Lecture #19: Second-Order Effects

Last time: perturbations = accidental degeneracy

Today: 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.
  
  $B \rightarrow D$  \hspace{1cm} [explicit R-dependence of $B(R)$]
  
  $A \rightarrow A_0$  \hspace{1cm} [implicit R-dependence of $A(R)$]
  
  [interaction with all $v$’s of same $\Lambda$-$S$ state]

* $\Lambda$-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

* $H^\text{eff}$ in terms of $E$, $B$, $A$, $(\lambda, \gamma)$, $\alpha$, $\beta$

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

* each term in van Vleck transformation is

  explicit function

  $f(v, J) \sum_{e', v'} \frac{H_{ev', e'v'} H_{e'v', ev}}{E_{ev'}^0 - E_{e'v'}^0}$

  new 2\textsuperscript{nd} order parameter

| $e/f$ | $^2\Pi_{3/2}$ | $^2\Pi_{1/2}$ | $^2\Sigma^s$
<table>
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<tbody>
<tr>
<td>$^2\Pi_{3/2}$</td>
<td>$E_{\Pi} + A\Pi/2 + B\Pi (y^2 - 2)$</td>
<td>$-B\Pi (y^2 - 1)^{1/2}$</td>
<td>$-\beta^s_{\Pi} (y^2 - 1)^{1/2}$</td>
</tr>
<tr>
<td>$^2\Pi_{1/2}$</td>
<td>$E_{\Pi} - A\Pi/2 + B\Pi (y^2)$</td>
<td>$\alpha^s + \beta^s [1 + (-1)^s y]$</td>
<td></td>
</tr>
<tr>
<td>$^2\Sigma^s$</td>
<td>$y \equiv J + 1/2$</td>
<td></td>
<td>$E_{\Sigma} + B_{\Sigma} [y^2 + (-1)^s y]$</td>
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For simplicity we do not include $\gamma$ terms ($\lambda$ terms are not possible for $S < 1$ states).
What do we do with these?

\[ \mathbf{H} = \begin{pmatrix} m & \text{interesting} & H'_{mn} \\ m' & \text{remote} & \vdots \\ n & \text{remote} & \vdots \\ n' & \text{remote} & \end{pmatrix} \]

follows rules for matrix multiplication

\[
H_{m,m'}^{VV} \equiv E^o_m \delta_{mm'} + \lambda^1 H'_{mm'} + \frac{\lambda^2}{2} \sum_n \left[ \frac{H'_{mn}H'_{nm'}}{E^o_m - E^o_n} + \frac{H'_{mn}H'_{nm'}}{E^o_{m'} - E^o_n} \right]
\]

\[
\sim \lambda^2 \sum_n \frac{H'_{mn}H'_{nm'}}{E^o_m + E^o_{m'} - 2E^o_n}
\]

We are going to write \( \mathbf{H}^{\text{eff}} \) in terms of

zero-order parameters \( E, B, A \)

perturbation parameters \( \alpha, \beta \)

second-order parameters \( D, A_D, o, p, q \)

\[ \hat{\mathbf{H}} = \hat{\mathbf{H}}^{\text{ROT}} + \hat{\mathbf{H}}^{\text{SO}} \]

\[ (\hat{\mathbf{H}})^2 = (\hat{\mathbf{H}}^{\text{ROT}})^2 \]

\[ + (\hat{\mathbf{H}}^{\text{SO}})^2 \]

\[ + (\hat{\mathbf{H}}^{\text{ROT}} \otimes \hat{\mathbf{H}}^{\text{SO}})^2 \]

e/f dependent q (\( \Lambda \)-doubling)
e/f independent D (centrifugal distortion of B)
e/f dependent o (\( \Lambda \)-doubling)
e/f independent \( \lambda \) (2nd-order spin-spin)
e/f dependent p (\( \Lambda \)-doubling)
e/f independent \( \gamma \) (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 $^2\Pi_{1/2}, v_\Pi$ to remote state and back to $^2\Pi_{1/2}, v_\Pi$.

