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5.80 Small-Molecule Spectroscopy and Dynamics
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<u>Lecture #19</u>: Second-Order Effects

<u>Last time</u>: perturbations = accidental degeneracy

<u>Today</u>: effects of "Remote Perturbers". What terms must we add to the effective **H** so that we can represent all usual behaviors with minimum number of parameters.

Use the van Vleck transformation.

Two effects to be discussed

* centrifugal distortion of all zero- and first-order parameters.
  e.g.
  $B \rightarrow D$ [explicit R-dependence of B(R)]
  $A \rightarrow A_D$ [implicit R-dependence of A(R)]
  [interaction with *all* v's of same Λ-S state]

* Λ-doubling and other 2nd-order parameters [interaction with *all* v's of *all* other states]

We will work with $^2\Pi$, $^2\Sigma^s$ example

Recipe

* $\mathbf{H}^{\text{eff}}$ in terms of E, B, A, (λ, γ), α, β

* van Vleck transformation: diagrammatically in the form of "railroads" for each location in $\mathbf{H}^{\text{eff}}$

* each term in van Vleck transformation is

explicit function

$$f(v,J) * \underbrace{\sum_{e',v'} \frac{H_{ev,e'v'}H_{e'v',ev}}{\bar{E}^o_{ev} - E^o_{e'v'}}}_{\text{new 2}^{\text{nd}}\text{ order parameter}}$$

e/f	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Sigma^s$
$^2\Pi_{3/2}$	$E_{v_\Pi} + A_\Pi/2 + B_{v_\Pi}\left(y^2-2\right)$	$-B_{v_\Pi}\left(y^2-1\right)^{1/2}$	$-\beta^s_{v_\Pi v_\Sigma}\left(y^2-1\right)^{1/2}$
$^2\Pi_{1/2}$		$E_{v_\Pi} - A_\Pi/2 + B_{v_\Pi}\left(y^2\right)$	$\alpha^s + \beta^s\left[1 \mp (-1)^s y\right]$
$^2\Sigma^s$			$E_{v_\Sigma} + B_{v_\Sigma}\left[y^2 \mp (-1)^s y\right]$

$y \equiv J + 1/2$

For simplicity we do not include γ terms (λ terms are not possible for S < 1 states).

What do we do with these?

$$\mathbf{H} = \begin{array}{c} m \\ m' \\ n \\ n' \end{array} \begin{pmatrix} \boxed{\text{interesting}} & H'_{mn} \\ & \\ & \boxed{\text{remote}} \\ & \end{pmatrix}$$

$$H^{VV}_{m,m'} \equiv E^o_m \delta_{mm'} + \lambda^1 H'_{mm'} + \underbrace{\frac{\lambda^2}{2} \sum_n \left[\overbrace{\frac{H'_{mn} H'_{nm'}}{E^o_m - E^o_n}}^{\text{follows rules for matrix multiplication}} + \frac{H'_{mn} H'_{nm'}}{E^o_{m'} - E^o_n} \right]}_{\sim \lambda^2 \sum_n \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm'}}{\frac{E^o_m + E^o_{m'}}{2} - E^o_n}}$$

We are going to write $\mathbf{H}^{eff}$ in terms of

zero-order parameters	E, B, A
perturbation parameters	α, β
second-order parameters	D, A_D, o, p, q

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^{ROT} + \hat{\mathbf{H}}^{SO}$$

$\left(\hat{\mathbf{H}}\right)^2 = \left(\hat{\mathbf{H}}^{ROT}\right)^2$
- e/f dependent — q (Λ-doubling)
- e/f independent — D (centrifugal distortion of B)

