

Transformation between $\mathbf{H}_{\text{Local}}^{\text{eff}}$ and $\mathbf{H}_{\text{Normal}}^{\text{eff}}$

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| Reading: Chapter 9.4.13, <i>The Spectra and Dynamics of Diatomic Molecules</i> , H. Lefebvre-Brion and R. Field, 2 nd Ed., Academic Press, 2004. |
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Last time:

2 identical coupled subsystems

1. Classical mechanical treatment of two 1 : 1 coupled local Harmonic Oscillators
Simple transformation decouples the sub-systems.
2. quantum Mechanical treatment of Morse oscillator
 $V(r) = D_e (1 - \exp - ar)^2$
 $E(v)/hc = \omega(v + 1/2) + x(v + 1/2)^2$ (x is usually negative)
Expand $V(r)$, use 1st-order p.t. for r^4 and 2nd-order for r^3 . Get exact result for energies!
Justifies use of harmonic oscillator basis set even when diagonal anharmonicity appears in $E^{(0)} + E^{(1)}$
3. 2 anharmonically coupled local Morse oscillators
3 parameter $\mathbf{H}_{\text{Local}}^{\text{eff}}$ (relationships or constraints among traditional fit parameters)

Today: Transformation $\mathbf{H}_{\text{Local}}^{\text{eff}} \leftrightarrow \mathbf{H}_{\text{Normal}}^{\text{eff}}$ Why? Good description of the pluck (e.g. overtone vs. SEP).

antagonism between term that lifts degeneracy in polyad vs. term that has off-diagonal intrapolyad matrix elements

2-level illustration

3 parameter model – some inconsistencies

6 parameter model $\mathbf{H}_{\text{Local}}^{\text{eff}} \leftrightarrow \mathbf{H}_{\text{Normal}}^{\text{eff}}$

Incompatible Terms in \mathbf{H}^{eff}

Often we have a choice between two zero-order basis sets. These correspond to two limiting cases for the dynamics. In one case, one term causes an on-diagonal energy splitting that preserves the limiting case and another term causes an off-diagonal matrix element that destroys the limiting case. In the other limiting case, the roles of the two terms are reversed.

Consider the following illustration for a 2 level system:

$$\mathbf{H} = \mathbf{H}^{\circ} + \mathbf{A} + \mathbf{B}$$

$$= \begin{pmatrix} \bar{E} & 0 \\ 0 & \bar{E} \end{pmatrix} + \begin{pmatrix} A & 0 \\ 0 & -A \end{pmatrix} + \begin{pmatrix} 0 & B \\ B & 0 \end{pmatrix}$$

Limit #1: Diagonalize $\mathbf{H}^{\circ} + \mathbf{B}$ (i.e. set $A = 0$)

$$|\pm\rangle = 2^{-1/2}[|1\rangle \pm |2\rangle] \quad (\text{diagonalize by inspection - often possible in a limiting case})$$

$$\langle \pm | (\mathbf{H}^{\circ} + \mathbf{B}) | \pm \rangle = \frac{1}{2}(2\bar{E} \pm 2B) = \bar{E} \pm B \quad (\text{as required})$$

$$\langle \pm | \mathbf{A} | \pm \rangle = \frac{1}{2}(A - A) = 0$$

$$\langle \pm | \mathbf{A} | \mp \rangle = \frac{1}{2}(A + A) = A$$

$$\mathbf{H}^1 \equiv \mathbf{T}^{\dagger} \mathbf{H} \mathbf{T} = \begin{pmatrix} \bar{E} + B & A \\ A & \bar{E} - B \end{pmatrix}$$

\mathbf{T} is the transformation that diagonalizes $\mathbf{H}^{\circ} + \mathbf{B}$

B lifts the degeneracy and preserves the #1 limit

A controls off-diagonal matrix elements that try to destroy the #1 limit

Choose instead to diagonalize $\mathbf{H}^{\circ} + \mathbf{A}$. It is already diagonal

$$\mathbf{H}^2 = \begin{pmatrix} \bar{E} + A & 0 \\ 0 & \bar{E} - A \end{pmatrix} + \begin{pmatrix} 0 & B \\ B & 0 \end{pmatrix} = \begin{pmatrix} \bar{E} + A & B \\ B & \bar{E} - A \end{pmatrix}$$

Here parameter A lifts the degeneracy and tries to preserve limit #2.

Parameter B controls the off-diagonal elements that try to destroy limit #2.

Parameters A and B play antagonistic roles, but their roles are reversed going from limit #1 to limit #2.

This sort of behavior is universal, even in much larger dimension problems than 2×2 .

