Normal ↔ Local Modes:
6-Parameter Models


Last time:

ω₁, τ, ω₂ (measure populations) experiment

(abc) ← ω₂ (AB) ← ω₁ g

two polyads.
populations in (1234) depend on τ.

could use 𝑓_𝑘 = \frac{E_{res,k}}{E_{res}} to devise optimal plucks for more complex situations

(choice of plucks and probes)

* multiple resonances
* more than 2 levels in polyad

Overtone Spectroscopy

nRH single resonance
nRH + 1RH double resonance
dynamics in frequency domain

Today:

Classical Mechanics: 2 1 : 1 coupled local harmonic oscillators
QM: Morse oscillator
2 Anharmonically Coupled Local Morse Oscillators

\( \mathbf{H}^{eff}_{Local} \cdot \text{ Antagonism. Local vs. Normal.} \)

Whenever you have two identical subsystems, energy will flow rapidly between them unless something special makes them dynamically different:

* anharmonicity
* interaction with surroundings
spontaneous symmetry - breaking

Next time: \( \mathbf{H}^{eff}_{Normal} \).
Two coupled identical harmonic oscillators: Classical Mechanics

\[ \mathcal{H} = \mathcal{T}(P_R, P_L) + \mathcal{V}(Q_R, Q_L) \]  
\[ \mathcal{T} = \frac{1}{2}(P_R, P_L)G\begin{pmatrix} P_R \\ P_L \end{pmatrix} \]

\[ = \frac{1}{2}[G_{rr}(P_R^2 + P_L^2) + 2G_{rr'}P_R P_L] \]

\[ \mathcal{V} = \frac{1}{2}(Q_R, Q_L)F\begin{pmatrix} Q_R \\ Q_L \end{pmatrix} \]

\[ = \frac{1}{2}[F_{rr}(Q_R^2 + Q_L^2) + 2F_{rr'}Q_R Q_L] \]

\[ \mathcal{H} = \left[ \frac{1}{2}G_{rr}P_R^2 + \frac{1}{2}F_{rr}Q_R^2 \right] + \left[ \frac{1}{2}G_{rr}P_L^2 + \frac{1}{2}F_{rr}Q_L^2 \right] \]

\[ + G_{rr'}P_R P_L + F_{rr'}Q_R Q_L \]

geometry and masses

force constants

kinetic coupling

potential (anharmonic) coupling
Each harmonic oscillator has a natural frequency, $\omega_0$:

$$\omega_0 = \frac{1}{2\pi c} \left[ F_{rr}G_{rr} \right]^{1/2} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}$$

and the coupling is via 1 : 1 kinetic energy and potential energy coupling terms.

Uncouple by going to symmetric and anti-symmetric normal modes.

$$Q_s = 2^{-1/2}[Q_R + Q_L] \quad Q_a = 2^{-1/2}[Q_R - Q_L]$$

$$P_s = 2^{-1/2}[P_R + P_L] \quad P_a = 2^{-1/2}[P_R - P_L]$$

plug this into $\mathcal{H}$ and do the algebra

$$\mathcal{H} = \left[ \frac{1}{2} \left( \frac{1}{\mu} + G_{rr}' \right) P_s^2 + \frac{1}{2} (k + k_{RL}) Q_s^2 \right]$$

$$+ \left[ \frac{1}{2} \left( \frac{1}{\mu} - G_{rr}' \right) P_a^2 + \frac{1}{2} (k - k_{RL}) Q_a^2 \right]$$

no coupling term!
\[
\begin{align*}
\omega_s &= \frac{1}{2\pi c} \left[ \left( \frac{1}{\mu} + G_{rr'} \right) (k + k_{RL}) \right]^{1/2} \\
\omega_a &= \frac{1}{2\pi c} \left[ \left( \frac{1}{\mu} - G_{rr'} \right) (k - k_{RL}) \right]^{1/2}
\end{align*}
\]

simplify to \( \omega = \omega_0 + \beta + \lambda \) (algebra, not power series)

\( \omega_s = \omega_0 + \beta + \lambda \)

\( \omega_a = \omega_0 + \beta - \lambda \)

\[
\beta = \frac{k_{RL} G_{rr'}}{2(2\pi c)^2 \omega_0}
\]

\[
\lambda = \frac{\omega_0}{2} \left( 1 - \frac{\beta}{\omega_0} \right) \left[ \frac{k_{RL}}{k} + \mu G_{rr'} \right]
\]

G_{rr'} can have either sign. It is usually negative because \( \phi > \pi/2 \).

Can have either sign. Positive if right bond gets stiffer when left bond is stretched.

