5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #16: Parity and e/f Basis for $^2\Pi$, $^2\Sigma^{\pm}$

Last Time: $\hat{\mathbf{H}} = \hat{\mathbf{H}}^{ROT} + \hat{\mathbf{H}}^{SO} + \hat{\mathbf{H}}^{SS} + \hat{\mathbf{H}}^{SR}$ for $^2\Pi$, $^2\Sigma$

* two identical blocks for $^2\Pi$ $\Omega > 0$ and $\Omega < 0$
* $^2\Pi \sim {}^2\Sigma$ matrix elements involve $L_{\pm}$ and cannot be evaluated explicitly.
Define:

$$\beta_{v_\Pi v_\Sigma} = B_{v_\Pi v_\Sigma} \langle n\Pi | \hat{L}_+ | n'\Sigma \rangle$$

$$\alpha_{v_\Pi v_\Sigma} = \langle v_\Pi | v_\Sigma \rangle \left\langle n\Pi \left| \frac{A}{2} \hat{L}_+ \right| n'\Sigma \right\rangle$$

Caution: we do not know relationship between two similar appearing symbols.

E.g. $$\langle n\Lambda = +1 | \hat{L}_+ | n'\Lambda = 0 \rangle \overset{?}{=} \langle n\Lambda = -1 | \hat{L}_- | n'\Lambda = 0 \rangle.$$

Another caution: The $^2\Sigma$ block of the matrix does not factor into $\Omega > 0$ and $\Omega < 0$ sub-blocks.

$$\begin{array}{c} {}^2\Sigma_{+1/2} \\ {}^2\Sigma_{-1/2} \end{array} \left| \begin{array}{cc} E_{v_\Sigma} - \gamma_\Sigma/2 + B_{v_\Sigma} y^2 & \text{sym} \\ (\gamma_\Sigma/2 - B_{v_\Sigma}) y & E_{v_\Sigma} - \gamma_\Sigma/2 + B_{v_\Sigma} y^2 \end{array} \right|$$

$y = J + 1/2$

$$\langle {}^2\Sigma_{+1/2} | \hat{\mathbf{H}} | {}^2\Sigma_{-1/2} \rangle = \left\langle {}^2\Sigma_{+1/2} \left| B_{v_\Sigma}(-J_-S_+) + \gamma_\Sigma \left(+\frac{1}{2} J_-S_+ \right) \right| {}^2\Sigma_{-1/2} \right\rangle$$

$$= (\gamma_\Sigma/2 - B_{v_\Sigma}) [\underbrace{J(J+1) - (1/2)(-1/2)}_{y}]^{1/2} [\underbrace{S(S+1) - (1/2)(-1/2)}_{1}]^{1/2}$$

So are we wrong about being able to factor **H** into two identical blocks? Not quite.

Today: Parity $\underline{\hat{\sigma}_v(xz)}$

HLB-RWF pages 74-75, 138-145
JTH, pages 15-22, 23-25

* apply $\hat{\sigma}_v$ to 3 parts of $|\rangle$ and to operators
* mysterious phases for α, β matrix elements
* $\pm$ parity and e/f basis functions

Derive full $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^- \binom{e}{f}$ Effective Hamiltonian expressed in terms of E, B, A, γ, α, β

What happens when we apply $\hat{\sigma}_v(xz)$ [reflection in body frame] to $|v\rangle$? Trivial.

What happens when we apply $\hat{\sigma}_v$ to $|\Omega JM\rangle$? Need to look at form of wavefunction.

Assertion $\hat{\sigma}_v(xz)\,|\Omega JM\rangle = (-1)^{J-\Omega}\,|J{-}\Omega M\rangle$

known as <u>Condon and Shortley phase convention</u>. This leads to $\hat{J}_x$ and $\hat{J}_\pm$ matrix elements real and positive.

Problem, what do we do about $|n\Lambda\rangle$? We have no L quantum number so what do we do to ensure the Condon and Shortley phase choice?

Assertion $\hat{\sigma}_v(xz)\,|n\Lambda^s S\Sigma\rangle = (-1)^{\Lambda+s+S-\Sigma}\,|n{-}\Lambda^s S{-}\Sigma\rangle$

What is s? A special index for Σ states. Necessary because

$$\hat{\sigma}_v|n\underbrace{\Pi}_{\Lambda=+1}\rangle = (-1)^1|n\underbrace{-\Pi}_{\Lambda=-1}\rangle$$

$$\text{but } \hat{\sigma}_v|n\underbrace{\Sigma}_{\Lambda=0}\rangle = (-1)^s|n\underbrace{\Sigma}_{\Lambda=0}\rangle$$

When $\Lambda \neq 0$ $\hat{\sigma}_v$ takes one basis state into another.

