# 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).]
  complete (2L + 1)(2S + 1) dimension for each L-S term [# of boxes]
* $n\ell^2$ pattern
* $(n\ell)^2$ $n'\ell'$
* method of ladders plus orthogonality

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TODAY:

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

* $\mathbf{L}^2 \rightarrow \mathbf{L}_+\mathbf{L}_-$ only for $M_L = 0$ block. Every L–S term 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 (block diagonalization), then diagonalize $\mathbf{L}^2$ by knowing (from crossing out boxes method) eigenvalues: L(L + 1)

other, strong spin-orbit basis sets

Modern calculations use projection operators: designed to project away all unwanted parts of $\psi$ 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 present once in the $M_L = M_S = 0$ block. Never try to get to this block by ladders and orthogonality!

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

Do $d^2$ in lecture

Cute trick that works especially well in $M_L = 0$ and $M_S = 0$ blocks because many otherwise awful terms vanish.

$$\mathbf{L}^2 = \mathbf{L}_z^2 + \frac{1}{2}\left(\mathbf{L}_+\mathbf{L}_- + \mathbf{L}_-\mathbf{L}_+\right) = \mathbf{L}_z^2 + \frac{1}{2}\left(\mathbf{L}_+\mathbf{L}_- + \mathbf{L}_+\mathbf{L}_- - \left[\mathbf{L}_+,\mathbf{L}_-\right]\right)$$

$$\left[\mathbf{L}_+,\mathbf{L}_-\right] = 2\hbar\mathbf{L}_z$$

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

So for $M_L = 0$ 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 $\mathbf{S}_+\mathbf{S}_-$.

For $f^2$:

ignore factors of $\hbar^2$

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

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

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

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

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

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

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

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

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

$$\psi_{4s} = \psi_7$$ ← This also has $\alpha\beta-\beta\alpha$ form

Confirm that these functions diagonalize $\mathbf{S}^2$ and give correct diagonal elements.

a diagonal element:

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

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

an off - diagonal element:

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

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

also

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

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

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

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

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

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NONLECTURE

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

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

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

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

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

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

Our goal is actually the eigen<u>vectors</u> not the eigen<u>values</u>

<u>TRIPLETS</u> $\quad \mathbf{L}^2 \left| {}^3H \;\; M_L = 0, M_S = 0 \right\rangle = \hbar^2 30 \left| {}^3H 00 \right\rangle$

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

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

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

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

$0a + 10b + 22c = 30c \; \rightarrow \; b = \dfrac{8}{10} c \qquad c = \dfrac{5}{21} b$

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

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

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

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

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

Similarly,

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

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

Note that each $\psi_{nt}$ basis state gets completely "used up" and all eigenvectors are normalized and mutually orthogonal. You check both "used up" and orthogonality.

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Nonlecture: **Singlets**

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

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

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

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

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

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

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

A lot of algebra skipped here:

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

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

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

Again note that each $\psi_{ns}$ is used up. Check for orthogonality!

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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).

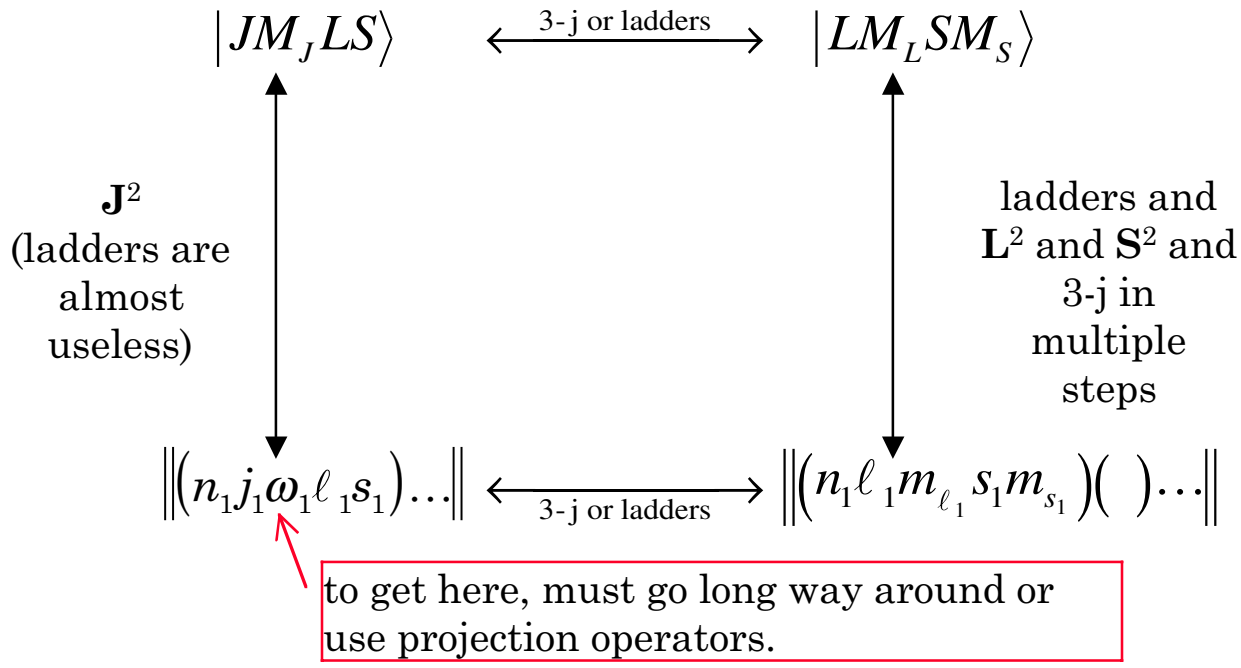
Before going to Projection Operators, look at the problems associated with getting 2 other kinds of basis states.

$m_j$

$|j\omega\ell s\rangle$

"coupled" orbitals — important for strong spin-orbit limit with HEAVY ATOMS.
($\mathbf{H}^{SO}$ is diagonal in jω and in JMLS)
$\zeta_{n\ell}$ >> energy separations between L-S terms
(all $\zeta_{n\ell}$ are ≥ 0)

$|JM_J LS\rangle$ 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 $\ell$ 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. 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 $M_J = J$.

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!]

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 $\boldsymbol{\ell}_i\cdot\mathbf{s}_i$

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

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 the 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

Alternative method to set up $|\,LM_LSM_S\rangle$ or $|\,JLSM_J\rangle$ basis sets in terms of either $n\ell m_\ell sm_s$ or $nj\omega\ell s$ orbital Slater basis sets.

1. Work out $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices for $n\ell m_\ell sm_s$ (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″ , 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 $\Psi = a\psi_{L'} + b\psi_{L''}$

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

4. Now recognize that one can build a projection operator that annihilates all 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 $\Psi$. 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 $\mathbf{S}^2$, can only 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 $\mathbf{J}^2$.