L-S Terms via L^2, S^2 and Projection

LAST TIME:

* method of M_L, M_S boxes. [For ^{3}L states, cross out boxes starting from both (M_L=L, M_S=1) and (M_L=L, M_S=0).]
* there must be a complete (2L + 1)(2S + 1) dimensionality for each L-S term [# of boxes]
* $n\ell^2$ pattern
* $(n\ell)^2$ $n'\ell'$ shortcut
* method of ladders plus orthogonality

TODAY:

$\mathbf{L}^2$, $\mathbf{S}^2$ method to obtain $|LM_LSM_S\rangle$, especially for the M_L,M_S boxes in which the method of ladders plus orthogonality is *most inconvenient*: e.g, $M_L = 0$, $M_S = 0$

* $\mathbf{L}^2 \rightarrow \mathbf{L}_+\mathbf{L}_-$ only for $M_L = 0$ block. Every L–S term in the configuration is represented in this most evil block.
* set up and diagonalize $\mathbf{S}^2$ — easy — by forming ± linear combinations
  (singlet and triplet)
  $\alpha\beta - \beta\alpha$ $\alpha\beta + \beta\alpha$
* transform $\mathbf{L}^2$ to singlet, triplet basis using the transformation that diagonalizes $\mathbf{S}^2$ (block diagonalization), then complete the diagonalization of $\mathbf{L}^2$ by knowing (from crossing out boxes method) the $\mathbf{L}^2$ eigenvalues: L(L + 1)

other, strong spin-orbit basis sets

Modern calculations use projection operators: designed to project away all unwanted parts of ψ yet preserve normalization.

Look at the $M_L = 0$, $M_S = 0$ block of f^2 and construct all L – S basis states. All extant L-S terms of f^2 are represented once in the $M_L = M_S = 0$ block. Never try to get to this block by ladders and orthogonality!

$$\psi_1 = \|3\alpha - 3\beta\|$$
$$\psi_2 = \|3\beta - 3\alpha\|$$
$$\psi_3 = \|2\alpha - 2\beta\|$$
$$\psi_4 = \|2\beta - 2\alpha\|$$
$$\psi_5 = \|1\alpha - 1\beta\|$$
$$\psi_6 = \|1\beta - 1\alpha\|$$
$$\psi_7 = \|0\alpha 0\beta\|$$

This is for f^2. Do d^2 in lecture

Exploit cute trick that works especially well in the $M_L = 0$, $M_S = 0$ block because many otherwise awful terms vanish.

$$L^2 = L_z^2 + \frac{1}{2}\left(L_+L_- + L_-L_+\right) = L_z^2 + \frac{1}{2}\left(L_+L_- + L_+L_- - \left[L_+, L_-\right]\right)$$

$$\left[L_+, L_-\right] = 2\hbar L_z$$

$$L^2 = \underbrace{L_z^2 - \hbar L_z}_{\substack{\text{diagonal but} \\ \text{vanishes in} \\ M_L = 0}} + \underbrace{L_+L_-}_{\text{nondiagonal}} \qquad \text{(same as } L^2 = L_z^2 + \hbar L_z + L_-L_+\text{)}$$

So for the $M_L = 0$ block *only*, can replace $\mathbf{L}^2$ by $\mathbf{L}_+\mathbf{L}_-$ (or $\mathbf{L}_-\mathbf{L}_+$) and, for $M_S = 0$ only, replace $\mathbf{S}^2$ by $\mathbf{S}_+\mathbf{S}_-$ (or $\mathbf{S}_-\mathbf{S}_+$).

