5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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

Last Time: effect of $\widehat{A^2}$, $\hat{A}_i$, $\hat{A}_\pm$ on $|A\ \alpha\ M_A\rangle$ basis set

case (a) basis set $\quad |n(L)\ \Lambda\ S\ \Sigma\rangle\ |v\rangle\ |\Omega JM\rangle$

L-destroyed, but not Λ: $\hat{L}_z$, $\hat{L}_\pm$, selection rules

$\hat{\mathbf{H}}^{ROT} = B(R)\widehat{R^2}$ matrix elements

Diagonal: $\left\langle n'\Lambda'S'\Sigma'\right|\left\langle v'\right|\left\langle \Omega JM\right|\hat{\mathbf{H}}^{ROT}\left|n\Lambda S\Sigma\right\rangle\left|v\right\rangle\left|\Omega JM\right\rangle = \delta_{n'n}\delta_{\Lambda'\Lambda}\delta_{S'S}\delta_{\Sigma'\Sigma}\delta_{v'v}\delta_{\Omega'\Omega}\delta_{J'J}\delta_{M'M}$

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

$\Delta\Omega = \Delta\Sigma = \pm 1$ within Λ–S multiplet state (**S-uncoupling**):

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

**** 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.

$$
^2\Pi \begin{cases}
 & \Lambda \quad S \quad \Sigma & \\
|n \quad 1 \quad 1/2 \quad 1/2\rangle & {}^2\Pi_{3/2} \\
|n \quad 1 \quad 1/2 \quad -1/2\rangle & {}^2\Pi_{1/2} \\
|n \quad -1 \quad 1/2 \quad -1/2\rangle & {}^2\Pi_{-3/2} \\
|n \quad -1 \quad 1/2 \quad 1/2\rangle & {}^2\Pi_{-1/2}
\end{cases}
$$

$$
\hat{\mathbf{H}}^{ROT}(^2\Pi) = B_v^\pi \times
\begin{array}{c} ^2\Pi_{3/2} \\ ^2\Pi_{1/2} \\ ^2\Pi_{-1/2} \\ ^2\Pi_{-3/2} \end{array}
\left(\begin{array}{cc|cc}
x - \frac{9}{4} + \frac{3}{4} - \frac{1}{4} & -[x - \frac{3}{4}]^{1/2}[\frac{3}{4} + \frac{1}{4}]^{1/2} & 0 & 0 \\
\text{sym} & x - \frac{1}{4} + \frac{3}{4} - \frac{1}{4} & \boxed{0} & 0 \\
\hline
0 & 0 & x - \frac{1}{4} + \frac{3}{4} - \frac{1}{4} - [x - \frac{3}{4}]^{1/2} & 1 \\
0 & 0 & \text{sym} & x - \frac{9}{4} + \frac{3}{4} - \frac{1}{4}
\end{array}\right)
$$

$\boxed{\Delta\Omega = \pm 1 \quad \Delta\Lambda = \pm 2}$

$$
B_v^\pi \left(\begin{array}{cc|cc}
x - \frac{7}{4} & (x - \frac{3}{4})^{1/2} & 0 & 0 \\
\text{sym} & x + \frac{1}{4} & 0 & 0 \\
\hline
0 & 0 & x + \frac{1}{4} & (x - \frac{3}{4})^{1/2} \\
0 & 0 & \text{sym} & x - \frac{7}{4}
\end{array}\right)
$$

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

What about $^2\Sigma^+$? Class should do this.