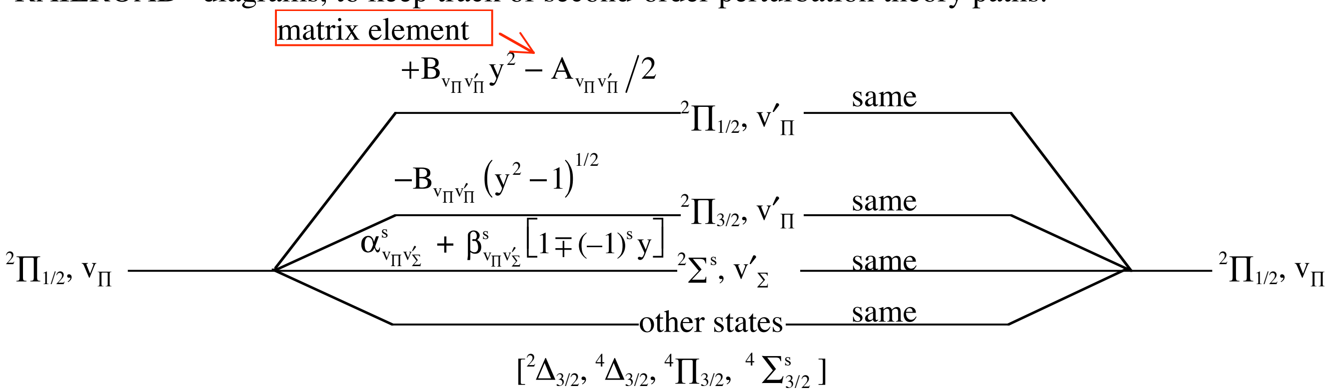
$+\left(\hat{\mathbf{H}}^{SO}\right)^2$
- e/f dependent — o (Λ-doubling)
- e/f independent — λ (2nd-order spin-spin)

$+\left(\hat{\mathbf{H}}^{ROT} \otimes \hat{\mathbf{H}}^{SO}\right)^2$
- e/f dependent — p (Λ-doubling)
- e/f independent — γ (2nd-order spin-rotation), A_D (centrifugal distortion of A)

Generate many 2nd-order parameters — not all are linearly independent.

Let's first work through all paths from ${}^2\Pi_{1/2}$, v_Π to remote state and back to ${}^2\Pi_{1/2}$, v_Π.

"RAILROAD" diagrams, to keep track of second-order perturbation theory paths.



collect terms and sum

$$H^{(2)}_{{}^2\Pi_{1/2},{}^2\Pi_{1/2}}\begin{pmatrix} e \\ f \end{pmatrix} = \sum_{v'_\Pi} \frac{B^2_{vv'}\left(y^4+y^2-1\right)+A^2_{vv'}/4 - B_{vv'}A_{vv'}y^2}{E^o_{v_\Pi}-E^o_{v'_\Pi}}$$

$$+\sum_{v'_\Sigma} \frac{\left(\alpha^s_{v_\Pi v'_\Sigma}\right)^2 + \left(\beta^s_{v_\Pi v'_\Sigma}\right)^2\left[1 \mp (-1)^s 2y + y^2\right] + \left(\alpha^s_{v_\Pi v'_\Sigma}\beta^s_{v_\Pi v'_\Sigma}\right)2\left[1 \mp (-1)^s y\right]}{E^o_{v_\Pi}-E^o_{v'_\Sigma}}$$

Now define some 2nd-order parameters.

$$D \equiv -\sum_{v'_\Pi \neq v_\Pi} \frac{B^2_{v_\Pi v'_\Pi}}{E^o_{v_\Pi}-E^o_{v'_\Pi}} \qquad \text{(defined so that } D>0 \text{ for } v_\Pi = 0)$$

$$A_D \equiv 2\sum_{v'_\Pi \neq v_\Pi} \frac{A_{v_\Pi v'_\Pi}B_{v_\Pi v'_\Pi}}{E^o_{v_\Pi}-E^o_{v'_\Pi}}$$

$$A_0 \equiv \sum_{v'_\Pi \neq v_\Pi} \frac{\left|A_{v_\Pi v'_\Pi}\right|^2}{E^o_{v_\Pi}-E^o_{v'_\Pi}}$$