When $\Lambda = 0$ $\hat{\sigma}_v$ takes a basis state into itself. Such a situation requires that a $|n\Sigma\rangle$ state be an eigenfunction of $\hat{\sigma}_v(xz)$ belonging to either the +1 (Σ^+) or the –1 (Σ^-) eigenvalue!

s = 0 for Σ^+
and s = 1
for Σ^-

Putting it all together:

$$\sigma_v|v\rangle|\Omega JM\rangle|n\Lambda^s S\Sigma\rangle = (-1)^{\underbrace{J-\Omega+\Lambda+s+S-\Sigma}_{J-S+s}}|v\rangle|-\Omega JM\rangle|n-\Lambda^s S-\Sigma\rangle$$

$$\left[\text{because } (-1)^{S-\Sigma} = (-1)^{\Sigma-S+2\underbrace{(S-\Sigma)}_{\text{an integer } (-1)^{2n}=+1}}\right]$$

So now we are ready to figure out the relationship between $\langle +\Pi|\hat{L}_+|\Sigma^s\rangle$ and $\langle -\Pi|\hat{L}_-|\Sigma^s\rangle$.

$$\left[\sigma_v, \widehat{\mathbf{H}}\right] = 0 \qquad \text{OR} \qquad \hat{\sigma}_v\,[\text{a number}] = [\text{same number}]$$

$$\hat{\sigma}_v(xz)\left[\left\langle {}^2\Pi_\Omega \middle| \widehat{L}_+ \middle| {}^2\Sigma^s_{\Omega-1}\right\rangle\right] = \left\langle {}^2\Pi_\Omega \middle| \widehat{L}_+ \middle| {}^2\Sigma^s_{\Omega-1}\right\rangle$$

$$\text{but also} \qquad \hat{\sigma}_v \quad \left\langle n\,{}^2\Pi_\Omega\right| = \qquad (-1)^{\overset{\Lambda}{\Lambda}+\overset{s}{0}+\overset{S}{1/2}-(\overset{\Sigma}{\Omega-\Lambda})}\left\langle n\,{}^2\Pi_{-\Omega}\right|$$

$$\hat{\sigma}_v(xz)\; x \to x$$
$$y \to -y$$
$$z \to z$$

$$\hat{\sigma}_v\widehat{L}_+ = \hat{\sigma}_v\left[\widehat{L}_x + i\widehat{L}_y\right] = \hat{\sigma}_v\left[yp_z - zp_y + i\left(xp_z - zp_x\right)\right]$$
$$= -\widehat{L}_x + i\widehat{L}_y = -\widehat{L}_-$$

$\hat{\sigma}_v L_\pm = -L_\mp$ turns out to be basis for $\Sigma^+ \sim \Sigma^-$ $\widehat{\mathbf{H}}^{SO}$ selection rule.

$$\sigma_v\left|{}^2\Sigma^s_{\underbrace{\Omega-1}_{\Sigma}}\right\rangle = (-1)^{0+s+1/2-(\overset{\Sigma}{\Omega-1})}\left|{}^2\Sigma^s_{-\Omega+1}\right\rangle$$

Putting it all together:

$$\left\langle n\,{}^2\Pi_\Omega \middle| \widehat{L}_+ \middle| n'\,{}^2\Sigma^s_{\Omega-1}\right\rangle = (-1)^{1/2-\Omega}\left\langle n\,{}^2\Pi_{-\Omega} \middle| (-1)^1\widehat{L}_-(-1)^{s+1/2-\Omega+1} \middle| n'\,{}^2\Sigma^s_{-\Omega+1}\right\rangle$$

$$= \underbrace{(-1)^{s+\underbrace{1/2+1/2+1+1}_{\text{odd integer}}\underbrace{-2\Omega}_{\text{even integer}}}}_{(-1)^S}\left\langle n\,{}^2\Pi_{-\Omega} \middle| \widehat{L}_- \middle| n'\,{}^2\Sigma^s_{-\Omega+1}\right\rangle$$

More generally:

$$\left\langle n\,{}^{2S+1}\Pi_\Omega \middle| \widehat{L}_+ \middle| n'\,{}^{2S+1}\Sigma^\pm_{\Omega-1}\right\rangle = \pm\left\langle n\,{}^{2S+1}\Pi_{-\Omega} \middle| \widehat{L}_- \middle| n'\,{}^{2S+1}\Sigma^s_{-\Omega+1}\right\rangle$$

Now return to ${}^2\Pi$, ${}^2\Sigma^+$ matrix and go to either +/– or e/f basis set in which every basis function is eigenfunction of $\hat{\sigma}_v(xz)$.

