Configuration and Resultant L-S-J "Terms" (States)

Last time: Matrix elements of Slater determinantal wavefunctions
Normalization: $(N!)^{-1/2}$
$\mathbf{F}(i)$: selection rule (Δs-o ≤ 1), sign depending on order
$\mathbf{G}(i,j)$: selection rule (Δs-o ≤ 2), two additive terms with opposite signs

TODAY: Configuration $\rightarrow$ which L-S terms? $\rightarrow$ L-S basis states $\rightarrow$ matrix elements

- Method of crossing out M_L, M_S boxes
- Ladders plus orthogonality
- Many worked out examples that will not be covered in lecture.

KEY IDEAS:

* $1/r_{ij}$ destroys spin-orbital labels as good quantum numbers.
* Configuration splits into widely spaced L-S-J "terms."
* $\sum_{i>j} 1/r_{ij}$ is a *scalar operator* with respect to **L, S,** and **J**, thus matrix elements are independent of M_L, M_S, and M_J.
* Configuration generates all possible M_L, M_S components of each L-S term.
* It can't matter which M_L, M_S component we use to evaluate the $1/r_{ij}$ matrix elements
* Method of microstates and boxes: Book-keeping for which L-S states are present, organizes the algebra to find eigenstates of L^2 and S^2, as basis for "sum rule" method (Lecture #33).

Longer term goals: represent "electronic structure" in terms of properties of atomic orbitals

1. Configuration $\rightarrow$ L,S terms
2. Derive correct linear combination of Slater determinants for each L,S term: several methods
3. $1/r_{ij}$ matrix elements $\rightarrow$ F_k, G_k Slater-Condon parameters, Slater sum rule trick
4. $\mathbf{H}^{SO}$ Spin-Orbit
   * $\zeta(NLS)$ — coupling constant for each L-S term in an electronic configuration
   * $\zeta(NLS) \leftrightarrow \zeta_{n\ell}$ a single spin-orbit orbital integral for the entire configuration
   * full H^{SO} matrix in terms of $\zeta_{n\ell}$
5. Stark effect, Zeeman effect, optical transitions
6. transition strengths

$$\left\langle n\ell \| r \| n'\ell+1 \right\rangle \ \left(\text{matrix elements of } \vec{\mathbf{r}}, \text{ magnetic g-values}\right)$$

There are a vastly smaller number of orbital parameters than the number of electronic states. The periodic table provides a basis for rationalization of orbital parameters (dependence on atomic number and on number of electrons.) Intuition vs. numerical description.

Which L-S terms belong to $(nf)^2$

* shorthand notation for spin-orbitals

  $n\ell m_\ell \alpha/\beta$ e.g. $4f3\alpha$, could suppress 4 and f

($\|$main diagonal$\|$ represents Slater determinant, $|\ \rangle|\ \rangle$...represents simple product of spin-orbitals)

* standard order (to get signs internally consistent): for f spin-orbitals

  $3\alpha 3\beta 2\alpha 2\beta \ldots -3\alpha\ -3\beta$ is my standard order for f ($\ell = 3$)

$(2\ell+1)(2s+1) = (7)(2) = 14$ spin-orbitals

* which Slater determinants are nonzero and distinct (i.e., not identical when spin-orbitals are permuted to a different ordering)?

f^2 - take any 2 s-o's and list in *standard order*

$\|2\alpha 0\alpha\|$ is OK, but $\|0\alpha 2\alpha\|$ is not in standard order, and $\|2\beta 2\beta\| = 0$.