Local Mode \leftrightarrow Normal Mode

Hund's Cases (antagonism between \mathbf{H}^{ROT} , \mathbf{H}^{SO} , and $\mathbf{H}^{\text{elect}}$.)

Stark Effect vs. Λ -doubling

Symmetric double minimum $\left\{ \begin{array}{l} \text{symmetry breaking} \\ \text{barrier height} \end{array} \right.$

Two-Coupled local Morse Oscillators

4 Physical parameters:

*Morse: a, D_e

* 1 : 1 Coupling: $G_{rr'}$ kinetic and k_{RL} potential

Fit Model:

$$\mathbf{H}_{\text{Local}}^{\text{eff}}/hc =$$

$$\begin{aligned} & |v_R v_L\rangle \langle v_R v_L| \left\{ \omega_M \left[1 - \frac{(D-C)^2}{8} \right] (v_R + v_L + 1) + \frac{\omega_M F}{2} \left[(v_R + v_L + 1)^2 + (v_R - v_L)^2 \right] \right\} \\ & + |v_R \pm 1 v_L \mp 1\rangle \langle v_R v_L| \left\{ \frac{\omega_M (D+C)}{2} \left[\left(v_R + \frac{1}{2} \pm \frac{1}{2} \right) \left(v_L + \frac{1}{2} \mp \frac{1}{2} \right) \right]^{1/2} \right\} \end{aligned}$$

$$\omega_M \left(1 - \frac{(D-C)^2}{8} \right) = \omega'$$

$$\omega_M F = x < 0$$

$$\frac{\omega_M (D+C)}{2} = H_{RL}/hc$$

3 independent fit parameters (ω', x, H_{RL}) derived from 4 physical parameters (a, D_e, G_{rr}, k_{RL}).

Polyad: $P = v_R + v_L = v_s + v_a$

Energy width of polyad:

$$\frac{\downarrow}{P^2 x/2} (P/2, P/2)$$

| | | | |
|--------------------------|-----------------------------------|---|--|
| | (0,P) ———— | ↑ | ————— (P,0) (degenerate!) |
| | (bottom of polyad) | | (top of polyad) |
| energy spacing: | large $\frac{x}{2}(4P - 4)$ | | small $\frac{x}{2}(4)$ |
| coupling matrix element: | small $\frac{H_{RL}}{hc} P^{1/2}$ | | large $\frac{H_{RL}}{hc} \left(\frac{P^2}{4} + \frac{P}{2}\right)^{1/2}$ |

High energy part of \mathbf{H}_{Local}^{eff} polyad goes toward normal mode limit faster than low energy part of polyad.

Anharmonicity creates large level spacings (between coupled levels) near bottom of polyad that resists transition toward normal mode limit.

Convert to normal mode limit:

- * analytic transformation of basis states
- * analytic transformation of \mathbf{H}
- * define $\mathbf{T}^\dagger \mathbf{H} \mathbf{T}$ transformation numerically: set case preserving constant to zero and diagonalize. Apply to \mathbf{H} where case preserving parameter is not zero.

First, rewrite the $\mathbf{a}, \mathbf{a}^\dagger$ operators:

$$\begin{aligned} \mathbf{a}_s &= 2^{-1/2}(\mathbf{a}_R + \mathbf{a}_L) & \mathbf{a}_s^\dagger &= 2^{-1/2}(\mathbf{a}_R^\dagger + \mathbf{a}_L^\dagger) \\ \mathbf{a}_a &= 2^{-1/2}(\mathbf{a}_R - \mathbf{a}_L) & (\mathbf{a}_a^\dagger) &= 2^{-1/2}(\mathbf{a}_R^\dagger - \mathbf{a}_L^\dagger) \end{aligned}$$

Transform basis states:

$$\begin{aligned} |00\rangle_{Normal} &= |00\rangle_{Local} \\ |v_s v_a\rangle_{Normal} &= [v_s! v_a!]^{-1/2} (\mathbf{a}_s^\dagger)^{v_s} (\mathbf{a}_a^\dagger)^{v_a} |00\rangle \\ & \text{(recall that } [\mathbf{a}_s^\dagger, \mathbf{a}_a^\dagger] = 0 \text{)} \end{aligned}$$

Transform $\mathbf{H}_{\text{Local}}^{\text{eff}}$ to $\mathbf{H}_{\text{Normal}}^{\text{eff}}$:

- * replace all v_i by $\mathbf{a}_i^\dagger \mathbf{a}_i$.
- * replace all $\{\mathbf{a}_R, \mathbf{a}_L, \mathbf{a}_R^\dagger, \mathbf{a}_L^\dagger\}$ by $\{\mathbf{a}_s, \mathbf{a}_a, \mathbf{a}_s^\dagger, \mathbf{a}_a^\dagger\}$
- * exploit $[\mathbf{a}, \mathbf{a}^\dagger] = 1$