For f^2:

$$\mathbf{S}^2\left|\left|3\alpha-3\beta\right|\right| = \mathbf{S}_+\mathbf{S}_-\left|\left|3\alpha-3\beta\right|\right| = \mathbf{S}_+\left|\left|3\beta-3\beta\right|\right| = \left|\left|3\alpha-3\beta\right|\right| + \left|\left|3\beta-3\alpha\right|\right|$$

$$\mathbf{L}^2\left|\left|3\alpha-3\beta\right|\right| = \mathbf{L}_+\mathbf{L}_-\left|\left|3\alpha-3\beta\right|\right| = \mathbf{L}_+ 6^{1/2}\left|\left|2\alpha-3\beta\right|\right| =$$

ignore factors of $\hbar^2$

$$6^{1/2}\left[\left[12-6\right]^{1/2}\left|\left|3\alpha-3\beta\right|\right| + \left[12-6\right]^{1/2}\left|\left|2\alpha-2\beta\right|\right|\right]$$

$$= 6\left[\left|\left|3\alpha-3\beta\right|\right| + \left|\left|2\alpha-2\beta\right|\right|\right]$$

etc.

$\psi_1 = \|3\alpha-3\beta\|$	$\mathbf{S}^2\psi_1 = \psi_1+\psi_2$	$\mathbf{L}^2\psi_1 = 6\psi_1+6\psi_3$
$\psi_2 = \|3\beta-3\alpha\|$	$\mathbf{S}^2\psi_2 = \psi_1+\psi_2$	$\mathbf{L}^2\psi_2 = 6\psi_2+6\psi_4$
$\psi_3 = \|2\alpha-2\beta\|$	$\mathbf{S}^2\psi_3 = \psi_3+\psi_4$	$\mathbf{L}^2\psi_3 = 6\psi_1+16\psi_3+10\psi_5$
$\psi_4 = \|2\beta-2\alpha\|$	$\mathbf{S}^2\psi_4 = \psi_3+\psi_4$	$\mathbf{L}^2\psi_4 = 6\psi_2+16\psi_4+10\psi_6$
$\psi_5 = \|1\alpha-1\beta\|$	$\mathbf{S}^2\psi_5 = \psi_5+\psi_6$	$\mathbf{L}^2\psi_5 = 10\psi_3+22\psi_5+12\psi_7$
$\psi_6 = \|1\beta-1\alpha\|$	$\mathbf{S}^2\psi_6 = \psi_5+\psi_6$	$\mathbf{L}^2\psi_6 = 10\psi_4+22\psi_6-12\psi_7$
$\psi_7 = \|0\alpha-0\beta\|$	$\mathbf{S}^2\psi_7 = 0$	$\mathbf{L}^2\psi_7 = 12\psi_5-12\psi_6+24\psi_7$
	all easy	require a bit more work

Now we know, for $2e^-$, $\mathbf{S}^2$ can only have $2\hbar^2$ and $0\hbar^2$ eigenvalues (triplet and singlet)

diagonalize $\mathbf{S}^2$ by inspection

$t : \alpha\beta+\beta\alpha$
$s : \alpha\beta-\beta\alpha$

$$\psi_{1t} = 2^{-1/2}\left(\psi_1+\psi_2\right) \qquad \psi_{1s} = 2^{-1/2}\left(\psi_1-\psi_2\right)$$

$$\psi_{2t} = 2^{-1/2}\left(\psi_3+\psi_4\right) \qquad \psi_{2s} = 2^{-1/2}\left(\psi_3-\psi_4\right)$$

$$\psi_{3t} = 2^{-1/2}\left(\psi_5+\psi_6\right) \qquad \psi_{3s} = 2^{-1/2}\left(\psi_5-\psi_6\right)$$

$$\psi_{4s} = \psi_7$$ → This also has αβ–βα form

Confirm that these functions diagonalize $\mathbf{S}^2$ and give correct values of diagonal elements. Also, they give orthogonality for singlets with triplets.