How many nonzero and distinct Slater determinants are there for f^2?

$$\left.\begin{array}{l}\text{14 spin-orbitals}\\ \text{2 identical electrons}\end{array}\right]\frac{14\cdot 13}{2} = \mathbf{91}$$ **Slater determinants!**

$$\text{general } (n\ell)^p : \prod_{n\ell} \frac{[2(2\ell+1)]!}{[2(2\ell+1)-p]!}\frac{1}{p!}$$

put p indistinguishable e⁻ *and* $2(2\ell+1)-p$ indistinguishable "holes" into $2(2\ell+1)$ boxes

subshell : one such factor for each subshell

How to generate all 91 linear combinations of Slater determinants that correspond to the 91 possible $|LM_L SM_S\rangle$ basis states that arise from f^2? Next lecture.

all of these are labor intensive:

* ladders plus orthogonality ← you know how to do this
* construct and diagonalize $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices
* projection operators
* 3-j, 6-j, 9-j coefficients ← you should begin to know this

updated August 27, 2020 @ 1:42 PM

Sometimes all we want to know is "which L-S terms"?
[WHY? $1/r_{ij}$ is scalar with respect to **L**,**S**, and **J**, thus eigenenergies are independent of M_L, M_S and M_J.]

EASY because we can read $\mathbf{L}_z = \sum_i \ell_{1z}$ and $\mathbf{S}_z = \sum_i \mathbf{s}_{1z}$ directly from the spin-orbital labels.

$$L_z \left\| 2\alpha 1\bar{\beta} \right\| = \sum_{i=1}^{2} \ell_{iz} \left\| 2\alpha 1\bar{\beta} \right\| = \hbar\left[2+1\right] \left\| 2\alpha 1\bar{\beta} \right\|$$

$$M_L = 3$$

M_L is sum of m_ℓ's
M_S is sum of m_S's

NONLECTURE

What about $\mathbf{L}^2$? Can do this in either of two ways:

* as below (very cumbersome)

* $\mathbf{L}^2 = \mathbf{L}_z^2 + (1/2)(\mathbf{L}_+\mathbf{L}_- + \mathbf{L}_-\mathbf{L}_+)$ [separately apply each $1e^-$ operator rather than treat entire operator as a $2e^-$ operator.]

very laborious because $\mathbf{L}^2 = \sum_{i,j} \ell_i \cdot \ell_j = \underbrace{\sum \ell_i^2}_{\text{one } e^-} + 2\underbrace{\sum_{i>j} \ell_i \ell_j}_{\text{two}-e^-}$

$$\mathbf{L}^2 \left\| 2\alpha 1\beta \right\| \neq \sum_i \hbar^2 \ell_i(\ell_i + 1) \left\| 2\alpha 1\beta \right\| \qquad \ell_i = 3 \text{ for } f$$

WORK OUT $\mathbf{L}^2$ matrix for $M_L = 3$, $M_S = 0$ block of f^2 for future reference

$$\mathbf{L}^2 = \sum_{i,j} \ell_i \cdot \ell_j = \underbrace{\sum_i \left[\ell_i^2\right] + 2\sum_{i>j}\left[\ell_{iz}\ell_{jz}\right.}_{\Delta\ell = 0,\ \Delta M_\ell = 0} + \underbrace{\left.\frac{1}{2}\left(\ell_{i+}\ell_{j-} + \ell_{i-}\ell_{j+}\right)\right]}_{\substack{\Delta\ell = 0,\ \Delta M_\ell = 0 \\ \Delta m_{\ell 1} = -\Delta m_{\ell 2} = \pm 1}}$$

all are $\Delta M_S = \Delta m_{s_1} = \Delta m_{s_2} = 0$

$\ell(\ell+1)$ → ; $m_{\ell 1} m_{\ell 2}$ → ; non-standard order →

$$\mathrm{L}^2\|2\alpha 1\beta\| = \hbar^2 \begin{bmatrix} (12+12)\|2\alpha1\beta\| + 2(2\cdot 1)\|2\alpha 1\beta\| + \\ [3\cdot 4 - 2\cdot 1]^{1/2}[3\cdot 4 - 1\cdot 2]^{1/2}\|1\alpha 2\beta\| + \\ [3\cdot 4 - 2\cdot 3]^{1/2}[3\cdot 4 - 1\cdot 0]^{1/2}\|3\alpha 0\beta\| \end{bmatrix}$$