ΔΩ = ΔΛ = ±1 between Λ-S multiplet states (**L-uncoupling**)

$$\left\langle n'\Lambda+1S\Sigma\left|\left\langle v'\left|\left\langle \Omega\pm1JM\left|\hat{\mathbf{H}}^{ROT}\right|n\Lambda S\Sigma\right\rangle\right|v\right\rangle\right|\Omega JM\right\rangle = -B_{v'v}[J(J+1)-(\Omega\pm1)\Omega]^{1/2}\times\underbrace{\left\langle n'\Lambda\pm1\left|L_\pm\right|n\Lambda\right\rangle}_{\beta}$$

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

<u>Today</u>: $\hat{\mathbf{H}}^{SO}, \hat{\mathbf{H}}^{SS}, \hat{\mathbf{H}}^{SR}$ $\begin{cases}\text{effective operators}\\ \text{matrix elements}\end{cases}$

Matrix elements of $^2\Pi$, $^2\Sigma$ effective **H**.

spin-orbit $\hat{\mathbf{H}}^{SO} = \sum_i a(r_i)\ell_i\cdot s_i \xrightarrow[\text{only}]{\text{for } \Delta S=0} A\hat{L}\cdot\hat{S}$ (restricted validity operator replacement)

spin-spin $\hat{\mathbf{H}}^{SS} = \xrightarrow[\text{only}]{\text{for } \Delta S=0} \frac{2}{3}\lambda\left[3\hat{S}_z^2-\hat{S}^2\right] +$ another term $\Delta\Sigma = -\Delta\Lambda = \pm 2$

spin-rotation $\hat{\mathbf{H}}^{SR} = \gamma\hat{R}\cdot\hat{S}$

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

$\hat{\mathbf{H}}^{SO}$ is very important

$$\hat{\mathbf{H}}^{SO} = \sum_i a(r_i)\hat{\ell}_i\cdot\hat{s}_i \qquad \left(\text{not} \sum_{i,j} a\hat{\ell}_i\cdot\hat{s}_j\right)$$

electron (not component)

L S

$\hat{\ell}_i, \hat{s}_i$ are vectors with respect to $\hat{J}$ → $\hat{\ell}_i\cdot\hat{s}_i$ is scalar (ΔJ = ΔM = ΔΩ = 0) with respect to $\hat{J}$.

$\hat{s}_i$ is vector with respect to $\hat{S}$ → $\hat{\ell}_i\cdot\hat{s}_i$ is vector with respect to $\hat{S}$ → ΔS = 0, ±1, ΔΣ = 0, ±1

Fine point!

$\ell_i\cdot s_i$ does not operate on $|\Omega JM\rangle$, only on $|n\Lambda S\Sigma\rangle$; it is therefore NOT INDEPENDENT of Ω because, as vector with respect to L and S, its matrix elements are not independent of Λ and Σ.

Selection rules (ASSERTED)

$\Delta J = 0$
$\Delta\Omega = 0$
$+ \not\leftrightarrow -$ (LAB INVERSION $\hat{I}$) (parity)
$g \not\leftrightarrow u$ (body inversion $\hat{i}$)
$\Sigma^+ \leftrightarrow \Sigma^-$ (σ_v)
$\Delta S = 0, \pm 1$
$\Delta\Sigma = -\Delta\Lambda = 0, \pm 1$

$\widehat{\mathbf{H}}^{SO}$ is a one-electron operator, so it has non-zero matrix elements only between electronic configurations differing by a single spin-orbital. (e.g. π orbital = 1α, 1β, -1α, -1β spin-orbitals)

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

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

E.g., for $^2\Pi$

$$\left\langle ^2\Pi_{\pm 3/2}\middle|\widehat{\mathbf{H}}^{SO}\middle|^2\Pi_{\pm 3/2}\right\rangle = A(\pm 1)\left(\pm\frac{1}{2}\right) = \frac{A}{2}$$
$$\left\langle ^2\Pi_{\pm 1/2}\middle|\widehat{\mathbf{H}}^{SO}\middle|^2\Pi_{\pm 1/2}\right\rangle = A(\pm 1)\left(\mp\frac{1}{2}\right) = -\frac{A}{2}$$

all $\Delta\Omega \neq 0$ matrix elements are = 0.

