Lecture #15: $^2\Pi$ and $^2\Sigma$ Matrices

Last Time:

- Effect of $\hat{\Lambda}^2$, $\hat{\Lambda}_z$, $\hat{\Sigma}$ on $|\Lambda \alpha M\rangle$ basis set
- Case (a) basis set $|n(L) \Lambda \Sigma \rangle |v\rangle |\OmegaJM\rangle$
- L-destroyed, but not $\Lambda$: $\hat{L}_z$, $\hat{L}_r$, selection rules

$$\hat{H}^\text{ROT} = B(R)\hat{R}^2$$

Diagonal:

$$\left\langle n\Lambda\Sigma \mid \hat{H}^\text{ROT} \mid n\Lambda\Sigma \right\rangle = \delta_{n'n}\delta_{\Lambda'\Lambda}\delta_{\Sigma'\Sigma}\delta_{v'v}\delta_{\OmegaJM\OmegaJM}$$

$$\times B_v[J(J + 1) - \Omega^2 + S(S + 1) - \Sigma^2 + L^2_\perp]$$

$$\Delta\Omega = \Delta\Sigma = \pm 1$$

within $\Lambda-S$ multiplet state (S-uncoupling):

$$\left\langle n\Lambda\Sigma \pm 1 \mid \hat{H}^\text{ROT} \mid n\Lambda\Sigma \right\rangle = -B_v[J(J + 1) - (\Omega \pm 1)\Omega]^{1/2}[S(S + 1) - (\Sigma \pm 1)\Sigma]^{1/2}$$

**** In some of my handouts I call $J + 1/2 = x$. Here, I'll call it $y$ ****

Here $x = J(J + 1)$, $y = J + 1/2$

For example: Start by listing all relevant basis states.

$^2\Pi$

$$\begin{align*}
|n 1 \ 1/2 \ 1/2\rangle & \quad ^2\Pi_{3/2} \\
|n 1 \ 1/2 \ -1/2\rangle & \quad ^2\Pi_{1/2} \\
|n -1 \ 1/2 \ -1/2\rangle & \quad ^2\Pi_{-3/2} \\
|n -1 \ 1/2 \ 1/2\rangle & \quad ^2\Pi_{-1/2}
\end{align*}$$

$\hat{H}^\text{ROT} (^2\Pi) = ^2\Pi_{3/2}$

$$B^x \times ^2\Pi_{1/2}$$

$$^2\Pi_{-1/2} \times ^2\Pi_{-3/2}$$

Two identical blocks for $\Omega > 0$ and $\Omega < 0$ - later we will consider parity basis.

What about $^2\Sigma^+$? Class should do this.
\[ \Delta \Omega = \Delta \Lambda = \pm 1 \] between \( \Lambda - S \) multiplet states (L-uncoupling)

\[
\begin{align*}
n' \Lambda + 1 S \Sigma & \left| \begin{array}{c}
\left. \Omega \pm 1 J M \right| H_\text{ROT} \left| n \Lambda S \Sigma \right| v \right| \Omega J M \right) = -B_\nu \gamma [J(J + 1) - (\Omega \pm 1)\Omega]^{1/2} \times \left| n' \Lambda \pm 1 \right| L_z | n \Lambda \right) \\
\beta
\end{align*}
\]

a perturbation parameter to be determined by a fit to the spectrum. ↑

Today: \( \hat{H}^\text{SO}, \hat{H}^\text{SS}, \hat{H}^\text{SR} \) \{ effective operators \} \{ matrix elements \}

Matrix elements of \( ^2\Pi, ^2\Sigma \) effective \( H \).

- **Spin-orbit** \( \hat{H}^\text{SO} = \sum_i a(r_i) \ell_i \hat{s}_i \) \( \ell_i \) \( \Lambda \) only → \( \Lambda \hat{S} \) \( \ell \) \( \Lambda \) \( S \) \( \hat{s}_i \) electron (not component)\)

- **Spin-spin** \( \hat{H}^\text{SS} = \sum_i^{\Delta S = 0} 2 \lambda \left[ 3S_z^2 - S^2 \right] \) another term \( \Delta \Sigma = -\Delta \Lambda = \pm 2 \)