Many steps skipped … $\ell_{1-}\ell_{2+}$, $\ell_{1+}\ell_{2-}$

$$= \hbar^2\left[28\|2\alpha1\beta\| - 10\|2\beta1\alpha\| + 6\cdot 2^{-1/2}\|3\alpha0\beta\|\right]$$

All of the 12, 21 exchange-type matrix elements are 0 because of m_s mismatch.

e.g. $$\left\langle 2\alpha(1)1\beta(1)\middle| \begin{matrix}\text{space only}\\ \text{operator}\end{matrix} \middle| 1\beta(1)2\alpha(2)\right\rangle = 0$$

Recall ± (⟨12|G|12⟩ – ⟨12|G|21⟩) for $2e^-$ operator.
We get:

$$\mathbf{L}^2\|2\beta1\alpha\| = \hbar^2\left[28\|2\beta1\alpha\| - 10\|2\alpha1\beta\| + \left(12\cdot 2^{-1/2}\right)\|3\beta0\alpha\|\right]$$

$$\mathbf{L}^2\|3\alpha0\beta\| = \hbar^2\left[(24+3\cdot 0)\|3\alpha0\beta\| + \left(12\cdot 2^{-1/2}\right)\|2\alpha1\beta\|\right]$$

$$\mathbf{L}^2\|3\beta0\alpha\| = \hbar^2\left[24\|3\beta0\alpha\| + \left(12\cdot 2^{-1/2}\right)\|2\beta1\alpha\|\right]$$

$$\mathrm{L}^2 = \hbar^2 \quad \begin{matrix} \|3\alpha0\beta\| \\ \|2\alpha1\beta\| \\ -\|1\alpha2\beta\| \\ -\|0\alpha3\beta\| \end{matrix} \begin{pmatrix} 24 & 6\cdot 2^{1/2} & 0 & 0 \\ 6\cdot 2^{1/2} & 28 & -10 & 0 \\ 0 & -10 & 28 & 6\cdot 2^{1/2} \\ 0 & 0 & 6\cdot 2^{1/2} & 24 \end{pmatrix}$$

[the bottom two Slater determinants are intentionally out of standard order to display effects of decreasing values of $m_\ell(1)$ and increasing values of $m_\ell(2)$.]

$\left|LSM_LM_S\right\rangle = \left|5130\right\rangle$

Example: found eigenvalues and eigenvectors of this block $M_L = 3$, $M_S = 0$ of f^2

$$\frac{\mathbf{L}^2}{\hbar^2}\left[3^{-1/2}\|3\alpha 0\beta\| + 3^{-1/2}\|3\beta 0\alpha\| + 6^{-1/2}\|2\alpha 1\beta\| + 6^{-1/2}\|2\beta 1\alpha\|\right] = 30[\;] \quad L = 5$$

$$\frac{\mathbf{L}^2}{\hbar^2}\left[6^{-1/2}\|3\alpha 0\beta\| + 6^{-1/2}\|3\beta 0\alpha\| - 3^{-1/2}\|2\alpha 1\beta\| - 3^{-1/2}\|2\beta 1\alpha\|\right] = 12[\;] \quad L = 3$$

$$\frac{\mathbf{L}^2}{\hbar^2}\left[11^{-1/2}\|3\alpha 0\beta\| - 11^{-1/2}\|3\beta 0\alpha\| + 3\cdot 22^{-1/2}\|2\alpha 1\beta\| - 3\cdot 22^{-1/2}\|2\beta 1\alpha\|\right] = 42[\;] \quad L = 6$$

$$\frac{\mathbf{L}^2}{\hbar^2}\left[3\cdot 22^{-1/2}\|3\alpha 0\beta\| - 3\cdot 22^{-1/2}\|3\beta 0\alpha\| - 11^{-1/2}\|2\alpha 1\beta\| + 11^{-1/2}\|2\beta 1\alpha\|\right] = 20[\;] \quad L = 4$$

(Note how easy it is to see that normalization is correct.) Look at the sum of the squares of each coefficient!

a lot of algebra is not presented here! (especially the derivation of the 4 eigenvectors)

* each Slater basis state gets "used up" [sum of squares of that basis set is 1]
* the first 2 eigenfunctions are in the form: $\alpha\beta + \beta\alpha \rightarrow S = 1$
* the second 2 eigenfunctions are in the form: $\alpha\beta - \beta\alpha \rightarrow S = 0$

You could prove these S = 1 and S = 0 results by applying $\mathbf{S}^2$ to above eigenfunctions of $\mathbf{L}^2$.