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

collect terms and sum

\[
H^{(2)}_{^2\Pi_{1/2} - ^2\Pi_{1/2}} (e \rightarrow f) = \sum_{v\ell} \left( \frac{B^2_{v\ell}(y^2 + y^2 - 1)}{E_v^0 - E_v^\ell} + \frac{A^2_{v\ell}}{4} - B_{v\ell} A_{v\ell} y^2 \right) + \sum_{v\ell} \left( \frac{(\alpha^s_{v\ell})^2}{E_v^0 - E_v^\ell} + (\beta^s_{v\ell})^2 [1 + (-1)^s 2y + y^2] + (\alpha^s_{v\ell} \beta^s_{v\ell}) 2 [1 + (-1)^s y] \right)
\]

Now define some 2nd-order parameters.

\[
D \equiv - \sum_{v\ell \neq v_\Pi} \frac{B^2_{v\ell v_\Pi}}{E_v^0 - E_v^\ell} \quad \text{(defined so that D > 0 for v_\Pi = 0)}
\]

\[
A_D \equiv 2 \sum_{v\ell \neq v_\Pi} \frac{A_{v\ell v_\Pi} B_{v\ell v_\Pi}}{E_v^0 - E_v^\ell}
\]

\[
A_0 \equiv \sum_{v\ell \neq v_\Pi} \frac{|A_{v\ell v_\Pi}|^2}{E_v^0 - E_v^\ell}
\]

\[
o^{(2 \Sigma^s)} \equiv \sum_{v\ell \neq v_\Pi} \left( \frac{\alpha^s_{v\ell}}{E_v^0 - E_v^\ell} \right)^2 [H^{SO} \otimes H^{SO}]
\]

\[
p^{(2 \Sigma^s)} \equiv 4 \sum_{v\ell \neq v_\Pi} \left( \frac{\alpha^s_{v\ell} \beta^s_{v\ell}}{E_v^0 - E_v^\ell} \right)^2 [H^{SO} \otimes H^{ROT}]
\]

\[
q^{(2 \Sigma^s)} \equiv 2 \sum_{v\ell \neq v_\Pi} \left( \frac{\beta^s_{v\ell}}{E_v^0 - E_v^\ell} \right)^2 [H^{ROT} \otimes H^{ROT}]
\]
Thus

\[
H_{\Pi_{1/2}, \Pi_{1/2}}^{\text{(2)}} \left( e_f \right) = -D(y^4 + y^2 - 1) - \frac{1}{2} A_D y^2 + A_0 / 4 + o(2 \Sigma^s) \\
+ \frac{1}{2} p(2 \Sigma^s)[1 \mp (-1)^s y] + \frac{1}{2} q(2 \Sigma^s)[1 \mp (-1)^s 2y + y^2]
\]

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

**Non-Lecture**

\[
\begin{align*}
2^\Pi_{3/2}, v_{\Pi} & \quad | \quad -B_{v\Pi} (y^2 - 1)^{1/2} \\
2^\Pi_{1/2}, v'_{\Pi} & \quad | \quad 2^\Pi_{1/2}, v'_{\Pi} & \quad | \quad \text{same} \\
A_{v\Pi} / 2 + B_{v\Pi} (y^2 - 2) & \quad | \quad 2^\Pi_{3/2}, v'_{\Pi} & \quad | \quad \text{same} \\
-\beta^{\text{spin}}_{v\Pi} (y^2 - 1)^{1/2} & \quad | \quad 2^\Sigma^s, v'_{\Sigma} & \quad | \quad \text{same} \\
\text{etc.} & \quad | \quad \text{other states} & \quad | \quad 2^\Pi_{3/2}, v_{\Pi}
\end{align*}
\]