- **Spin-rotation** \( \hat{H}^\text{SR} = \gamma \hat{R} \hat{S} \)

usually \( \lambda, \gamma \) are very small with respect to \( A \) and are dominated by second-order spin-orbit effects (thru van Vleck transformation)—discussed later

\( \hat{H}^\text{SO} \) is very important

\[
\begin{align*}
\hat{H}^\text{SO} &= \sum_i a(r_i) \ell_i \hat{s}_i \\
&= \left( \begin{array}{c}
\text{not} \\
\sum_{i,j}
\end{array} \right) \left( \begin{array}{c}
a \ell_i \cdot \hat{s}_j \\
\end{array} \right)
\end{align*}
\]

\( \ell_i, \hat{s}_i \) are vectors with respect to \( \hat{J} \) → \( \ell_i \hat{s}_i \) is scalar \( \Delta J = \Delta M = \Delta \Omega = 0 \) with respect to \( \hat{J} \).

\( \hat{s}_i \) is vector with respect to \( \hat{S} \) → \( \ell_i \hat{s}_i \) is vector with respect to \( \hat{S} \) → \( \Delta S = 0, \pm 1, \Delta \Sigma = 0, \pm 1 \)

**Fine point!**

\( \ell_i \hat{s}_i \) does not operate on \( |\Omega J M \rangle \), only on \( |n \Lambda S \Sigma \rangle \); it is therefore NOT INDEPENDENT of \( \Omega \) because, as vector with respect to \( L \) and \( S \), its matrix elements are not independent of \( \Lambda \) and \( \Sigma \).
Selection rules (ASSERTED)

\[ \Delta J = 0 \]
\[ \Delta \Omega = 0 \]
\[ + \leftrightarrow \ - \ (\text{LAB INVERSION } \hat{I}) \ (\text{parity}) \]
\[ g \leftrightarrow u \ (\text{body inversion } \hat{i}) \]
\[ \Sigma^+ \leftrightarrow \Sigma^- \ (\sigma_i) \]
\[ \Delta S = 0, \pm 1 \]
\[ \Delta \Sigma = -\Delta \Lambda = 0, \pm 1 \]

\( \hat{H}^{SO} \) is a one-electron operator, so it has non-zero matrix elements only between electronic configurations differing by a single spin-orbital. (e.g. \( \pi \) orbital = \( 1\alpha, 1\beta, -1\alpha, -1\beta \) spin-orbitals)

Special simplification (due to simple form of Wigner-Eckart Theorem). If \( \hat{B} \) is vector with respect to \( \hat{A} \), then \( \Delta \hat{B} = 0 \) matrix elements of a vector operator (\( \hat{B} \)) with respect to angular momentum (\( \hat{A} \)) may be evaluated by replacing \( \hat{B} \) by \( b \hat{A} \) (where \( b \) is a constant, often called a reduced matrix element)!

\( a(r_i) \hat{\ell}_i \) is vector with respect to \( \hat{L} \)
\( \hat{s}_i \) is vector with respect to \( \hat{S} \)

For \( \Delta L = 0, \Delta S = 0 \) matrix elements

\[ \sum_i a(r_i) \hat{\ell}_i \cdot \hat{s}_i \rightarrow A \hat{L} \cdot \hat{S} \]

(limited validity operator replacement)

\[ \hat{H}^{SO} = A \left[ L_z S_z + \frac{1}{2} (L_+ S_- + L_- S_+) \right] \]

E.g., for \( ^2\Pi \)

\[ \left\langle ^2 \Pi_{\pm 3/2} | \hat{H}^{SO} | ^2 \Pi_{\pm 3/2} \right\rangle = A (\pm 1) \left( \pm \frac{1}{2} \right) = \frac{A}{2} \]
\[ \left\langle ^2 \Pi_{\pm 1/2} | \hat{H}^{SO} | ^2 \Pi_{\pm 1/2} \right\rangle = A (\pm 1) \left( \mp \frac{1}{2} \right) = -\frac{A}{2} \]

all \( \Delta \Omega \neq 0 \) matrix elements are = 0.