We have obtained $\left|LSM_LM_S\right\rangle = \left|5130\right\rangle, \left|3130\right\rangle, \left|6030\right\rangle$, and $\left|4030\right\rangle$ eigenstates.

END OF NON-LECTURE

Non-lecture pages were intended to show that applying $\mathbf{L}^2$ and $\mathbf{S}^2$ to Slater determinants is laborious — much more so than applying $\mathbf{L}_z$ and $\mathbf{S}_z$.

This is one reason why we use the "crossing out M_L, M_S microstates" method to figure out which L,S states must be considered. Often this is sufficient — and it can be the basis for some shortcut tricks!

The M_L, M_S method works because:

* each configuration generates the full (2L + 1) (2S + 1) manifold of M_L, M_S states associated with each L,S term. Why? If you have one $|M_L M_S\rangle$ member of $|LM_L SM_S\rangle$ you can generate all of the others for that L,S using $\mathbf{L}_\pm$ and $\mathbf{S}_\pm$ operators.
* This must be true because, starting with $M_L = L$, $M_S = S$, $\mathbf{L}_-$ and $\mathbf{S}_-$ can be used to generate all M_L, M_S components of the full L,S term without the need to go outside the specific configuration.

M_L, M_S method

	$M_L = L_{MAX}$	$L_{MAX} - 1$	$L_{MAX} - 2$ …	0
$M_S = S_{MAX}$	list all Slater determinants			
$S - 1$				
0				

$S_{MAX} = (\#\text{ of } e^-)/2.$

No need to include negative values of M_S or M_L. Why? They are accessed by $\mathbf{L}_- + \mathbf{S}_-$ and contain no new information.

f^2

M_S \ M_L	6(I)	5(H)	4(G)	3(F)	2(D)	1(P)	0(S)
1	~~‖3α3α‖~~	‖3α2α‖	‖3α1α‖	‖3α0α‖	‖2α0α‖	‖3α − 2α‖	‖3α − 3α‖
exclusively S = 1 states			~~‖2α2α‖~~	‖2α1α‖	‖3α − 1α‖	‖2α − 1α‖	‖2α − 2α‖
					~~‖1α1α‖~~	‖1α0α‖	‖1α − 1α‖
							~~‖0α0α‖~~
0	‖3α3β‖	‖3α2β‖	‖3α1β‖	‖3α0β‖	‖2α0β‖	‖3α − 2β‖	‖3α − 3β‖
		‖3β2α‖	‖3β1α‖	‖3β0α‖	‖2β0α‖	‖3β − 2α‖	‖3β − 3α‖
Both S = 1 and S = 0 states			‖2α2β‖	‖2α1β‖	‖3α − 1β‖	‖2α − 1β‖	‖2α − 2β‖
				‖2β1α‖	‖3β − 1α‖	‖2β − 1α‖	‖2β − 2α‖
					‖1α1β‖	‖1α0β‖	‖1α − 1β‖
						‖1β0α‖	‖1β − 1α‖
							‖0α0β‖

Slaters for f^2

Need not include $M_S < 0$ or $M_L < 0$ because these are identical to the $M_L > 0$ and $M_S > 0$ quadrant.

Notice that as you go down by 1 in M_L, the number of Slater determinants in each M_L, M_S box increases only by 1. This is a prerequisite for using the $\mathbf{L}_-$ plus orthogonality method! This useful simplicity does not occur as you go down a column in M_S.