Thus

\[
H_{\Pi_{3/2}, \Pi_{3/2}}^{\text{(2)}} \left( e_f \right) = -D[y^4 - 3y^2 + 3] + \frac{1}{2} A_D (y^2 - 2) + A_0 / 4 + \frac{1}{2} q(2 \Sigma^s)[y^2 - 1]
\]

\[
\begin{align*}
2^\Pi_{3/2}, v_{\Pi} & \quad | \quad -B_{v\Pi} (y^2 - 1)^{1/2} \\
2^\Pi_{1/2}, v'_{\Pi} & \quad | \quad 2^\Pi_{1/2}, v'_{\Pi} & \quad | \quad -A_{v\Pi} / 2 + B_{v\Pi} y^2 \\
A_{v\Pi} / 2 + B_{v\Pi} (y^2 - 2) & \quad | \quad 2^\Pi_{3/2}, v'_{\Pi} & \quad | \quad -B_{v\Pi} (y^2 - 1)^{1/2} \\
-\beta^{\text{spin}}_{v\Pi} (y^2 - 1)^{1/2} & \quad | \quad 2^\Sigma^s, v'_{\Sigma} & \quad \alpha^{\text{spin}}_{v\Pi} + \beta^{\text{spin}}_{v\Pi} [1 \mp (-1)^s y] & \quad | \quad 2^\Pi_{1/2}, v_{\Pi}
\end{align*}
\]

Thus

\[
H_{\Pi_{3/2}, \Pi_{3/2}}^{\text{(2)}} \left( e_f \right) = +D[y^2 (y^2 - 1)^{1/2} + (y^2 - 2) (y^2 - 1)^{1/2}] + \frac{1}{2} A_D \left[ \frac{1}{2} (y^2 - 1)^{1/2} - \frac{1}{2} (y^2 - 1)^{1/2} \right] \\
+ \frac{1}{4} p(2 \Sigma^s)[-(y^2 - 1)^{1/2}] + \frac{1}{2} q(2 \Sigma^s)[-1 \mp (-1)^s y] (y^2 - 1)^{1/2} \\
= +D2(y^2 - 1)^{3/2} - \frac{1}{4} p(y^2 - 1)^{1/2} - \frac{1}{2} q(2 \Sigma^s)(1 \mp (-1)^s y)(y^2 - 1)^{1/2}
\]
\[ H_{\Sigma, \Sigma}^{(2)} = -D_\Sigma \left[ y^4 \mp (-1)^s 2y^3 + y^2 \right] + \frac{1}{2} q_\Sigma \left( \frac{1}{2} \Pi \right) \left[ y^2 - 1 + \mp (-1)^s 2y + y^2 \right] + \frac{1}{4} p_\Sigma \left( \frac{1}{2} \Pi \right) \left[ 2(1 \mp (-1)^s y) \right] + o_\Sigma \left( \frac{1}{2} \Pi \right) \]

\( q_\Sigma \left( \frac{1}{2} \Pi \right) \) is exactly correlated with \( B_\Sigma \) because it has same J-dependence.

\( o_\Sigma \left( \frac{1}{2} \Sigma \right) \) is exactly correlated with \( E_\Sigma \).

\( \frac{1}{3} p_\Sigma \left( \frac{1}{2} \Pi \right) \) is exactly correlated with \( \gamma_\Sigma \).

These second-order parameters cannot be determined by a fit to the observed energy levels. They also cause the microscopic mechanical meaning of the \( E, B, \gamma \) parameters to be contaminated.
Now that I have worked out all of the correction terms for the $^2\Pi, \ ^2\Sigma^+ \text{H}^{\text{eff}}$, we can examine the structure of this matrix. For simplicity, specialize to $^2\Sigma^+$ ($s = 0$).

\[
\begin{array}{|c|c|c|c|}
\hline
H^{(2)}(e) & ^2\Pi_{3/2} & ^2\Pi_{1/2} & ^2\Sigma^+ \\
\hline
^2\Pi_{3/2} & -D_\Pi(y^3 - 3y^2 + 3) & +D_\Pi(y^2 - 1)^{3/2} & \\
 & +\frac{1}{2}A_\Pi(y^2 - 2) & -\frac{1}{2}p_\Pi(y^2 - 1)^{1/2} & \\
 & +\frac{1}{2}q_\Pi(y^2 - 1) & -\frac{3}{2}q_\Pi(1 \mp y)(y^2 - 1)^{1/2} & \\
 & +A_0/4 & & \\
\hline
^2\Pi_{1/2} & \text{sym} & -D_\Pi(y^4 + y^2 - 1) + A_0/4 & \\
 & & +\frac{1}{2}A_\Pi y^2 + o_\Pi & \\
 & & +\frac{1}{2}p_\Pi(1 \mp y) + \frac{1}{2}q_\Pi[1 \mp 2y + y^2] & \\
\hline
^2\Sigma^+ & & & -D_\Sigma(y^4 \mp 2y^3 + y^2) \\
 & & & +q_\Sigma(y^2 \mp y) \\
 & & & +\frac{1}{2}p_\Sigma(1 \mp y) + o_\Sigma \\
\hline
\end{array}
\]