a diagonal element: $\left\langle \psi_{1t} \middle| \mathbf{S}^2 \middle| \psi_{1t} \right\rangle = \frac{1}{2}\left\langle \left(\psi_1 + \psi_2\right) \middle| \mathbf{S}^2 \middle| \left(\psi_1 + \psi_2\right) \right\rangle$

$$= \frac{1}{2}\hbar^2 \left\langle \left(\psi_1 + \psi_2\right)\left(2\psi_1 + 2\psi_2\right) \right\rangle = \frac{1}{2}\hbar^2 (2+2) = 2\hbar^2$$

an off-diagonal element: $\left\langle \psi_{1t} \middle| \mathbf{S}^2 \middle| \psi_{1s} \right\rangle = \frac{1}{2}\left\langle \left(\psi_1 + \psi_2\right) \middle| \mathbf{S}^2 \middle| \left(\psi_1 - \psi_2\right) \right\rangle$

$$= \frac{1}{2}\hbar^2 \left\langle \left(\psi_1 + \psi_2\right)\left(\psi_1 + \psi_2 - \psi_1 - \psi_2\right) \right\rangle = 0 \text{ as expected}$$

also $\left\langle \psi_{1s} \middle| \mathbf{S}^2 \middle| \psi_{1s} \right\rangle = 0$

$$\mathbf{S}^2 = \hbar^2 \begin{pmatrix} 2 & & & & & & & \\ & 2 & & & & & \mathbf{0} & \\ & & 2 & & & & & \\ & & & 0 & & & & \\ & & & & 0 & & & \\ & & \mathbf{0} & & & 0 & & \\ & & & & & & 0 & \end{pmatrix} \begin{matrix} 1t \\ 2t \\ 3t \\ 1s \\ 2s \\ 3s \\ 4s \end{matrix}$$

What does $\mathbf{L}^2$ look like when expressed in the basis set that diagonalizes $\mathbf{S}^2$?

$$\mathbf{L}^2\psi_{1t} = 2^{-1/2}\hbar^2\left[6\psi_1 + 6\psi_3 + 6\psi_2 + 6\psi_4\right]$$

$$\left\langle \psi_{1t} \middle| \mathbf{L}^2 \middle| \psi_{1t} \right\rangle = \frac{1}{2}\hbar^2[6+6] = 6\hbar^2$$

NONLECTURE

$$\left\langle \psi_{2t} \middle| \mathbf{L}^2 \middle| \psi_{1t} \right\rangle = \frac{1}{2}\hbar^2 \left\langle \psi_3 + \psi_4 \middle| 6\psi_1 + 6\psi_3 + 6\psi_2 + 6\psi_4 \right\rangle = \frac{1}{2}\hbar^2\left[6+6\right] = 6\hbar^2$$

$$\left\langle \psi_{2t} \middle| \mathbf{L}^2 \middle| \psi_{2t} \right\rangle = \frac{1}{2}\hbar^2\left[\left\langle \psi_3 + \psi_4 \middle| \mathbf{L}^2 \middle| \psi_3 + \psi_4 \right\rangle\right]$$

$$= \frac{1}{2}\hbar^2 \left\langle \psi_3 + \psi_4 \middle| 6\psi_1 + 16\psi_3 + 10\psi_5 + 6\psi_2 + 16\psi_4 + 10\psi_6 \right\rangle$$

$$= \frac{1}{2}\hbar^2\left(16+16\right) = 16\hbar^2$$

$$\mathbf{L}^2 = \hbar^2 \left(\begin{array}{ccc|cccc} 6 & 6 & 0 & & & & \\ 6 & 16 & 10 & & \mathbf{0} & & \\ 0 & 10 & 22 & & & & \\ \hline & & & 6 & 6 & 0 & 0 \\ & \mathbf{0} & & 6 & 16 & 10 & 0 \\ & & & 0 & 10 & 22 & 24\cdot 2^{-1/2} \\ & & & 0 & 0 & 24\cdot 2^{-1/2} & 24 \end{array}\right) \begin{array}{c} 1t \\ 2t \\ 3t \\ \hline 1s \\ 2s \\ 3s \\ 4s \end{array}$$

These 2 matrices are easier to diagonalize than the full 7 × 7 matrix, especially because we know the eigenvalues in advance!