This convenient situation does not occur for d^3 or f^3. Why? Because there can be more than one *L*-*S* term of a specified symmetry. For example, for d^2 there are ${}^1S$, ${}^3P$, ${}^1D$, ${}^3F$, ${}^1G$ terms, but for d^3 there are ${}^2P$, ${}^4P$, **two** ${}^2D$, ${}^2F$, ${}^4F$, ${}^2G$ and ${}^2H$ terms.

No J by convention (I, K)

	S	P	D	F	G	H	I	K
L =	0,	1,	2,	3,	4,	5,	6,	7

Start in extreme M_L, M_S corner — This generally contains only one Slater determinant

$L = M_{L_{MAX}}$, $S = M_{S_{MAX}}$ so we have one of the L - S terms

This L-S term includes one of each M_L, M_S in the range

$$-L \le M_L \le L$$
$$-S \le M_S \le S$$

This means this L-S term will "use up" the equivalent of one Slater determinant in each M_L,M_S box.

Bookkeeping: cross out one Slater determinant, any one, from each relevant M_L,M_S box.

Now repeat, again starting at the remaining extreme M_L,M_S corner

etc.	* ^1I	1×13	= 13
	* ^3H	3×11	= 33
	* ^1G	1×9	= 9
	* ^3F	3×7	= 21
	* ^1D	1×5	= 5
	* ^3P	3×3	= 9
	* ^1S	1×1	= 1
			91

91 as required! [It is a good idea to use this total degeneracy of the configuration as a check.]

Since there is only one Slater determinant in the $M_L = 5$, $M_S = 1$ box, generate all triplets by repeated application of $\mathbf{L}_-$ to $||3\alpha\, 2\alpha||$ (plus orthogonality) and generate all singlets by $\mathbf{L}_-$ on $||3\alpha\, 3\beta||$. Many orthogonalization steps are needed! Especially for singlets. Need to use $\mathbf{S}_-$ also.

Before illustrating the ladders plus orthogonality method, it is useful to show some patterns and list some valuable tricks.

The most difficult cases are $(n\ell)^m$ where m = 2, 3,… 2ℓ.

Easy to combine $n\ell$ with $n'\ell'$ because no need for special bookkeeping.

ℓ	$(n\ell)^2$	$(n\ell)^3$
s	^1S	—
p	^1D, ^3P, ^1S	^4S, ^2D, ^2P
d	^1G, ^3F, ^1D, ^3P, ^1S	^2H, ^2G, ^2F, ^4F, $^2D(2)$, ^4P, ^2P
f	^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S	
	A simple, memorable pattern	Rather complicated

Get the same L-S states for 2 and 3 "holes" (e.g. $p^4 \leftrightarrow p^2$, $d^3 \leftrightarrow d^7$) instead of electrons.

$$\text{Also } (n\ell)^2 n'\ell' \rightarrow \left[n\ell^{2\ 2S+1}L\right] \otimes \left({}^2\ell'\right) = {}^{(2S+2,\text{ and }2S)}\left(L+\ell', L+\ell'-1, \cdots |L-\ell'|\right)$$

Simple vector coupling of the $n'\ell'$ electron to the two-electron $n\ell^{2\ 2S+1}L$ term. No Pauli exclusion because $n'\ell'$ is distinguished from $n\ell$.

When the e^- are in distinct subshells (different values of ℓ and n), there is no need to be as careful about the exclusion principle.

<u>Ladders plus Orthogonality Method</u>

f^2 example

Start with 2 extreme <u>UNIQUE</u> states

1. $\left|{}^3\text{H}\, M_L = 5, M_s = 1\right\rangle = \left\|3\alpha 2\alpha\right\|$

Use this to generate all triplet states by applying **L_** repeatedly and using orthogonality when necessary. Note that # of determinants in each M_L,M_S=1 box increases no faster than in steps of 1.

To get to ^{3}P, must not only apply orthogonality several times, but must follow each L state down to the M_L = 1 box!