Since $\hat{\sigma}_v\left|n\Lambda^s S\Sigma\right\rangle|\Omega JM\rangle|v\rangle = (-1)^{J-S+s}\left|n-\Lambda S-\Sigma\right\rangle|-\Omega JM\rangle|v\rangle$

try $\psi = 2^{-1/2}\left[|n\Lambda^{s}S\Sigma\rangle|\Omega JM\rangle|v\rangle \pm (-1)^{J-S+s}|n-\Lambda S-\Sigma\rangle|-\Omega JM\rangle|v\rangle\right]$.

So what do we get?

$$\hat{\sigma}_v\psi = 2^{-1/2}\left[(-1)^{J-S+s}|n-\Lambda^{s}S-\Sigma\rangle|-\Omega JM\rangle|v\rangle \pm \underbrace{(-1)^{J-S+s}(-1)^{J-S+s}}_{+1}|n\Lambda S\Sigma\rangle|\Omega JM\rangle|v\rangle\right]$$

$$= \pm\psi$$

So these are the **Parity Basis Functions**

E.g. $\quad |{}^{2}\Pi_{3/2}\pm\rangle \equiv 2^{-1/2}\left[|{}^{2}\Pi_{+3/2}\rangle \pm (-1)^{J-S}|{}^{2}\Pi_{-3/2}\rangle\right]$

Or more generally

$$|n\underbrace{|\Lambda^{s}|S\Sigma\pm\rangle||\Omega|}_{\text{note |absolute value| on }\Lambda\text{ and }\Omega\text{ only}}JM\rangle \equiv 2^{-1/2}\left[|n\Lambda^{s}\geq 0S\Sigma\rangle|\Omega=|\Lambda|+\Sigma JM\rangle \pm (-1)^{J-S+s}|n\Lambda^{s}\leq 0S-\Sigma\rangle|\Omega=-|\Lambda|-\Sigma JM\rangle\right]$$

need careful notation to deal with case where $S > |\Lambda|$ e.g. ${}^{4}\Pi$ where $|\Omega|$ = 5/2, 3/2, 1/2, **–1/2**

NOTE that the phase factor in front of the second term alternates with J (and S). This turns out to be inconvenient for labeling spectroscopic transitions and spectroscopic perturbations. Alternative form of parity: e/f symmetry labels.

$$\text{Want}\quad \text{e:}\quad \sigma_v(xz)\psi_e = +(-1)^{J-1/2}\psi_e$$
$$\text{f:}\quad \sigma_v(xz)\psi_f = -(-1)^{J-1/2}\psi_f$$

use J–1/2 for even multiplicity systems S = 1/2, 3/2, etc.
use J for odd multiplicity systems S = 0, 1, 2, etc.

For our problems we will use e/f labeled basis functions. Check that the following conform to the above definition.

$$\left|{}^{2}\Pi_{3/2}\,{}^{e}_{f}\right\rangle = 2^{-1/2}\left[|{}^{2}\Pi_{+3/2}\rangle \pm |{}^{2}\Pi_{-3/2}\rangle\right]$$

$$\left|{}^{2}\Pi_{1/2}\,{}^{e}_{f}\right\rangle = 2^{-1/2}\left[|{}^{2}\Pi_{1/2}\rangle \pm |{}^{2}\Pi_{-1/2}\rangle\right]$$

$$\left|{}^{2}\Sigma^{\pm}_{1/2}\,{}^{e}_{f}\right\rangle = 2^{-1/2}\left[|{}^{2}\Sigma^{\pm}_{+1/2}\rangle \pm (-1)^{s}|{}^{2}\Sigma^{\pm}_{-1/2}\rangle\right]$$

(Recall s = 0 for Σ^+ and s = 1 for Σ^-)

Now we can write down the full $^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$ matrix in the case (a) e/f basis.

$$
\begin{array}{c|cccc}
\text{e/f} & {}^2\Pi_{3/2} & {}^2\Pi_{1/2} & {}^2\Sigma^+ & {}^2\Sigma^- \\
\hline
{}^2\Pi_{3/2} & \begin{array}{c} E_{v_\Pi} + \frac{1}{2}A_\Pi + B_{v_\Pi} \times \\ \left(y^2-2\right) - \frac{1}{2}\gamma_\Pi \end{array} & \begin{array}{c} \left(\frac{1}{2}\gamma_\Pi - B_{v_\Pi}\right)\times \\ \left[y^2-1\right]^{1/2} \end{array} & -\beta^+_{v_\Pi v_{\Sigma^+}}\left[y^2-1\right]^{1/2} & -\beta^-_{v_\Pi v_{\Sigma^-}}\left[y^2-1\right]^{1/2} \\
{}^2\Pi_{1/2} & & E_{v_\Pi} - \frac{1}{2}A_\Pi + B_{v_\Pi}y^2 - \frac{1}{2}\gamma_\Pi & \alpha^+_{v_\Pi v_{\Sigma^+}} + \beta^+_{v_\Pi v_{\Sigma^+}}[1 \mp y] & \alpha^-_{v_\Pi v_{\Sigma^-}} + \beta^-_{v_\Pi v_{\Sigma^-}}[1 \pm y] \\
{}^2\Sigma^+ & & & \begin{array}{c} E_{v_{\Sigma^+}} + B_{v_{\Sigma^+}}\left(y^2 \mp y\right) \\ -\frac{1}{2}\gamma_{\Sigma^+}(1 \mp y) \end{array} & \alpha_{v_{\Sigma^+} v_{\Sigma^-}} \\
{}^2\Sigma^- & & & & \begin{array}{c} E_{v_{\Sigma^-}} + B_{v_{\Sigma^-}}\left(y^2 \pm y\right) \\ -\frac{1}{2}\gamma_{\Sigma^-}(1 \pm y) \end{array}
\end{array}
$$