But our goal is actually the eigen<u>vectors</u> not the eigen<u>values:</u>

$$\underline{\text{TRIPLETS}} \quad \mathrm{L}^2 \left| {}^3\mathrm{H}\ M_L = 0, M_S = 0 \right\rangle = \hbar^2 30 \left| \ {}^3\mathrm{H} \quad 00 \ \right\rangle$$

$$\begin{pmatrix} 6 & 6 & 0 \\ 6 & 16 & 10 \\ 0 & 10 & 22 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = 30 \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$(\mathbf{L}^2)$ eigenvector equation

$$6a + 6b + 0c = 30a \qquad \rightarrow b = \frac{24}{6} a = 4a \qquad a = b/4$$

$$6a + 16b + 10c = 30b$$

$$0a + 10b + 22c = 30c \quad \rightarrow b = \frac{8}{10} c$$

$$1 = [a^2 + b^2 + c^2]^{1/2}$$

$$a = 42^{-1/2}$$

$$b = (8/21)^{1/2}$$

$$c = (25/42)^{1/2}$$

$$\left|{}^3\mathrm{H}\quad 00\right\rangle = 42^{-1/2}\psi_{1t} + (8/21)^{1/2}\psi_{2t} + (25/42)^{1/2}\psi_{3t}$$

Similarly,

$$\left|{}^3\mathrm{F}\quad 00\right\rangle = 3^{-1/2}\left(\psi_{1t} + \psi_{2t} - \psi_{3t}\right)$$

$$\left|{}^3\mathrm{P}\quad 00\right\rangle = -\left(\frac{9}{14}\right)^{-1/2}\psi_{1t} + \left(\frac{2}{7}\right)^{1/2}\psi_{2t} - 14^{-1/2}\psi_{3t}$$

Note that each ψ_{nt} basis state gets completely "used up" and all eigenvectors are normalized and mutually orthogonal. You should verify both "used up" and orthogonality.

Nonlecture: **Singlets**

$$\mathrm{L}^2\left|{}^1\mathrm{I}\quad 00\right\rangle = \hbar^2 42\left|{}^1\mathrm{I}\quad 00\right\rangle$$

$$\begin{pmatrix} 6 & 6 & 0 & 0 \\ 6 & 16 & 10 & 0 \\ 0 & 10 & 22 & 24\bullet 2^{-1/2} \\ 0 & 0 & 24\bullet 2^{-1/2} & 24 \end{pmatrix}\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 42\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix}$$

$6a + 6b = 42a \qquad 6b = 36a \Rightarrow \qquad \boxed{a = b/6}$

$6a + 16b + 10c = 42b \qquad 6a + 10c = 26b \qquad 10c = 25b \qquad \boxed{c = \frac{5}{2}b}$

$24\cdot 2^{-1/2}c + 24d = 42d \qquad 24\cdot 2^{-1/2}c = 18d \qquad \boxed{d = \frac{10}{3\cdot 2^{1/2}}b}$

normalization: $\qquad 1 = b\left[\frac{1}{36} + 1 + \frac{25}{4} + \frac{50}{9}\right]^{1/2} \qquad \boxed{b = (6/77)^{1/2}}$

$$\left|{}^1\mathrm{I}\ 00\right\rangle = \frac{1}{6}\left(\frac{6}{77}\right)^{1/2}\psi_{1s} + \left(\frac{6}{77}\right)^{1/2}\psi_{2s} + \frac{5}{2}\left(\frac{6}{77}\right)^{1/2}\psi_{3s} + \frac{10}{3}\left(\frac{3}{77}\right)^{1/2}\psi_{4s}$$