2. To get singlets, start with the unique $|{}^1\text{I}\, M_L = 6, M_s = 0\rangle$ state.

Again, as **L_** takes us to successively lower-M_L boxes, # of determinants increases in steps of 1. But some of these steps are due to triplets with M_S = 0. Need to step triplets down into M_S = 0 territory using **S_** once. Lots more orthogonality steps, lots more trails being followed. AWFUL, but do-able.

<u>Nonlecture</u>

$$\left|{}^3\text{H}\; M_L M_S\right\rangle =$$

$$\mathbf{L}_-\left|{}^3\text{H}\; 51\right\rangle = \sum_i \ell_{i^-}\left\|3\alpha 2\alpha\right\|$$

$$\hbar\left[5\cdot 6 - 5\cdot 4\right]^{1/2}\left|{}^3\text{H}\; 41\right\rangle = \hbar\left[3\cdot 4 - 3\cdot 2\right]^{1/2}\left\|2\alpha 2\alpha\right\| + \hbar\left(3\cdot 4 - 2\cdot 1\right)^{1/2}\left\|3\alpha 1\alpha\right\|$$

($\left\|2\alpha 2\alpha\right\| \rightarrow 0$)

$$\left|{}^3\text{H}\; 41\right\rangle = \left\|3\alpha 1\alpha\right\| \qquad \text{big surprise!}$$

$$\mathbf{L}_-\left|{}^3\text{H}\; 41\right\rangle = \Sigma\ell_{i^-}\left\|3\alpha 1\alpha\right\|$$

$$\left|{}^3\text{H}\; 31\right\rangle = \left(1/3\right)^{1/2}\left\|2\alpha 1\alpha\right\| + \left(2/3\right)^{1/2}\left\|3\alpha 0\alpha\right\|$$

orthogonality: $$\left|{}^3\text{F}\; 31\right\rangle = \left(\frac{2}{3}\right)^{1/2}\left\|2\alpha 1\alpha\right\| - \left(\frac{1}{3}\right)^{1/2}\left\|3\alpha 0\alpha\right\|$$

and so on, to get all $|{}^3\text{L}\; L\; 1\rangle$ many-electron functions (L = M_L, 1 = M_S)

$M_S = 0$

Try a detour into singlet territory, and then check for self-consistency.

$$\mathbf{S}_{-}\left|{}^3F\quad 31\right\rangle = \sum_i \mathbf{s}_{i^-}\left[\left(\frac{2}{3}\right)^{1/2}\|2\alpha 1\alpha\| - \left(\frac{1}{3}\right)^{1/2}\|3\alpha 0\alpha\|\right]$$

(by orthogonality with) $\left|{}^3H\quad 31\right\rangle$

$$\hbar\left[1\cdot 2 - 1\cdot 0\right]^{1/2}\left|{}^3F\quad 30\right\rangle = \hbar\left[\left(\frac{2}{3}\right)^{1/2}\left[\frac{1}{2}\cdot\frac{3}{2} - \frac{1}{2}\left(-\frac{1}{2}\right)\right]^{1/2}\left(\|2\beta 1\alpha\| + \|2\alpha 1\beta\|\right) - \left(\frac{1}{3}\right)^{1/2}\left[1\right]^{1/2}\left(\|3\beta 0\alpha\| + \|3\alpha 0\beta\|\right)\right]$$

this factor is always 1 or 0

$$\left|{}^3F\,30\right\rangle = \left(\frac{1}{3}\right)^{1/2}\left(\|2\beta 1\alpha\| + \|2\alpha 1\beta\|\right) - \left(\frac{1}{6}\right)^{1/2}\left(\|3\beta 0\alpha\| + \|3\alpha 0\beta\|\right)$$

$$\mathbf{S}_{-}\left|{}^3H\,31\right\rangle = \sum_i s_{i^-}\left[\left(\frac{1}{3}\right)^{1/2}\|2\alpha 1\alpha\| + \left(\frac{2}{3}\right)^{1/2}\|3\alpha 0\alpha\|\right]$$

$$\left|{}^3H\,30\right\rangle = \left(\frac{1}{6}\right)^{1/2}\left(\|2\beta 1\alpha\| + \|2\alpha 1\beta\|\right) + \left(\frac{1}{3}\right)^{1/2}\left(\|3\beta 0\alpha\| + \|3\alpha 0\beta\|\right)$$