$$o\left({}^2\Sigma^s\right) \equiv \sum_{\substack{v'_\Sigma \\ (\neq v_\Sigma)}} \frac{\left(\alpha^s_{v_\Pi v'_\Sigma}\right)^2}{E^o_{v_\Pi}-E^o_{v'_\Sigma}} \qquad [H^{SO} \otimes H^{SO}]$$

$$p\left({}^2\Sigma^s\right) \equiv 4\sum_{\substack{v'_\Sigma \\ (\neq v_\Sigma)}} \frac{\alpha^s_{v_\Pi v'_\Sigma}\beta^s_{v_\Pi v'_\Sigma}}{E^o_{v_\Pi}-E^o_{v'_\Sigma}} \qquad [H^{SO} \otimes H^{ROT}]$$

$$q\left({}^2\Sigma^s\right) \equiv 2\sum_{\substack{v'_\Sigma \\ (\neq v_\Sigma)}} \frac{\left(\beta^s_{v_\Pi v'_\Sigma}\right)^2}{E^o_{v_\Pi}-E^o_{v'_\Sigma}} \qquad [H^{ROT} \otimes H^{ROT}]$$

Thus

$$H^{(2)}_{^2\Pi_{1/2},\,^2\Pi_{1/2}}\begin{pmatrix}e\\ f\end{pmatrix} = -D\left(y^4+y^2-1\right)-\frac{1}{2}A_D y^2 + A_0/4 + o\left(^2\Sigma^s\right)$$

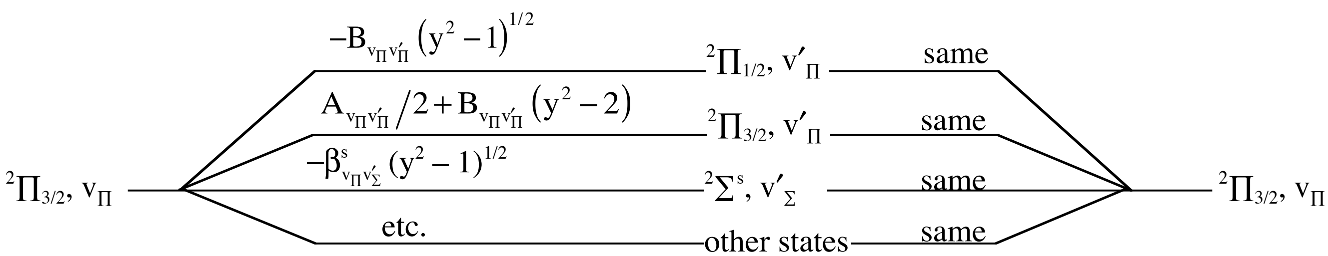
(no Λ-doubling)

$$+\frac{1}{2}p\left(^2\Sigma^s\right)\left[1\mp(-1)^s y\right]+\frac{1}{2}q\left(^2\Sigma^s\right)\left[1\mp(-1)^s 2y+y^2\right]$$

(Λ-doubling) (Λ-doubling)

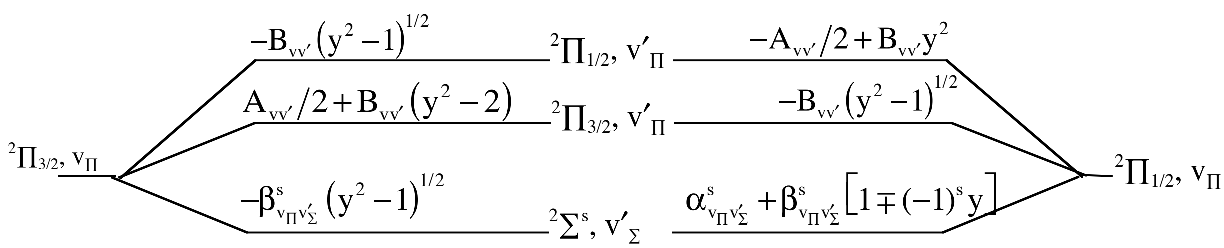
These same parameters appear in other locations in $^2\Pi$ $\mathbf{H}^{\text{eff}}$.