\[ \hat{H}^{SS} \xrightarrow{\Delta S = 0} \frac{2}{3} \lambda \left[ 3 \hat{S}_z^2 - \hat{S}^2 \right] = \frac{2}{3} \lambda \left[ 3 \hat{S}_z^2 - S(S + 1) \right] + \text{additional term} \]
Selection rules

\[ \Delta S = 0 \]
\[ \Delta \Omega = 0 \]
\[ \Delta S = 0 \quad \text{[also } \pm 1, \pm 2 \text{ neglected here]} \]
\[ \Delta \Sigma = 0 \quad \text{[also } \Delta \Sigma = -\Delta \Lambda = \pm 2 \text{ (} \Lambda \text{-doubling in } ^3\Pi_0 \text{ neglected here)}] \]
\[ g \leftrightarrow u \]
\[ \Sigma^* \leftrightarrow \Sigma^- \]

\[ \hat{H}^{SR} = \gamma \hat{R} \cdot \hat{S} = \gamma (\hat{J} - \hat{L} - \hat{S}) \cdot \hat{S} = \gamma \left[ J \cdot S - L \cdot S - S^2 \right] \]

we already know how to deal with all three of these!

Now we are ready to set up full \(^2\Pi, ^3\Sigma^+\) matrix. Start with all matrix elements of \(^2\Pi_{3/2}\) and then \(^2\Pi_{1/2}\) and then \(^3\Sigma_{1/2}\) etc.

\[ \langle v, n, \ ^2\Pi_{3/2} \mid \hat{H} = \hat{H}^{\text{elect}} + \hat{H}^{\text{vib}} + \hat{H}^{\text{ROT}} + \hat{H}^{\text{SO}} + \hat{H}^{\text{SS}} + \hat{H}^{\text{SR}} \mid n, \ ^2\Pi_{3/2}, v \rangle = \]

\[ T_e (n^2 \Pi) + G(v_\Pi) + A_\Pi (11/2) + \frac{2}{3} \lambda \left( \frac{3}{2} \right) ^2 \left( \frac{1}{2} \right) ^2 - \frac{3}{4} + \gamma_\Pi \left( \frac{3}{2} - 1 \right) ^2 \left( \frac{1}{2} - 3 \right) \]

always \(= 0\) for \( S = 1/2 \) states!

\[ + B_{v_\Pi} \left[ J(J + 1) - \frac{9}{4} + \frac{3}{4} + \frac{1}{4} + \frac{L_{\perp}^2}{y^2} \right] = E_{v_\Pi} + \frac{1}{2} A_\Pi - \frac{1}{2} \gamma_\Pi + B_{v_\Pi} \left( J(J + 1) - \frac{7}{4} \right) \]

\[ y \equiv J + 1/2, \text{ thus } y \text{ is an integer since } J \text{ is half-integer for } ^3\Pi \text{ and } ^2\Sigma. \]

Get same results for \( \langle \ ^2\Pi_{3/2} \mid \hat{H} \mid \ ^2\Pi_{3/2} \rangle \).

\[ \langle \ ^2\Pi_{1/2} \mid \hat{H} \mid \ ^2\Pi_{1/2} \rangle = E_{v_\Pi} - \frac{1}{2} A_\Pi - \frac{1}{2} \gamma_\Pi + B_{v_\Pi} \left[ \frac{J(J + 1) + 1}{4} \right] \]
Get same results for $\langle 2 \Pi_{-1/2} | \hat{H} | 2 \Pi_{1/2} \rangle$.

$$\langle 2 \Sigma_{1/2} | \hat{H} | 2 \Sigma_{1/2} \rangle = \langle 2 \Sigma_{-1/2} | \hat{H} | 2 \Sigma_{-1/2} \rangle = E_{\Sigma} - A_{\Sigma} \frac{1}{2} - \frac{1}{2} \gamma_{\Sigma} + B_{\Sigma} \left[ J(J+1) - 1/4 + 3/4 - 1/4 \right]$$

$\uparrow$ always for $\Sigma$-states

[ASIDE: we have two explicit cases where, by evaluation of matrix elements, we see that $\langle \Lambda \Sigma \Omega | \hat{H} | \Lambda \Sigma \Omega \rangle = \langle -\Lambda - \Sigma - \Omega | \hat{H} | -\Lambda - \Sigma - \Omega \rangle$. But be careful, this is not true for $\langle \Lambda' | \hat{H} | \Lambda \rangle$! Non-automatically-evaluable matrix elements.]