There are 4 Slater determinants in the $M_L = 3$, $M_S = 0$ box. We can't find the other two singlet linear combinations uniquely without using $\mathbf{L}_{-}$ on the extreme singlets.

$$L_{-}\left|{}^1I\quad 60\right\rangle = \Sigma\ell_{i^-}\|3\alpha 3\beta\|$$

$$\hbar\left[6\cdot 7 - 6\cdot 5\right]^{1/2}\left|{}^1I\quad 50\right\rangle = \hbar\left[3\cdot 4 - 3\cdot 2\right]^{1/2}\left(\|2\alpha 3\beta\| + \|3\alpha 2\beta\|\right)$$

wrong order: must change sign to reverse order

$$\left|{}^1I\quad 50\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha 2\beta\| - \|3\beta 2\alpha\|\right]$$

orthogonality

$$\left|{}^3H\quad 50\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha 2\beta\| + \|3\beta 2\alpha\|\right]$$

$$L_{-}\left|{}^1I\quad 50\right\rangle = \Sigma\ell_{i^-}\left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha 2\beta\| - \|3\beta 2\alpha\|\right]$$

wrong order

$$\left|{}^{1}\text{I}\,40\right\rangle = \left(\frac{1}{44}\right)^{1/2}\left[(10)^{1/2}\left(\|3\alpha 1\beta\| - \|3\beta 1\alpha\|\right) + 6^{1/2}\left(\|2\alpha 2\beta\| - \|2\beta 2\alpha\|\right)\right]$$

$$\left|{}^{1}\text{I}\,40\right\rangle = \left(\frac{5}{22}\right)^{1/2}\left[\left(\|3\alpha 1\beta\| - \|3\beta 1\alpha\|\right) + \left(\frac{6}{11}\right)\|2\alpha 2\beta\|\right]$$

$$\left|{}^{3}\text{H}\,40\right\rangle = \left(\frac{1}{20}\right)^{1/2}\left[(6)^{1/2}\left(\|2\alpha 2\beta\| + \|2\beta 2\alpha\|\right) + 10^{1/2}\left(\|3\alpha 1\beta\| + \|3\beta 1\alpha\|\right)\right]$$

wrong order

$$\left|{}^{3}\text{H}\,40\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left(\|3\alpha 1\beta\| + \|3\beta 1\alpha\|\right)$$

orthogonality

$$\left|{}^{1}\text{G}\,40\right\rangle = \left(\frac{3}{11}\right)^{1/2}\left[\left(\|3\alpha 1\beta\| - \|3\beta 1\alpha\|\right) - \left(\frac{5}{11}\right)^{1/2}\|2\alpha 2\beta\|\right]$$

At last we are ready to enter the $M_L = 3$, $M_S = 0$ block!

It is clear that if we apply $\mathbf{L}_-$ to $|{}^3\text{H}\ 40\rangle$, we will get the same form that we already derived starting from $|{}^3\text{H}\ 51\rangle$ Instead, let's lower $|{}^1\text{I}\ 40\rangle$.

$$\mathbf{L}_-\left|{}^{1}\text{I}\ \ 40\right\rangle = \sum_i \ell_{i^-}\left\{\left(\frac{5}{22}\right)^{1/2}\left[\|3\alpha 1\beta\| - \|1\beta 3\alpha\|\right] + \left(\frac{6}{11}\right)^{1/2}\|2\alpha 2\beta\|\right\}$$

$$\left|{}^{1}\text{I}\ \ 30\right\rangle = (30)^{1/2}\left\{\left(\frac{5}{22}\right)^{1/2}(6)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right) + \left(\frac{5}{22}\right)^{1/2}(12)^{1/2}\left(\|3\alpha 0\beta\| - \|3\beta 0\alpha\|\right)\right.$$
$$\left. + \left(\frac{6}{11}\right)^{1/2}(10)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right)\right\}$$