Lots of Algebra!

$$\mathbf{H}_{\text{Normal}}^{\text{eff}}/hc = |v_s v_a\rangle\langle v_s v_a| \left\{ \omega'(v_s + v_a + 1) + x_M \left[\frac{3}{4}(v_s + v_a + 1)^2 - \frac{1}{4}(v_s - v_a)^2 - \frac{1}{4} \right] + \frac{H_{RL}}{hc}(v_s - v_a) \right\} \\ + |v_s \pm 2, v_a \mp 2\rangle\langle v_s v_a| \left\{ \frac{x_M}{2} \left[\left(v_s + \frac{1}{2} \pm \frac{1}{2} \right) \left(v_s + \frac{1}{2} \pm \frac{3}{2} \right) \left(v_a + \frac{1}{2} \mp \frac{1}{2} \right) \left(v_a + \frac{1}{2} \mp \frac{3}{2} \right) \right] \right\}$$

Notice that degeneracy is lifted by both x_M and $\frac{H_{RL}}{hc}$ terms, and that the off-diagonal matrix elements are controlled by x_M rather than H_{RL} !

The roles of x_M and H_{RL} are (mostly) reversed between $\mathbf{H}_{\text{Local}}^{\text{eff}}$ and $\mathbf{H}_{\text{Normal}}^{\text{eff}}$.

If we compare this to a standard fit model for $\mathbf{H}_{\text{Normal}}^{\text{eff}}$

$$\mathbf{H}_{\text{Normal}}^{\text{eff,fit}}/hc = |v_s v_a\rangle\langle v_s v_a| \left\{ \omega_s \left(v_s + \frac{1}{2} \right) + \omega_a \left(v_a + \frac{1}{2} \right) + x_{ss} \left(v_s + \frac{1}{2} \right)^2 \right. \\ \left. + x_{aa} \left(v_a + \frac{1}{2} \right)^2 + x_{sa} \left(v_s + \frac{1}{2} \right) \left(v_a + \frac{1}{2} \right) + E^0 / hc \right\} \\ + |v_s \pm 2, v_a \mp 2\rangle\langle v_s v_a| \left\{ \frac{K_{ssaa}}{16hc} \left[\left(v_s + \frac{1}{2} \pm \frac{1}{2} \right) \left(v_s + \frac{1}{2} \pm \frac{3}{2} \right) \left(v_a + \frac{1}{2} \mp \frac{1}{2} \right) \left(v_a + \frac{1}{2} \mp \frac{3}{2} \right) \right] \right\}$$

we find (algebra) that:

$$\omega_s = \omega' + \frac{H_{RL}}{hc} = \omega' + \lambda$$

$$\omega_a = \omega' - \frac{H_{RL}}{hc} = \omega' - \lambda$$

$$E^0/hc = -x_M/4$$

$$x_{ss} = x_{aa} = x_M/2$$

$$x_{sa} = 2x_M$$

$$\frac{K_{ssaa}}{16hc} = \frac{x_M}{2}$$

A total of only 3 independent fit parameters (ω', λ, x_M)!

But we have a small problem because we have only kept the $\frac{K_{ssaa}}{16hc} [\mathbf{a}_s \mathbf{a}_s \mathbf{a}_a^\dagger \mathbf{a}_a^\dagger + \mathbf{a}_s^\dagger \mathbf{a}_s^\dagger \mathbf{a}_a \mathbf{a}_a]$ part of the $\frac{K_{ssaa}}{4hc} [\hat{\mathbf{Q}}_s^2 \hat{\mathbf{Q}}_a^2]$ Darling-Dennison coupling term.

The neglected terms are:

- * out-of-polyad: $\frac{K_{ssaa}}{16hc} \left[\mathbf{a}_s^\dagger^2 \mathbf{a}_a^\dagger^2 + \mathbf{a}_s^2 \mathbf{a}_a^2 + 2 \left(v_s + \frac{1}{2} \right) (\mathbf{a}_a^\dagger^2 + \mathbf{a}_a^2) + 2 \left(v_a + \frac{1}{2} \right) (\mathbf{a}_s^\dagger^2 + \mathbf{a}_s^2) \right]$ which would have to be corrected for via a Van Vleck transformation
- * and a diagonal term: $\underbrace{\frac{K_{ssaa}}{4hc}}_{2x_M} \left(v_s + \frac{1}{2} \right) \left(v_a + \frac{1}{2} \right)$

These out-of-polyad and diagonal corrections spoil the microscopic definitions of ω' , λ , x_{ss} , x_{aa} , x_{sa} in terms of the 3 fit parameters from $\mathbf{H}_{\text{Local}}^{\text{eff}}$ or the 4 parameters $\{a, D_e, G_{rr'}, k_{RL}\}$.

