L = 3\ M_S = 1 \left| \mathrm{H}^{\mathrm{SO}} \right| {}^3H\ 31 \right\rangle = \zeta\left( nf^2, {}^3H \right) \hbar^2 3 \cdot 1$

but we already showed that $\zeta(nf^2, {}^3H) = \zeta_{n\ell}/2$

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

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

sum for the $M_L = 3$, $M_S = 1$ box

$$= \left\langle {}^3F\ 31 \left| \mathbf{H}^{\mathrm{SO}} \right| {}^3F\ 31 \right\rangle = \zeta\left( nf^2, {}^3F \right)\left( 3 \cdot 1 \right)\hbar^2$$

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

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

[not true for all configurations]

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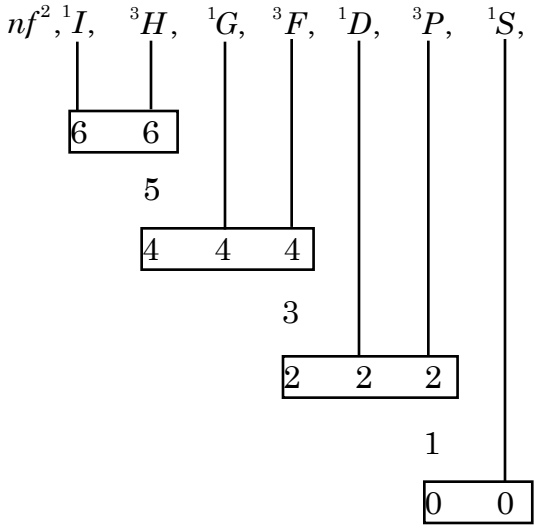
We are not done. There are some $\Delta J = 0$ *off-diagonal in L,S matrix elements* among the L-S-J terms of the same configuration.

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



set up the J = 6 matrix because it is simplest

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

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

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

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

$$= \left\langle 3\beta\left|\frac{1}{2}\ell_+ s_-\right|2\alpha\right\rangle$$

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

zero for all singlet states

$$\mathbf{H}^{\mathrm{SO}}_{J=6} = \begin{matrix} \\ {}^1I_6 \\ {}^3H_6 \end{matrix}\begin{matrix} \begin{matrix} \downarrow \end{matrix} \\ \begin{pmatrix} 0 & (3/2)^{1/2} \\ (3/2)^{1/2} & 5/2 \end{pmatrix} \end{matrix}$$

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

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

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for more complex configurations such as $(n\ell)^a(n'\ell')^b \rightarrow \varsigma_{n\ell}$ and $\varsigma_{n'\ell'}$: two ς parameters needed, 1 for each of the two open subshell orbitals.

But can use the value of $\varsigma_{n\ell}$ determined from some other configuration:
e.g. $\varsigma_{3d}$ from $3d^6 4s^2$ can be used to predict the 3d part of $\mathbf{H}^{\mathrm{SO}}$ in $3d^6\ 4s4p$. Unexpected *inter-relationships* between superficially unrelated observables. Small number of control parameters. Magic decoder!

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**Hund's 3rd Rule**: lowest energy J level of lowest energy L – S term is J = |L – S| if subshell is less than ½ full, but it is J = L + S if subshell is more than ½ full, and J = S (no spin-orbit splitting) because L = 0 for a half-filled subshell. Sign of ζ(n,L,S) as diagnostic!

NEXT TIME!

5.73 Quantum Mechanics I
Fall 2018