$$\left|{}^{1}\text{I}\ \ 30\right\rangle = \left[\left(\frac{1}{22}\right)^{1/2} + \left(\frac{4}{22}\right)^{1/2}\right]\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right) + \left(\frac{2}{22}\right)^{1/2}\left(\|3\alpha 0\beta\| - \|3\beta 0\alpha\|\right)$$

$$\left|{}^{1}\text{I}\ \ \ 30\right\rangle = \left(\frac{9}{22}\right)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right) + \left(\frac{2}{22}\right)^{1/2}\left(\|3\alpha 0\beta\| - \|3\beta 0\alpha\|\right)$$

Finally, by orthogonality:

IMPORTANT →

$$\left|{}^{1}\text{G}\ \ \ 30\right\rangle = -\left(\frac{1}{11}\right)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right) + \left(\frac{9}{22}\right)^{1/2}\left(\|3\alpha 0\beta\| - \|3\beta 0\alpha\|\right)$$

Does this match what one would get from $\mathbf{L}_-|{}^1G\ 40\rangle$?

$$\mathbf{L}_-\left|{}^1\mathrm{G}\ \ 40\right\rangle = \sum_i \ell_{i^-}\left\{\left(\frac{3}{11}\right)^{1/2}\left[\|3\alpha1\beta\| - \|1\beta3\alpha\|\right] - \left(\frac{5}{11}\right)^{1/2}\|2\alpha2\beta\|\right\}$$

$$\left|{}^1\mathrm{G}\ \ 30\right\rangle = (8)^{1/2}\left\{\left(\frac{5}{11}\right)^{1/2}(6)^{1/2}\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right) + \left(\frac{3}{11}\right)^{1/2}(12)^{1/2}\left(\|3\alpha0\beta\| - \|3\beta0\alpha\|\right)\right.$$

$$\left. - \left(\frac{5}{11}\right)^{1/2}(10)^{1/2}\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right)\right\}$$

IMPORTANT $\longrightarrow$

$$\left|{}^1\mathrm{G}\ \ 30\right\rangle = -\left(\frac{1}{11}\right)^{1/2}\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right) + \left(\frac{9}{22}\right)^{1/2}\left(\|3\alpha0\beta\| - \|3\beta0\alpha\|\right)$$

checks!

End of Non-Lecture

As you see, this ladders plus orthogonality method is extremely laborious. There is a much better way!

** [There are several patterns: singlets for $M_S = 0$ always have the form $(\alpha\beta - \beta\alpha)$ and $M_S = 0$ triplets always $(\alpha\beta + \beta\alpha)$.

This can be generalized for any value of S (page 151 of Hélène Lefebvre-Brion-Robert Field Perturbations 2004 book)
[Also M. Yamazaki, Sci. Rep. Kanezawa Univ. 8, 371 (1963).]

2. **Failure and Inconvenience of ladder method**
The ladder method is OK when you have a single target $|LM_L SM_S\rangle$ state, especially when it is near an edge of the M_L,M_S box diagram. Essential that # of Slater determinants in each $M_L M_S$ box increases in steps of 1 as you step down in M_L or M_S.

Fails when there are two L-S terms of same L and S in a given configuration. Then we must set up a 2 × 2 secular equation anyway.

e.g. $(nd)^3\ \ {}^2\mathrm{H}, {}^2\mathrm{G}, {}^2\mathrm{F}, {}^4\mathrm{F}, \boxed{{}^2\mathrm{D}(2),} {}^4\mathrm{P}, {}^2\mathrm{P}$

3. **$\mathbf{L}^2$ and $\mathbf{S}^2$ Matrix Method**
Another method is based on constructing $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices in the Slater determinantal basis set. This is no cakewalk either (but this is easier)!

Since usually $S_{MAX} \ll L_{MAX}$ for a configuration when using $\mathbf{L}^2 + \mathbf{S}^2$ matrices method, it is best to start with the $\mathbf{S}^2$ matrix because it is simpler.