So we go to a pair of slightly more flexible and less microscopic 6 parameter models.

But before we look at these 6 parameter models, reconsider the roles of x_M and K_{ssaa}/hc .

| | | |
|----------|---|---|
| x_M | $\mathbf{H}_{\text{LOCAL}}^{\text{eff}}$ lifts degeneracy, drives toward local (preserves basis) | $\mathbf{H}_{\text{NORMAL}}^{\text{eff}}$ { lifts degeneracy, { couples s and a mostly drives toward local (destroys basis) |
| H_{LR} | couples L and R derives toward normal (destroys basis) | lifts degeneracy: $\omega' \pm \lambda$ drives toward normal (preserves basis) |

Roles are reversed

K_{ssaa} actually comes (largely) from x_M

6 parameter models (basis for classical mechanics treatment next lecture)

$$\mathbf{H}_{\text{Normal}}^{\text{eff}}/hc = |v_s v_a\rangle\langle v_s v_a| \left\{ \frac{\omega_s + \omega_a}{2} (v_s + v_a + 1) + \frac{x_{ss} + x_{aa} + x_{sa}}{4} [(v_s + v_a)(v_s + v_a + 1) + 1] \right.$$

two degeneracy-lifting terms

$$\left. \begin{aligned}
 &+ \left[\frac{\omega_s - \omega_a}{2} + \frac{x_{ss} - x_{aa}}{2} (v_s + v_a + 1) \right] (v_s - v_a) \\
 &+ \frac{x_{ss} + x_{aa} - x_{sa}}{4} (v_s - v_a)^2 \}
 \end{aligned}$$

****most important**

one off-diagonal term

$$+ |v_s \pm 2, v_a \mp 2\rangle\langle v_s v_a| \left\{ \frac{K_{ssaa}}{16hc} \left[(v_s + \frac{1}{2} \pm \frac{1}{2})(v_s + \frac{1}{2} \pm \frac{3}{2})(v_a + \frac{1}{2} \mp \frac{1}{2})(v_a + \frac{1}{2} \mp \frac{3}{2}) \right]^{1/2} \right\}$$

$$\mathbf{H}_{\text{Local}}^{\text{eff}}/hc = |v_R v_L\rangle\langle v_R v_L| \left\{ \frac{\omega_s + \omega_a}{2} (v_R + v_L + 1) + \frac{3x_{ss} + 3x_{aa} + x_{sa} - K_{ssaa}/8hc}{2} \right.$$

one degeneracy-lifting term

$$\left. + \frac{3K_{ssaa}/16hc - x_{ss} - x_{aa} + x_{sa}}{4} (v_R - v_L)^2 \right\}$$

two off-diagonal terms

$$\left\{ \begin{aligned}
 &+ |v_R \pm 1, v_L \mp 1\rangle\langle v_R v_L| \left[\left[\frac{\omega_s - \omega_a}{2} + \frac{x_{ss} - x_{aa}}{2} (v_R + v_L + 1) \right] \left[(v_R + \frac{1}{2} \pm \frac{1}{2})(v_L + \frac{1}{2} \mp \frac{1}{2}) \right]^{1/2} \right\} \\
 &+ |v_R \pm 2, v_L \mp 2\rangle\langle v_R v_L| \left\{ \frac{K_{ssaa}/32hc + x_{ss} + x_{aa} - x_{sa}}{4} \right. \\
 &\left. \times \left[(v_R + \frac{1}{2} \pm \frac{1}{2})(v_R + \frac{1}{2} \pm \frac{3}{2})(v_L + \frac{1}{2} \mp \frac{1}{2})(v_L + \frac{1}{2} \mp \frac{3}{2}) \right]^{1/2} \right\}
 \end{aligned}$$

It is insightful to know relationships among fit parameters

- * recognize unlikely assignments
- * simplify dynamics. simplest possible description of a pluck.
- * recognize opposing forces toward or away from opposite limits

But it is difficult to map out the local vs. normal character of the individual eigenstates in each polyad and the evolution toward global normal or local dynamics.

What are we supposed to look for, especially when there is more than one coupling mechanism?

- * division between mostly-local and mostly-normal eigenstates
- * appearance of qualitatively new (and unexpected) classes of motion.
- * chaos. Fraction of phase space that is chaotic.
- * statistical measures $\left\{ \begin{array}{l} \text{level spacing distribution} \\ \text{relative intensity distribution} \end{array} \right.$