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

Selection rules

$\Delta S = 0$

$\Delta\Omega = 0$

$\Delta S = 0$ [also ±1, ±2 neglected here]

$\Delta\Sigma = 0$ [also $\Delta\Sigma = -\Delta\Lambda = \pm 2$ (Λ-doubling in ${}^3\Pi_0$ neglected here)]

$+ \not\leftrightarrow -$

$g \not\leftrightarrow u$

$\Sigma^+ \not\leftrightarrow \Sigma^-$

$$\hat{\mathbf{H}}^{SR} = \gamma\hat{R}\cdot\hat{S} = \gamma\left(\hat{J}-\hat{L}-\hat{S}\right)\cdot\hat{S} = \gamma[\underbrace{J\cdot S - L\cdot S - S^2}_{\text{we already know how to deal with all three of these!}}]$$

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

$$\left\langle v,n,{}^2\Pi_{3/2}\middle|\hat{\mathbf{H}} = \hat{\mathbf{H}}^{elect} + \hat{\mathbf{H}}^{vib} + \hat{\mathbf{H}}^{ROT} + \hat{\mathbf{H}}^{SO} + \hat{\mathbf{H}}^{SS} + \hat{\mathbf{H}}^{SR}\middle|n,{}^2\Pi_{3/2},v\right\rangle =$$

$$T_e\left(n^2\Pi\right) + G\left(v_\Pi\right) + A_\Pi\overbrace{(1\cdot 1/2)}^{\Lambda\Sigma} + \frac{2}{3}\lambda\left(\underbrace{3\cdot\left(\frac{1}{2}\right)^2 - \frac{3}{4}}_{\substack{\text{always = 0 for}\\ \text{S = 1/2 states!}}}\right)^{\boxed{3\Sigma^2 - S(S+1)}} + \gamma_\Pi\left(\overset{\Omega}{\frac{3}{2}}\cdot\overset{\Sigma}{\frac{1}{2}} - \overset{\Lambda\Sigma}{1\cdot\frac{1}{2}} - \overset{S(S+1)}{\frac{3}{4}}\right)$$

$$+B_{v_\Pi}\left[J(J+1) \overset{-\Omega^2}{-\frac{9}{4}} \overset{+S^2-\Sigma^2}{+\frac{3}{4}-\frac{1}{4}} + \underbrace{L_\perp^2}_{\boxed{\substack{\text{include with } T_e\\ +\text{ G in } E_{v_\Pi}}}}\right] = E_{v_\Pi} + \frac{1}{2}A_\Pi - \frac{1}{2}\gamma_\Pi + B_{v_\Pi}\left(\underbrace{J(J+1) - \frac{7}{4}}_{y^2-2}\right)$$

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

Get same results for $\left\langle {}^2\Pi_{-3/2}\middle|\hat{\mathbf{H}}\middle|{}^2\Pi_{-3/2}\right\rangle$.

$$\left\langle {}^2\Pi_{1/2}\middle|\hat{\mathbf{H}}\middle|{}^2\Pi_{1/2}\right\rangle = E_{v_\Pi} - \frac{1}{2}A_\Pi - \frac{1}{2}\gamma_\Pi + B_{v_\Pi}\left[\underbrace{J(J+1)+1/4}_{y^2}\right]$$

Get same results for $\left\langle {}^2\Pi_{-1/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{-1/2}\right\rangle$.

$$\left\langle {}^2\Sigma_{1/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Sigma_{1/2}\right\rangle = \left\langle {}^2\Sigma_{-1/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Sigma_{-1/2}\right\rangle = E_{v_\Sigma} - A_\Sigma 0\cdot\frac{1}{2} - \frac{1}{2}\gamma_\Sigma + B_{v_\Sigma}\Big[\underbrace{J(J+1) - 1/4 + 3/4 - 1/4}_{y^2}\Big]$$