y = J + 1/2

See derivations below for details regarding Σ states.

There are some surprising terms here.

Consider

1 $$\left\langle {}^2\Sigma^+ {}^{e}_{f} \middle| \hat{\mathbf{H}} \middle| {}^2\Sigma^+ {}^{e}_{f} \right\rangle = \frac{1}{2}\left[\underbrace{\mathbf{H}_{1/2\ 1/2} + \mathbf{H}_{-1/2\ -1/2}}_{\boxed{[-\gamma/2 + By^2]}} \underbrace{\pm \mathbf{H}_{1/2\ -1/2} \pm \mathbf{H}_{-1/2\ 1/2}}_{\boxed{\pm(\gamma/2 - B)y}}\right] = B\left(y^2 \mp y\right) + \gamma/2\,(\pm y - 1)$$

$$\left\langle {}^2\Sigma^+ {}^{e}_{f} \middle| \hat{\mathbf{H}} \middle| {}^2\Sigma^+ {}^{f}_{e} \right\rangle = \frac{1}{2}\left[\mathbf{H}_{1/2\ 1/2} - \mathbf{H}_{-1/2\ -1/2} + \mathbf{H}_{-1/2\ 1/2} - \mathbf{H}_{1/2\ -1/2}\right] = 0$$

Factorization into separate e/f blocks!

2 $$\left\langle {}^2\Sigma^- {}^{e}_{f} \middle| \hat{\mathbf{H}} \middle| {}^2\Sigma^- {}^{e}_{f} \right\rangle = \frac{1}{2}\left[\mathbf{H}_{1/2\ 1/2} + \mathbf{H}_{-1/2\ -1/2} \mp \mathbf{H}_{1/2\ -1/2} \mp \mathbf{H}_{-1/2\ 1/2}\right] = B\left(y^2 \pm y\right) + \gamma/2\,(\mp y - 1)$$

Also

3 $$\left\langle {}^2\Sigma^+ {}^{e}_{f} \middle| \hat{\mathbf{H}} \middle| {}^2\Pi_{1/2} {}^{e}_{f} \right\rangle = \frac{1}{2}\left[\overset{L_-S_+}{\mathbf{H}_{\Sigma_{1/2}\,\Pi_{1/2}}} + \overset{L_+S_-}{\mathbf{H}_{\Sigma_{-1/2}\,\Pi_{-1/2}}} \pm \overset{J_+L_-}{\mathbf{H}_{\Sigma_{-1/2}\,\Pi_{1/2}}} \pm \overset{J_-L_+}{\mathbf{H}_{\Sigma_{1/2}\,\Pi_{-1/2}}}\right]$$

$$= \frac{1}{2}\left[(\alpha+\beta) + (\alpha+\beta) \pm (y^2)^{1/2}\beta \pm y\beta\right]$$

$$= \alpha + \beta(1 \pm y)$$

4 $$\left\langle {}^2\Sigma^{-}\,{}^{e}_{f}\middle|\widehat{\mathbf{H}}\middle|\,{}^2\Pi_{1/2}\,{}^{e}_{f}\right\rangle = \frac{1}{2}\left[\mathbf{H}_{\Sigma_{1/2}\,\Pi_{1/2}} - (1)^{s}\,\mathbf{H}_{\Sigma_{-1/2}\,\Pi_{-1/2}} \pm \mathbf{H}_{\Sigma_{1/2}\,\Pi_{-1/2}} \mp \mathbf{H}_{\Sigma_{-1/2}\,\Pi_{1/2}}\right]$$

$$= \frac{1}{2}\left[(\alpha+\beta) - (-1)^{1}(\alpha+\beta) \pm y\beta(-1)^{1} \mp y\beta\right]$$

$$= \alpha + \beta(1 \mp y)$$