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

TODAY: Configuration ∅ which L-S terms? ∅ L-S basis states ∅ matrix elements

Method of crossing out M_L, M_S boxes
ladders plus orthogonality
Many worked out examples 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 which L-S states are present, organize the algebra to find eigenstates of L^2 and S^2, basis for "sum rule" method (next lecture).

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

1. Configuration $\rightarrow$ L,S terms
2. 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. $\mathbf{H}^{SO}$
   * ζ(NLS) — coupling constant for each L-S term in an electronic configuration
   * ζ(NLS) $\leftrightarrow$ $\zeta_{n\ell}$ one spin-orbit orbital integral for entire configuration
   * full H^{SO} matrix in terms of $\zeta_{n\ell}$
5. Stark, Zeeman, optical transitions
6. transition strengths $\langle n\ell \| r \| n'\ell+1\rangle$ (matrix elements of $\vec{\mathbf{r}}$, g - values)

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.)

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

* shorthand notation for spin - orbitals

  $n\mathbf{l}m_{\mathbf{l}}\alpha/\beta$ e.g. $4f3\alpha$, could suppress 4 and f

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

* standard order (to get signs internally consistent)

  $3\alpha3\beta2\alpha2\beta\ \ldots\ -3\alpha\ -3\beta$ is my standard order for f

$(2\mathbf{l}+1)(2s+1) = (7)(2) = 14$ spin orbitals

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

$\boxed{f^2 \text{ - take any 2 s-o's and list in standard order}}$

$\|2\alpha0\alpha\|$ is OK but $\|0\alpha2\beta\|$ is not in standard order and $\|2\beta2\beta\| \equiv 0$

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

$$\left.\begin{array}{l}\text{14 spin - orbitals}\\ \text{2 identical electrons}\end{array}\right] \frac{14\cdot13}{2} = \mathbf{91} \quad \textbf{Slater determinants!}$$

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

put p indistinguishable e^- and $2(2\ell+1)$-p 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 $|LM_LSM_S\rangle$ basis states that arise from f^2? Next lecture.

all of these are labor intensive

* ladders plus orthogonality
* construct and diagonalize $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices
* projection operators
* 3-j, 6-j, 9-j coefficients

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 can read $\mathbf{L}_z = \sum \mathbf{l}_{iz}$ and $\mathbf{S}_z = \sum \mathbf{s}_{iz}$ directly from the spin-orbital labels.

$$\mathbf{L}_z \|2\alpha 1\beta\| = \sum_{i=1}^{2} \boldsymbol{\ell}_{iz} \|2\alpha 1\beta\| = \hbar[2+1]\|2\alpha 1\beta\|$$

$$M_L = 3$$

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
$$\mathbf{L}^2 = \sum_{\mathrm{i,j}} \boldsymbol{\ell}_{\mathrm{i}} \cdot \boldsymbol{\ell}_{\mathrm{j}} = \underbrace{\sum_{\mathrm{i}} \boldsymbol{\ell}_{\mathrm{i}}^2}_{\text{one } e^-} + 2\underbrace{\sum_{\mathrm{i>j}} \boldsymbol{\ell}_{\mathrm{i}}\boldsymbol{\ell}_{\mathrm{j}}}_{\text{two–}e^-}$$

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

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

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

all are $\Delta M_S = \Delta m_{S1} = \Delta m_{S2} = 0$

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

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

$\boldsymbol{\ell}_{1-}\boldsymbol{\ell}_{2+}$
$\boldsymbol{\ell}_{1+}\boldsymbol{\ell}_{2-}$

$$= \hbar^2\left[28\|2\alpha 1\beta\| - 10\|2\beta 1\alpha\| + 12\cdot 2^{-1/2}\|3\alpha 0\beta\|\right]$$

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

e.g. $\langle \|2\alpha 1\beta\| \text{spatial part} \|1\beta 2\alpha\| \rangle = 0$

Recall $\pm(\langle 12|G|12\rangle - \langle 12|G|21\rangle)$.

$$\mathbf{L}^2\|2\beta 1\alpha\| = \hbar^2\left[28\|2\beta 1\alpha\| - 10\|2\alpha 1\beta\| + 12\cdot 2^{-1/2}\|3\beta 0\alpha\|\right]$$
$$\mathbf{L}^2\|3\alpha 0\beta\| = \hbar^2\left[(24+3\cdot 0)\|3\alpha 0\beta\| + (12\cdot 2^{-1/2})\|2\alpha 1\beta\|\right]$$
$$\mathbf{L}^2\|3\beta 0\alpha\| = \hbar^2\left[24\|3\beta 0\alpha\| + (12\cdot 2^{-1/2})\|2\beta 1\alpha\|\right]$$