A lot of algebra skipped here:

$$\left|{}^1\mathrm{G}\ 00\right\rangle = \left[\frac{9}{77}\right]^{1/2}\psi_{1s} + \left[\frac{49}{77}\right]^{1/2}\psi_{2s} + \left(\frac{1}{77}\right)^{1/2}\psi_{3s} - \left(\frac{18}{77}\right)^{1/2}\psi_{4s}$$

$$\left|{}^1\mathrm{D}\ 00\right\rangle = -\left(\frac{25}{42}\right)^{1/2}\psi_{1s} + 0\psi_{2s} + \left(\frac{9}{42}\right)^{1/2}\psi_{3s} - \left(\frac{8}{42}\right)^{1/2}\psi_{4s}$$

$$\left|{}^1\mathrm{S}\ 00\right\rangle = -\left(\frac{2}{7}\right)^{1/2}\psi_{1s} + \left(\frac{2}{7}\right)^{1/2}\psi_{2s} - \left(\frac{2}{7}\right)^{1/2}\psi_{3s} + \left(\frac{1}{7}\right)^{1/2}\psi_{4s}$$

Again note that each ψ_{ns} is used up. You should verify orthogonality!

Two opposite strategies:

1. ladder down from extreme M_L, M_S
2. $\mathbf{L}^2 + \mathbf{S}^2$ matrices are large but easy to write out for $M_L = 0$ and $M_S = 0$ ONLY — could then ladder up from any $\mathbf{L}^2$, $\mathbf{S}^2$ eigenfunction (no need to use orthogonality because every L–S state is present in the $M_L = 0$, $M_S = 0$ block).

Before going to Projection Operators, look briefly at the problems associated with deriving 2 other kinds of basis states.

m_j

$|j\omega\ell s\rangle$

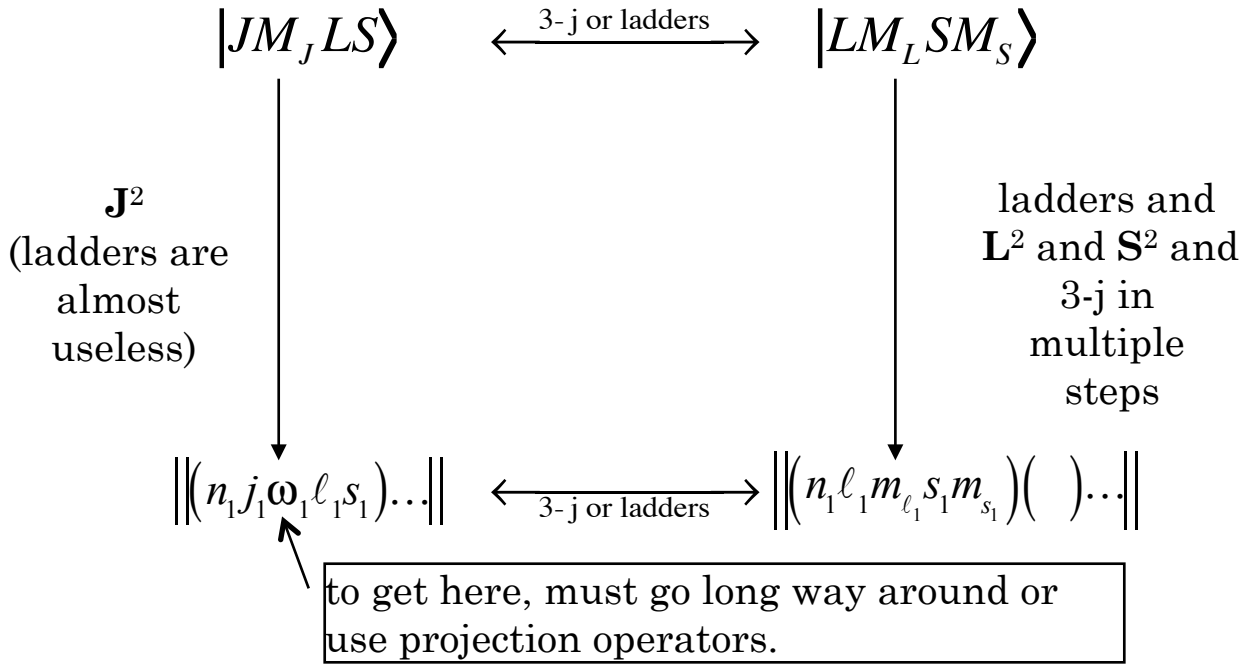
"coupled" orbitals — important for strong spin-orbit limit with HEAVY ATOMS.