** 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 $H^{(2)}$

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

Now apply perturbation theory to $H^{(0)} + H^{(1)} + H^{(2)}$ 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 $H^{\text{eff}}$

**IMPLICIT**  e/f dependence off-diagonal in $H^{\text{eff}}$

$E_{\Sigma,\Pi}^e - E_{\Sigma,\Pi}^f = -y\pi - 2yq\pi + \text{“second order”}$

$E_{\Sigma,\Pi}^e - E_{\Sigma,\Pi}^f = 0 + \text{“second order”}$

“second order” = \( \frac{H_{3/2,1/2}^2}{E_{3/2} - E_{1/2}^o} \approx \) largest parity dependent term + largest parity independent term

**largest term**

\[
H_{3/2,1/2} = -B_{\Pi}(y^2 - 1)^{1/2} + D_{\Pi}2(y^2 - 1)^{3/2} - \frac{1}{4}p_{\Pi}(y^2 - 1)^{1/2} - \frac{1}{2}q_{\Pi}(1 \mp y)(y^2 - 1)
\]

Parity dependent part of $H_{3/2,1/2}^2$

\[
H_{3/2,1/2}^2 = \mp 2 \frac{1}{2}B_{\Pi}q_{\Pi}y(y^2 - 1)^{1/2} = \mp B_{\Pi}q_{\Pi}y(y^2 - 1)
\]

\[
E_{3/2}^o - E_{1/2}^o \approx A_{\Pi}
\]

So

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

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

\[
E_{1/2}^e - E_{1/2}^f \approx -\left( p_{\Pi} + 2q_{\Pi} \right)y + \frac{2}{A} qJ^3
\]

\[
\text{from } H_{\Pi/2, \Pi/2}^{(2)}
\]

\[
\text{from } (H_{3/2,1/2}^2)^2 / A
\]

Usually $|p_{\Pi}| \gg |q_{\Pi}|$ because $p \propto \alpha \beta$

$q \propto \beta$

$p / q \approx \frac{\alpha}{\beta} = \frac{A}{B}$
At low-J, leading contribution to \( \Lambda \)-doubling

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

Structure of \( ^2\Sigma^+ \) state

\[
E\left( ^2\Sigma^+ \right) = \left( E_{v}\Sigma + o\Sigma \right) + \left( B_{v}\Sigma + q\Sigma \right) \left( y^2 + y \right) + \frac{1}{2} p\Sigma (1+y) - D\Sigma \left( y^4 + 2y^3 + y^2 \right)
\]

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

Finally, replace \( y \) by \( N \) as follows:

For \( ^2\Sigma^+ \):

<table>
<thead>
<tr>
<th>( J )</th>
<th>( y )</th>
<th>( N(N+1) )</th>
<th>( -N )</th>
<th>( N^2(N+1)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e )</td>
<td>( J = N + 1/2 (F_1) )</td>
<td>( y = N + 1 )</td>
<td>( N(N+1) )</td>
<td>( -N )</td>
</tr>
<tr>
<td>( f )</td>
<td>( J = N - 1/2 (F_2) )</td>
<td>( y = N )</td>
<td>( N(N+1) )</td>
<td>( 1 + N )</td>
</tr>
</tbody>
</table>

[F 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 \( J \).]

\[
E\left( ^2\Sigma^+ \right) = E_{v}\Sigma + B_{v}\Sigma N(N+1) - D\Sigma \left[ N(N+1) \right]^2 + \frac{1}{2} p\Sigma \left[ \frac{1}{2} \mp (N + 1/2) \right]
\]

\( N \) is pattern-forming quantum number!

\[
E_{\Sigma^+} - E_{\Sigma^+} = -yp\Sigma = -(N+1/2)p\Sigma
\]

for same \( N \) (different \( J \))