**Off-Diagonal Matrix Elements**

Always ask what operator do we need to get non-zero matrix element between specified basis states?

$$\langle 2 \Pi_{3/2} | \hat{H} | 2 \Pi_{1/2} \rangle = \langle 2 \Pi_{-3/2} | \hat{H} | 2 \Pi_{-1/2} \rangle = -0A_{\Pi} + \left[ \frac{1}{2} \left( x - \frac{3}{4} \right)^{1/2} \right] \gamma_{\Pi} - B_{\Pi} \left[ x - \frac{3}{2} \right]^{1/2} \left[ \frac{3}{4} - \frac{1}{2} \left( -\frac{1}{2} \right) \right]^{1/2}$$

$\Delta \Omega = 0$

$$\langle 2 \Pi_{3/2} | \hat{H} | 2 \Pi_{-1/2} \rangle = 0 \quad \Delta \Omega = 2$$

$$\langle 2 \Pi_{3/2} | \hat{H} | 2 \Pi_{-3/2} \rangle = 0 \quad \Delta \Omega = 3$$

$$\langle 2 \Pi_{3/2} | \hat{H} | 2 \Sigma_{1/2}^{+} \rangle = -\langle \nu_{\Pi} | B(\mathbf{R}) | \nu_{\Sigma} \rangle \left[ J(J+1) - \frac{3}{2} \right]^{1/2} \langle n \Pi | L_{+} | n' \Sigma \rangle$$

$$= -\beta_{\nu_{\Pi} \nu_{\Sigma}} \left[ y^{2} - 1 \right]^{1/2}$$

$$\langle 2 \Pi_{3/2} | \hat{H} | 2 \Sigma_{-1/2} \rangle = 0 \quad \Delta \Omega = 2$$

all done with $^2\Pi_{3/2}$

$$\langle 2 \Pi_{1/2} | \hat{H} | 2 \Pi_{-3/2} \rangle = 0 \quad \Delta \Omega = 2$$
\[ \langle \frac{2}{3} \Pi_{1/2} | \hat{H} | \frac{2}{3} \Sigma_{1/2} \rangle = \langle v_{\Pi} | \frac{2}{3} \Pi_{1/2} \left[ \frac{1}{2} A + B(R) \right] L_+ S_- | v_{\Sigma} \rangle \]

\[ = \left[ S(S+1) - \Sigma_{\Pi} \Sigma_{\Sigma} \right]^{1/2} \left[ \langle v_{\Pi} | n_{\Pi} \mid \frac{A}{2} L_+ \mid n'_{\Sigma} \rangle \alpha + B_{v_{\Pi} v_{\Sigma}} \langle n_{\Pi} \mid L_+ \mid n'_{\Sigma} \rangle \beta \right] \]

\[ = 1 \left[ \alpha_{v_{\Pi} v_{\Sigma}} + \beta_{v_{\Pi} v_{\Sigma}} \right] \]

\[ \langle \frac{2}{3} \Pi_{1/2} | \hat{H}^2 | \frac{2}{3} \Sigma_{1/2} \rangle = -B_{v_{\Pi} v_{\Sigma}} \left[ J(J+1) - \frac{1}{2} \left( -\frac{1}{2} \right) \right]^{1/2} \langle n_{\Pi} \mid L_+ \mid n'_{\Sigma} \rangle \]

\[ = -\beta_{v_{\Pi} v_{\Sigma}} y^2 \]

all done with $^3\Pi_{1/2}$

\[ \langle \frac{2}{3} \Sigma_{1/2} | \hat{H}^2 | \frac{2}{3} \Sigma_{1/2} \rangle = -B_{v_{\Sigma}} \left[ J(J+1) - \frac{1}{2} \left( -\frac{1}{2} \right) \right]^{1/2} \left[ \frac{3}{4} - \frac{1}{2} \left( -\frac{1}{2} \right) \right]^{1/2} \]

\[ = -B_{v_{\Sigma}} y^2 \]

all done with $^3\Sigma_{1/2}$.

Are we done? Not quite. Must worry about $^3\Sigma^+ \sim ^3\Pi_{3/2}$ and $^3\Sigma^- \sim ^3\Pi_{1/2}$ matrix elements. What happens to the $\langle \Pi[L_\pm] \Sigma \rangle$ unevaluable factor? Need to consider effects of $\sigma_v(xz)$ reflections and $\Sigma^+, \Sigma^-$ symmetry in order to get the correct relative signs of off-diagonal matrix elements.