Many steps skipped …

$$\mathbf{L}^2 = \hbar^2 \begin{array}{r} \|3\alpha 0\beta\| \\ \|2\alpha 1\beta\| \\ -\|1\alpha 2\beta\| \\ -\|0\alpha 3\beta\| \end{array} \begin{pmatrix} 24 & 0 & 12\cdot 2^{-1/2} & 0 \\ 0 & 24 & 0 & 12\cdot 2^{-1/2} \\ 12\cdot 2^{-1/2} & 0 & 28 & -10 \\ 0 & 12\cdot 2^{-1/2} & -10 & 28 \end{pmatrix}$$

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

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

L = 5

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

L = 3

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

L = 6

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

L = 4

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

(Note how easy it is to see that normalization is correct.)

a lot of algebra is not presented here!

* each Slater basis state gets "used up"
* first 2 eigenfunctions are in form $\alpha\beta + \beta\alpha \rightarrow S = 1$

  second 2 eigenfunctions are in form $\alpha\beta - \beta\alpha \rightarrow S = 0$

prove this by applying $\mathbf{S}^2$ to above eigenfunctions of $\mathbf{L}^2$

END OF NON-LECTURE

Nonlecture pages were intended to show that applying $\mathbf{L}^2$ and $\mathbf{S}^2$ to Slater determinants is laborious — much moreso than $\mathbf{L}_z$ 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 — or can be the basis for some shortcut tricks!

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 a given L,S term. Why? If you have one $|M_L M_S\rangle$ you can generate all of the others using $\mathbf{L}_\pm$ and $\mathbf{S}_\pm$ operators.
* This must be true because, starting with $M_L = L$, $M_S = S$, L_- and S_- can be used to generate the full L,S term without the need to go outside the specific configuration.

M_L, M_S method

	$M_L = L_{MAX}$	$L - 1$	$L - 2$	…	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.

$\boxed{f^2}$

M_S \ M_L	6(I)	5(H)	4(G)	3(F)	2(D)	1(P)	0(S)
1	$\cancel{\|3\alpha 3\alpha\|}$	$\|3\alpha 2\alpha\|$	$\|3\alpha 1\alpha\|$	$\|3\alpha 0\alpha\|$	$\|2\alpha 0\alpha\|$	$\|3\alpha -2\alpha\|$	$\|3\alpha -3\alpha\|$
			$\cancel{\|2\alpha 2\alpha\|}$	$\|2\alpha 1\alpha\|$	$\|3\alpha -1\alpha\|$	$\|2\alpha -1\alpha\|$	$\|2\alpha -2\alpha\|$
					$\cancel{\|1\alpha 1\alpha\|}$	$\|1\alpha 0\alpha\|$	$\|1\alpha -1\alpha\|$
							$\cancel{\|0\alpha 0\alpha\|}$
0	$\|3\alpha 3\beta\|$	$\|3\alpha 2\beta\|$	$\|3\alpha 1\beta\|$	$\|3\alpha 0\beta\|$	$\|2\alpha 0\beta\|$	$\|3\alpha -2\beta\|$	$\|3\alpha -3\beta\|$
		$\|3\beta 2\alpha\|$	$\|3\beta 1\alpha\|$	$\|3\beta 0\alpha\|$	$\|2\beta 0\alpha\|$	$\|3\beta -2\alpha\|$	$\|3\beta -3\alpha\|$
			$\|2\alpha 2\beta\|$	$\|2\alpha 1\beta\|$	$\|3\alpha -1\beta\|$	$\|2\alpha -1\beta\|$	$\|2\alpha -2\beta\|$
				$\|2\beta 1\alpha\|$	$\|3\beta -1\alpha\|$	$\|2\beta -1\alpha\|$	$\|2\beta -2\alpha\|$
					$\|1\alpha 1\beta\|$	$\|1\alpha 0\beta\|$	$\|1\alpha -1\beta\|$
						$\|1\beta 0\alpha\|$	$\|1\beta -1\alpha\|$
							$\|0\alpha 0\beta\|$

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 in M_L, the number of Slater determinants in each M_L, M_S box increases only by one. This is a prerequisite for using the 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 are more than one L-S term of a given symmetry.