Non-Lecture



Thus

$$H^{(2)}_{^2\Pi_{3/2},\,^2\Pi_{3/2}}\begin{pmatrix}e\\ f\end{pmatrix} = -D\left[y^4-3y^2+3\right]+\frac{1}{2}A_D\left(y^2-2\right)+A_0/4+\frac{1}{2}q\left(^2\Sigma^s\right)\left[y^2-1\right]$$



Thus

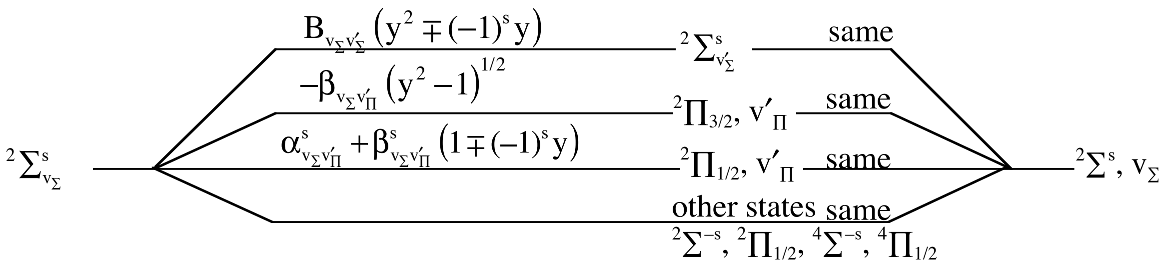
$$H^{(2)}_{^2\Pi_{3/2},\,^2\Pi_{1/2}}\begin{pmatrix}e\\ f\end{pmatrix} = +D\underbrace{\left[y^2\left(y^2-1\right)^{1/2}+\left(y^2-2\right)\left(y^2-1\right)^{1/2}\right]}_{\boxed{2(y^2-1)(y^2-1)^{1/2}}}+\frac{1}{2}A_D\underbrace{\left[\frac{1}{2}\left(y^2-1\right)^{1/2}-\frac{1}{2}\left(y^2-1\right)^{1/2}\right]}_{\boxed{0}}$$

$$+\frac{1}{4}p\left(^2\Sigma^s\right)\left[-\left(y^2-1\right)^{1/2}\right]+\frac{1}{2}q\left(^2\Sigma^s\right)\left[-\left[1\mp(-1)^s y\right]\left(y^2-1\right)^{1/2}\right]$$

$$= +D2\left(y^2-1\right)^{3/2}-\frac{1}{4}p\left(y^2-1\right)^{1/2}-\frac{1}{2}q\left(^2\Sigma^s\right)\left(1\mp(-1)^s y\right)\left(y^2-1\right)^{1/2}$$

Λ-doubling

Non-Lecture



$$
\begin{aligned}
H^{(2)}_{^2\Sigma^s,\,^2\Sigma^s} &= -D_\Sigma\left[y^4 \mp (-1)^s 2y^3 + y^2\right] \\
&+ \frac{1}{2} q_\Sigma\left(^2\Pi\right)\left[y^2 - 1 + \left(1 \mp (-1)^s 2y + y^2\right)\right] \qquad = \left\{\frac{1}{2} q_\Sigma\left(^2\Pi\right)\left[2y^2 \mp (-1)^s 2y\right]\right\} \\
&+ \frac{1}{4} p_\Sigma\left(^2\Pi\right)\left[2\left(1 \mp (-1)^s y\right)\right] \\
&+ o_\Sigma\left(^2\Pi\right)
\end{aligned}
$$

$q_\Sigma(^2\Pi)$ is exactly correlated with B_Σ because it has same J-dependence.

$o_\Sigma(^2\Sigma)$ is exactly correlated with E_Σ.

$\frac{1}{2}p_\Sigma(^2\Pi)$ is exactly correlated with γ_Σ.