($\mathbf{H}^{SO}$ is diagonal in $|j\omega\rangle$ and in $|JM_JLS\rangle$)

$\zeta_{n\ell} \gg$ energy separations between L-S terms

(all $\zeta_{n\ell}$ are ≥ 0)

$|JM_JLS\rangle$ coupled many-electron L-S-J states.
Again — useful in strong spin-orbit limit



NONLECTURE

BOX METHOD FOR $|j\omega\ell s\rangle$ orbital basis: $(nf)^2$ example
No need to specify ℓ and s.

Standard Order: (7/2 7/2), (7/2 5/2), (7/2 3/2), (7/2 1/2), (7/2, -1/2), (7/2, -3/2), (7/2 -5/2), (7/2 -7/2), (5/2 5/2), (5/2 3/2), (5/2 1/2), (5/2 -1/2), (5/2 -3/2), (5/2 -5/2)

14 functions $\left|j_1\omega_1 j_2\omega_2\right\rangle$ List only Slater determinants with $M_J \geq 0$.

Suppress the /2's

#	M_J								
(0)	7	~~$\|7777\|$~~							
(2)	6	$\|7775\|$	$\|7755\|$						
(3)	5	$\|7773\|$	$\|7753\|$	$\|7555\|$					
(6)	4	$\|7771\|$	$\|7751\|$	$\|7573\|$	$\|7553\|$	$\|7355\|$	$\|5553\|$		
(7)	3	$\|777-1\|$	$\|775-1\|$	$\|7571\|$	$\|7551\|$	$\|7353\|$	$\|5551\|$	$\|7155\|$	
(10)	2	$\|777-3\|$	$\|775-3\|$	$\|777-1\|$	$\|775-1\|$	$\|7371\|$	$\|7351\|$	$\|7153\|$	$\|7-155\|$
		$\|555-1\|$	$\|5351\|$						
(11)	1	$\|777-5\|$	$\|775-5\|$	$\|757-3\|$	$\|755-3\|$	$\|737-1\|$	$\|735-1\|$	$\|7151\|$	$\|7-153\|$
		$\|7-355\|$	$\|555-3\|$	$\|535-1\|$					
(13)	0	$\|777-7\|$	$\|757-5\|$	$\|755-5\|$	$\|737-3\|$	$\|735-3\|$	$\|717-1\|$	$\|715-1\|$	~~$\|7-171\|$~~
		$\|7-151\|$	~~$\|7-373\|$~~	$\|7-353\|$	$\|7-555\|$	$\|555-5\|$	$\|535-3\|$	$\|515-1\|$	

AWFUL! The number of Slater determinants increases in steps larger than 1 as you move down from $M_J = J$. Ladders plus orthogonality cannot work.

Work in the 13 member $M_J = 0$ block

Worst possible one for ladders plus orthogonality.

$\mathbf{J}^2 = \underbrace{\mathbf{J}_z^2 - \hbar\mathbf{J}_z}_{\text{diagonal}} + \mathbf{J}_+\mathbf{J}_-$ [Hopeless to attempt to set up $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices!] Why?

Dimension of Various J blocks:

J =	Dimension =
6	2
5	1
4	3
3	1
2	3
1	1
0	2

All blocks are manageable! Ladder up from $M_J = 0$.

coupled basis sets are convenient for $\mathbf{L} \cdot \mathbf{S}$ and $\ell_i \cdot \mathbf{s}_i$ (spin-orbit)

uncoupled basis sets are convenient for $(\mathbf{L}_z + 2\mathbf{S}_z)$ (Zeeman)

Either of the two many-electron basis sets is OK for $\frac{e^2}{r_{ij}}$.
The big problem for e^2/r_{ij} is that it has
many off-diagonal matrix elements in the Slater determinantal basis set. These are extremely tedious to evaluate. The solution to this is the
"Slater Sum Rule" method.
It is based on the fact that the trace of a matrix is equal to the sum of its eigenvalues. This is true regardless of what representation is used to express the matrix.