No J

$$\begin{array}{lcccccccc} & S & P & D & F & G & H & I & K \\ L = & 0, & 1, & 2, & 3, & 4, & 5, & 6, & 7 \end{array}$$

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

$$-L \leq M_L \leq L$$
$$-S \leq M_S \leq S$$

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 extreme M_L,M_S corner

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

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 needed! Especially for singlets. Need $\mathbf{S}_-$ also.

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

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, $\boxed{^2D(2)}$, ^4P, ^2P
f	^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S	
g		
	a simple, memorable pattern	rather complicated

same L-S states for 2 and 3 "holes" instead of electrons.

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

simple vector coupling

Ladder and Orthogonality Method

f^2 example

Start with 2 extreme UNIQUE states
$\left|{}^3H\ M_L = 5, M_S = 1\right\rangle = \|3\alpha 2\alpha\|$

Use this to generate all triplets 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 ^3P, must not only apply orthogonality several times, but must follow each L state down to the $M_L = 1$ box!

To get singlets, start with $\left|{}^1I\ M_L = 6, M_S = 0\right\rangle$.
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.

Nonlecture

$$\left|{}^3\mathrm{H}\ \mathrm{M_L M_S}\right\rangle$$

$$\mathbf{L}_-\left|{}^3\mathrm{H}\ 51\right\rangle = 2\boldsymbol{\ell}_{i^-}\|3\alpha 2\alpha\| \qquad\qquad 0$$

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

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

$$\mathbf{L}_-\left|{}^3\mathrm{H}\ 41\right\rangle = \Sigma\boldsymbol{\ell}_{i^-}\|3\alpha 1\alpha\|$$

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

orthogonality: $$\left|{}^3F\ 31\right\rangle = \left(\frac{2}{3}\right)^{1/2}\|2\alpha1\alpha\| - \left(\frac{1}{3}\right)^{1/2}\|3\alpha0\alpha\|$$

M_L M_S

and so on, to get all $\left|{}^3L\ \ L\ \ 1\right\rangle$ many electron functions.

$M_S = 0$

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

$$\mathbf{S}_-\left|{}^3F\ 31\right\rangle = \sum_i \mathbf{s}_{i^-}\left[\left(\frac{2}{3}\right)^{1/2}\|2\alpha1\alpha\| - \left(\frac{1}{3}\right)^{1/2}\|3\alpha0\alpha\|\right]$$

$$\hbar[1\cdot2-1\cdot0]^{1/2}\left|{}^3F\ 30\right\rangle = \hbar\left[\left(\frac{2}{3}\right)^{1/2}\left[\frac{1}{2}\cdot\frac{3}{2}-\frac{1}{2}\left(-\frac{1}{2}\right)\right]^{1/2}\left(\|2\beta1\alpha\| + \|2\alpha1\beta\|\right)\right.$$

$$\left. -\left(\frac{1}{3}\right)^{1/2}[1]^{1/2}\left(\|3\beta0\alpha\| + \|3\alpha0\beta\|\right)\right]$$

$$\left|{}^3F\ 30\right\rangle = \left(\frac{1}{3}\right)^{1/2}\left[\|2\beta1\alpha\| + \|2\alpha1\beta\|\right] - \left(\frac{1}{6}\right)^{1/2}\left[\|3\beta0\alpha\| + \|3\alpha0\beta\|\right]$$

$$\mathbf{S}_-\left|{}^3H\ 31\right\rangle = \sum_i \mathbf{s}_{i^-}\left[\left(\frac{1}{3}\right)^{1/2}\|2\alpha1\alpha\| + \left(\frac{2}{3}\right)^{1/2}\|3\alpha0\alpha\|\right]$$

$$\left|{}^3H\ 30\right\rangle = \left(\frac{1}{6}\right)^{1/2}\left[\|2\beta1\alpha\| + \|2\alpha1\beta\|\right] + \left(\frac{1}{3}\right)^{1/2}\left[\|3\beta0\alpha\| + \|3\alpha0\beta\|\right]$$

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

$$\mathbf{L}_-\left|{}^1I\ 60\right\rangle = \sum \ell_{i^-}\|3\alpha3\beta\|$$

$$\hbar[6\cdot7-6\cdot5]^{1/2}\left|{}^1I\ 50\right\rangle = \hbar[3\cdot4-3\cdot2]^{1/2}\left(\|2\alpha3\beta\| + \|3\alpha2\beta\|\right)$$

wrong order

$$\left|{}^1I\ 50\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha2\beta\| - \|3\beta2\alpha\|\right] \quad \text{orthogonality} \quad \left|{}^3H\ 50\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha2\beta\| + \|3\beta2\alpha\|\right]$$