These second-order parameters cannot be determined by a fit to the observed energy levels. They also cause the microscopic mechanical meaning of the E, B, γ parameters to be contaminated.

Now that I have worked out all of the correction terms for the ${}^2\Pi$, ${}^2\Sigma^s$ $\mathbf{H}^{\text{eff}}$, we can examine the structure of this matrix. For simplicity, specialize to ${}^2\Sigma^+$ (s = 0).

$\mathbf{H}^{(2)}\binom{e}{f}$	${}^2\Pi_{3/2}$	${}^2\Pi_{1/2}$	${}^2\Sigma^+$
${}^2\Pi_{3/2}$	$-D_\Pi(y^4 - 3y^2 + 3)$ $+\frac{1}{2}A_D(y^2 - 2)$ $+\frac{1}{2}q_\Pi(y^2 - 1)$ $+ A_0/4$	$+D_\Pi 2(y^2 - 1)^{3/2}$ $-\frac{1}{4}p_\Pi(y^2 - 1)^{1/2}$ $-\frac{1}{2}q_\Pi(1 \mp y)(y^2 - 1)^{1/2}$	
${}^2\Pi_{1/2}$	sym	$-D_\Pi(y^4 + y^2 - 1) + A_0/4$ $+\frac{1}{2}A_D y^2 + o_\Pi$ $+\frac{1}{2}p_\Pi(1 \mp y) + \frac{1}{2}q_\Pi[1 \mp 2y + y^2]$	
${}^2\Sigma^+$			$-D_\Sigma(y^4 \mp 2y^3 + y^2)$ $+q_\Sigma(y^2 \mp y)$ $+\frac{1}{2}p_\Sigma(1 \mp y) + o_\Sigma$

NOTE: ** Centrifugal Distortion matrix elements are not trivial replacement of B by [B – DJ(J + 1)]

** e/f degeneracy in ${}^2\Pi$ is lifted in $\mathbf{H}^{(2)}$

** all Λ-doubling in ${}^2\Pi$ states comes from ${}^2\Sigma^\pm$, none from ${}^2\Pi$, ${}^2\Delta$, ${}^4\Pi$, ${}^4\Delta$, etc.

Now apply perturbation theory to $\mathbf{H}^{(0)} + \mathbf{H}^{(1)} + \mathbf{H}^{(2)}$ matrices to analyze where specific effect (e.g. Λ-doubling) originates.

Often want to do this in order to:

* identify parameter responsible for an observed splitting with a certain J-dependence;
* prove that two fit parameters are correlated and therefore not independently determinable;
* build in correction for expected not-quite-remote perturber;
* determine whether a certain fit parameter can actually be determined by the information contained in your specific data set.

EXAMPLE - Λ-Doubling

EXPLICIT e/f dependence on-diagonal in $\mathbf{H}^{\mathrm{eff}}$
IMPLICIT e/f dependence off-diagonal in $\mathbf{H}^{\mathrm{eff}}$

$$E_{{}^2\Pi_{1/2}\,e} - E_{{}^2\Pi_{1/2}\,f} = -yp_{\Pi} - 2yq_{\Pi} + \text{“second order”}$$
$$E_{{}^2\Pi_{3/2}\,e} - E_{{}^2\Pi_{3/2}\,f} = 0 \qquad + \text{“second order”}$$
$$\text{“second order”} = \frac{H^2_{3/2,1/2}}{E^{\circ}_{3/2} - E^{\circ}_{1/2}} \approx \begin{matrix}\text{largest parity}\\ \text{dependent term}\end{matrix} + \begin{matrix}\text{largest parity}\\ \text{independent term}\end{matrix}$$