SUM RULE METHOD: Diagonal matrix elements of e^2/r_{ij} in the Slater determinantal basis set

NEXT TIME

NONLECTURE: Projection Operators

This is an alternative method to set up $|LM_L SM_S\rangle$ or $|\ JLSM_J\rangle$ basis sets in terms of either $n\ell m_\ell s m_s$ or $nj\omega\ell s$ spin-orbital Slater basis sets.

1. Work out $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices for $n\ell m_\ell s m_s$ (or $\mathbf{J}^2$ for $nj\omega\ell s$). These matrices are block diagonal in M_L, M_S (or M_J).

2. Construct an operator which, when applied to an arbitrary function, annihilates the undesired part of that function.

   e.g. annihilate L″ by $\left[\hat{\mathbf{L}}^2 - \hbar^2 L''(L''+1)\right]\Psi$

3. Modify the above operator so that it preserves the amplitude of the L′ component of ψ.

   e.g. annihilate L″ , and preserve amplitude of L′

$$\left[\frac{\hat{\mathbf{L}}^2 - \hbar^2 L''(L''+1)}{\hbar^2\left[L'(L'+1) - L''(L''+1)\right]}\right]\Psi \equiv \mathbf{P}\Psi$$

   show how this works by applying it to $\Psi = a\psi_{L'} + b\psi_{L''}$

$$\begin{aligned}\mathbf{P}(a\psi_{L'} + b\psi_{L''}) &= a\frac{L'(L'+1) - L''(L''+1)}{L'(L'+1) - L''(L''+1)}\psi_{L'} + b\frac{L''(L''+1) - L''(L''+1)}{L'(L'+1) - L''(L''+1)}\psi_{L''} \\ &= a\psi_{L'} + 0\psi_{L''}\end{aligned}$$

4. Now recognize that one can build a projection operator that annihilates all of the undesired L″ components by taking a product of operators like that in #3, one for each L″ .

$$\mathbf{P}_{L'} = \prod_{\text{all } L'' \neq L'} \frac{\hat{\mathbf{L}}^2 - \hbar^2 L''(L''+1)}{\hbar^2 L'(L'+1) - \hbar^2 L''(L''+1)}$$

5. Recognize that $\mathbf{P}_{L'}\psi = a_{L'}\psi_{L'}$, which is not normalized, because $a_{L'}$ is the amplitude of $\psi_{L'}$ in ψ. Get a normalized $\psi_{L'}$ by recognizing that $\langle \psi_{L'} | \Psi \rangle = a_{L'}$

$$\psi_{L'} = \frac{\mathbf{P}_{L'}\Psi}{\langle \psi_{L'} | \Psi \rangle}$$

This method is useful for dealing with $|JM_JLS\rangle$ in the $|j\omega\ell s\rangle$ orbital basis because there is no *simple* way of block diagonalizing $\mathbf{J}^2$ in terms of $\mathbf{L}^2$ and $\mathbf{S}^2$. It is only possible to block diagonalize $\mathbf{J}^2$ in terms of M_J.

Modern calculations will simply set up the $\mathbf{J}^2$,$\mathbf{J}_z$ matrix, diagonalize $\mathbf{J}^2$, and then discover to which eigenvalues of $\mathbf{L}^2$ and $\mathbf{S}^2$ each $\mathbf{J}^2$, $\mathbf{J}_z$ basis function belongs. In many cases two or more L–S terms will contain L–S–J components which belong to the same eigenvalue of $\mathbf{J}^2$.

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