$$\mathbf{L}_-\left|{}^1I\ 50\right\rangle = \sum \ell_{i^-}\left(\frac{1}{2}\right)^{1/2}\left[\|3\alpha2\beta\| - \|3\beta2\alpha\|\right]$$

wrong order

$$\left|{}^1I\ 40\right\rangle = \left(\frac{1}{44}\right)^{1/2}\left[(10)^{1/2}\left(\|3\alpha1\beta\| - \|3\beta1\alpha\|\right) + 6^{1/2}\left(\|2\alpha2\beta\| - \|2\beta2\alpha\|\right)\right]$$

$$\left|{}^1I\ 40\right\rangle = \left(\frac{5}{22}\right)^{1/2}\left[\left(\|3\alpha1\beta\| - \|3\beta1\alpha\|\right) + \left(\frac{6}{11}\right)^{1/2}\|2\alpha2\beta\|\right]$$

$$\left|{}^3H\ 40\right\rangle = \left(\frac{1}{20}\right)^{1/2}\left[(6)^{1/2}\left(\|2\alpha2\beta\| + \|2\beta2\alpha\|\right) + (10)^{1/2}\left(\|3\alpha1\beta\| + \|3\beta1\alpha\|\right)\right]$$

wrong order

$$\left|{}^3H\ 40\right\rangle = \left(\frac{1}{2}\right)^{1/2}\left(\|3\alpha1\beta\| + \|3\beta1\alpha\|\right)$$

orthogonality

$$\left|{}^1G\ 40\right\rangle = \left(\frac{3}{11}\right)^{1/2}\left(\|3\alpha1\beta\| - \|3\beta1\alpha\|\right) - \left(\frac{5}{11}\right)^{1/2}\|2\alpha2\beta\|$$

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 $\left|{}^3H\ 40\right\rangle$ we will get the same form we already derived starting from $\left|{}^3H\ 51\right\rangle$. Let's lower $\left|{}^1I\ 40\right\rangle$

$$\mathbf{L}_-\left|{}^1I\ 40\right\rangle = \sum_i \ell_{i^-}\left\{\left(\frac{5}{22}\right)^{1/2}\left[\|3\alpha1\beta\| - \|3\beta1\alpha\|\right] + \left(\frac{6}{11}\right)^{1/2}\|2\alpha2\beta\|\right\}$$

$$\left|{}^1I\ 30\right\rangle = (30)^{1/2}\left\{\left(\frac{5}{22}\right)^{1/2}(6)^{1/2}\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right) + \left(\frac{5}{22}\right)^{1/2}(12)^{1/2}\left(\|3\alpha0\beta\| - \|3\beta0\alpha\|\right)\right.$$
$$\left. + \left(\frac{6}{11}\right)^{1/2}(10)^{1/2}\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right)\right\}$$

$$\left|{}^1I\ 30\right\rangle = \left[\left(\frac{1}{22}\right)^{1/2} + \left(\frac{4}{22}\right)^{1/2}\right]\left(\|2\alpha1\beta\| - \|2\beta1\alpha\|\right) + \left(\frac{2}{22}\right)^{1/2}\left(\|3\alpha0\beta\| - \|3\beta0\alpha\|\right)$$

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

Finally, by orthogonality:

IMPORTANT →

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

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

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

$$\left|{}^{1}G\ 30\right\rangle = (8)^{-1/2}\left\{\left(\frac{3}{11}\right)^{1/2}(6)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right) + \left(\frac{3}{11}\right)^{1/2}(12)^{1/2}\left(\|3\alpha 0\beta\| - \|3\beta 0\alpha\|\right)\right.$$
$$\left. - \left(\frac{5}{11}\right)^{1/2}(10)^{1/2}\left(\|2\alpha 1\beta\| - \|2\beta 1\alpha\|\right)\right\}$$

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

checks!

End of Non-Lecture

As you see, this is extremely laborious. There is a better way!

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

This can be generalized for any value of S (page 61 of Hélène Lefebvre-Brion-Robert Field Perturbations book)
[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 $|LM_LSM_S\rangle$ state, especially when it is near an edge of the M_L,M_S box diagram. Essential that # of Slater determinants in each M_LM_S box increases in steps of 1 as you step down in M_L or M_S.

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

eg. $(nd)^3$ $\ {}^2H, {}^2G, {}^2F, {}^4F,\quad \boxed{{}^2D(2),}\ {}^4P, {}^2P$

3. **L^2 and 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!

Since usually $S_{MAX} << L_{MAX}$ for a configuration, it is best to start with $\mathbf{S}^2$ because it is simpler.