$\boxed{\text{largest term}}$

$$H_{3/2,1/2} = -B_{v_{\Pi}}\underbrace{\left(y^2-1\right)}^{1/2} + D_{\Pi}2\left(y^2-1\right)^{3/2} - \frac{1}{4}p_{\Pi}\left(y^2-1\right)^{1/2} - \frac{1}{2}q_{\Pi}\left(1\mp y\right)\underbrace{\left(y^2-1\right)}$$

parity dependent part of $H^2_{3/2,1/2}$

$$H^2_{3/2,1/2} = \mp 2\frac{1}{2}B_{v_{\Pi}}q_{\Pi}y\left(y^2-1\right)^{1/2}\left(y^2-1\right)^{1/2} = \mp B_{v_{\Pi}}q_{\Pi}y\left(y^2-1\right)$$
$$E^{\circ}_{3/2} - E^{\circ}_{1/2} \approx A_{\Pi}$$

So

$$E_{3/2e} - E_{3/2f} \approx -2\frac{B}{A}qy\left(y^2-1\right) \approx -2\frac{B}{A}qJ^3$$

Similar algebra for ${}^2\Pi_{1/2}$:

$$E_{1/2e} - E_{1/2f} \approx \underbrace{-\left(p_{\Pi} + 2q_{\Pi}\right)\overset{\boxed{J}}{y}}_{\text{from } H^{(2)}_{{}^2\Pi_{1/2},{}^2\Pi_{1/2}}} + \underbrace{2\frac{B}{A}qJ^3}_{\text{from } \left(H_{3/2,1/2}\right)^2/A}$$

Usually $|p_{\Pi}| \gg |q_{\Pi}|$ because
$$p \propto \alpha\beta$$
$$q \propto \beta^2$$
$$p/q \approx \frac{\alpha}{\beta} = \frac{A}{B}$$

At low-J, leading contribution to Λ-doubling

in $^2\Pi_{1/2}$	is	$-Jp_\Pi$	linear in J
in $^2\Pi_{3/2}$	is	$-(2Bq/A)J^3$	cubic in J

Structure of $^2\Sigma^+$ state

$$E\left({}^2\Sigma^+ \begin{matrix} e \\ f \end{matrix}\right) = \left(E_{v_\Sigma} + \overbrace{o_\Sigma}^{\text{lumped into } E_{v_\Sigma}}\right) + \left(B_{v_\Sigma} + \underbrace{q_\Sigma}_{\text{lumped into } B_{v_\Sigma}}\right)\left(y^2 \mp y\right) + \underbrace{\frac{1}{2}p_\Sigma(1 \mp y)}_{\text{same as } \gamma \mathbf{R}\cdot\mathbf{S}} - D_\Sigma\left(y^4 \mp 2y^3 + y^2\right)$$

A mixture of mechanical and magnetic significance is what we determine by fitting a spectrum!

Finally, replace y by N as follows:

	for $^2\Sigma^+ \begin{pmatrix} e \\ f \end{pmatrix}$		$y^2 \mp y$	$1 \mp y$	$y^4 \mp 2y^3 + y^2$
e	$J = N + 1/2\ (F_1)$	$y = N + 1$	$N(N + 1)$	$-N$	$N^2(N + 1)^2$
f	$J = N - 1/2\ (F_2)$	$y = N$	$N(N + 1)$	$1 + N$	$N^2(N + 1)^2$

[F_i labels: for isolated $^{2S+1}\Sigma$ state, F_1 is $N = J - S$ and lies at lowest E for given J and F_{2S+1} is $N = J + S$ and lies at highest E for given J.]

$$E\left({}^2\Sigma^+ \begin{matrix} e \\ f \end{matrix}\right) = E_{v_\Sigma} + B_{v_\Sigma}\underbrace{N(N+1)} - D_\Sigma\left[\underbrace{N(N+1)}\right]^2 + \frac{1}{2}p_\Sigma\left[\frac{1}{2} \mp \underbrace{(N+1/2)}\right]$$

N is pattern-forming quantum number!

$$\boxed{E_{^2\Sigma^+ e} - E_{^2\Sigma^+ f} = -yp_\Sigma = -(N+1/2)p_\Sigma}$$

for same N (different J)