$\uparrow$ always for Σ-states

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

<u>Off-Diagonal Matrix Elements</u>

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

$$\left\langle {}^2\Pi_{3/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{1/2}\right\rangle = \left\langle {}^2\Pi_{-3/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{-1/2}\right\rangle = \underbrace{-0A_\Pi}_{\Delta\Omega=0} + \overbrace{\left[\frac{1}{2}\left(x-\frac{3}{4}\right)^{1/2}\right]}^{\frac{1}{2}(J_+S_- + J_-S_+)}\gamma_\Pi - B_{v_\Pi}\underbrace{\left[x-\frac{1}{2}\frac{3}{2}\right]^{1/2}}_{[y^2-1]^{1/2}}\underbrace{\left[\frac{3}{4}-\frac{1}{2}\left(-\frac{1}{2}\right)\right]^{1/2}}_{1}$$

$\left\langle {}^2\Pi_{3/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{-1/2}\right\rangle = 0 \qquad \Delta\Omega = 2$

$\left\langle {}^2\Pi_{3/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{-3/2}\right\rangle = 0 \qquad \Delta\Omega = 3$

$$\left\langle {}^2\Pi_{3/2}\middle|\overset{\boxed{-BJ_-L_+}}{\widehat{\mathbf{H}}}\middle|{}^2\Sigma^+_{1/2}\right\rangle = -\underbrace{\left\langle v_\Pi\middle|\mathbf{B(R)}\middle|v_\Sigma\right\rangle}_{B_{v_\Pi v_\Sigma}}\overset{\boxed{J_+}}{\left[J(J+1)-\frac{3}{2}\frac{1}{2}\right]^{1/2}}\underbrace{\left\langle n\Pi\middle|L_+\middle|n'\Sigma\right\rangle}_{\beta(\Pi,\Sigma)}$$
$$= -\beta_{v_\Pi v_\Sigma}\left[y^2-1\right]^{1/2}$$

$\left\langle {}^2\Pi_{3/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Sigma_{-1/2}\right\rangle = 0 \qquad \Delta\Omega = 2$

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

$\left\langle {}^2\Pi_{1/2}\middle|\widehat{\mathbf{H}}\middle|{}^2\Pi_{-3/2}\right\rangle = 0 \qquad \Delta\Omega = 2$

$$\left\langle {}^2\Pi_{1/2}\middle|\hat{\mathbf{H}}\middle|{}^2\Sigma_{1/2}\right\rangle = \left\langle v_\Pi\, {}^2\Pi_{1/2}\middle|\left[\overset{\boxed{\text{from } AL\cdot S}}{\frac{1}{2}A} \overset{\boxed{\text{from } 2BL\cdot S}}{+} B(R)\right]L_+S_-\middle|v_\Sigma\, {}^2\Sigma^+_{1/2}\right\rangle$$

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

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

$$\left\langle {}^2\Pi_{1/2}\middle|\overset{\boxed{-BJ\_L_+}}{\hat{\mathbf{H}}}\middle|{}^2\Sigma_{-1/2}\right\rangle = -B_{v_\Pi v_\Sigma}\left[\underbrace{J(J+1)-\frac{1}{2}\left(-\frac{1}{2}\right)}_{y^2}\right]^{1/2}\langle n\Pi|L_+|n'\Sigma\rangle$$

$$= -\beta_{v_\Pi v_\Sigma}\, y$$

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

$$\left\langle {}^2\Sigma_{1/2}\middle|\overset{\boxed{-BJ\_S_+}}{\hat{\mathbf{H}}}\middle|{}^2\Sigma_{-1/2}\right\rangle = -B_{v_\Sigma}\overset{\boxed{J_+}}{\left[\underbrace{J(J+1)-\frac{1}{2}\left(-\frac{1}{2}\right)}_{y^2}\right]^{1/2}}\overset{\boxed{S_+}}{\left[\frac{3}{4}-\frac{1}{2}\left(-\frac{1}{2}\right)\right]^{1/2}}$$

$$= -B_{v_\Sigma}\, y$$

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

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