Sign of \( \lambda \) determined by whether potential or kinetic coupling is larger (or by the signs of \( k_{RL} \) and \( G_{rr'} \)).
Morse Oscillator

The Morse oscillator has a physically appropriate and mathematically convenient form. It turns out to give a vastly more convenient representation of an anharmonic vibration than

\[ V(r) = \frac{1}{2} f_{rr}x^2 + \frac{1}{6} f_{rrr}x^3 + \frac{1}{24} f_{rrrr}x^4 \]

treated by perturbation theory.

\[ V_{\text{Morse}}(r) = D_e \left[ 1 - e^{-ar} \right]^2 \quad (V(0) = 0, \ V(\infty) = D_e) \]

\[ r = R - R_e \]

Power series expansion of \( V_{\text{Morse}}(r) = \frac{1}{2} (2a^2D_e)r^2 - \frac{1}{6} (6a^3D_e)r^3 + \frac{1}{24} (14a^4D_e)r^4 \).

If we use

\[ f_r = 2a^2D_e \]
\[ f_{rr} = -6a^3D_e \]
\[ f_{rrr} = 14a^4D_e \]

in the framework of nondengenerate perturbation theory, we get much better results than we expect or deserve.

Why? Because the energy levels of a Morse oscillator have a very simple form:

\[ E_{\text{Morse}}(\nu)/\hbar c = E_{\text{Morse}}^0/\hbar c + \omega_m(\nu + 1/2) + x_m(\nu + 1/2)^2 \]

and an exact solution for the energy levels gives

\[ E_{\text{Morse}}^0 = 0 \]

\[ \omega_m = \frac{1}{2\pi c} \left( \frac{2a^2D_e}{\mu} \right)^{1/2} \]

\[ \mu = \frac{m_1m_2}{m_1 + m_2} \]

\[ x_m = -\frac{a^2\hbar}{4\pi c\mu} \]

we get the exact same relationship between \((D_e,a)\) and \( (E_{\text{Morse}}^0, \omega_m, x_m) \) by perturbation theory (with a twist).
\[ H^{(0)} = \frac{1}{2} f_{rr} r'^2 + \frac{1}{2\mu} P^2 \]
\[ E_v^{(1)} = \frac{1}{24} f_{rrr} \braket{v}{r^4}{v} \]
\[ E_v^{(2)} = \left( \frac{f_{rrr}}{6} \right)^2 \frac{1}{\omega_m} \left[ \frac{\braket{v - 1}{r^3}{v} - \braket{v + 1}{r^3}{v}}{1} + \frac{\braket{v - 3}{r^3}{v} - \braket{v + 3}{r^3}{v}}{3} \right] \]

This works better than we could ever have hoped, and therefore we should never look a gift horse in the mouth. We always use Morse rather than an arbitrary power series representation of V(r). Sometimes we even use a power series \( \sum_n a_n [1 - \exp(-ar)]^n \).

Armed with this simplification, consider **two anharmonically coupled local stretch oscillators.** WHY?
What promotes or inhibits energy flow between two identical subsystems?

* ubiquitous
* Local and Normal Mode Pictures are opposite limiting cases
* \( H_{\text{eff}} \) contains antagonistic terms that preserve and destroy limiting behavior
* the roles are reversed for \( H_{\text{Local}}^{\text{eff}} \) and \( H_{\text{Normal}}^{\text{eff}} \)

See Section 9.4.12.3 of HLB-RWF
Extremely complicated algebra

1. \( H_{\text{Local}} \) defined identically to \( H_{\text{Local}}^{\text{Local}} \), but with diagonal anharmonicity.
2. Convert to dimensionless \( P, Q, H \) and then to \( a, a^\dagger \).
3. exploit the convenient \( V(Q) \leftrightarrow E(v) \) properties of \( V_{\text{Morse}} \).
4. van Vleck transformation to account for the effect of out of polyad coupling terms from \( [G_\nu P_\nu P_\lambda + k_{RL} Q_\lambda Q_\lambda] \) BUT NOT from \( V_{\text{Morse}} \).
5. Simplest possible fit model — relationships (constraints) between fit parameters imposed by the identical Morse oscillator model.
6. Next time — transformation from \( H_{\text{Local}} \) to \( H_{\text{Normal}} \).
1. 

\[ \mathbf{H}^{\text{Local}} = \left[ \frac{1}{2\mu} \mathbf{P}^2_R + \frac{1}{2\mu} \mathbf{Q}^2_R + V^{\text{anh}}(\mathbf{Q}_R) \right] \]

\[ + \left[ \frac{1}{2\mu} \mathbf{P}^2_L + \frac{1}{2\mu} \mathbf{Q}^2_L + V^{\text{anh}}(\mathbf{Q}_L) \right] \]

\[ + G_{rr'} \mathbf{P}_R \mathbf{P}_L + k_{RL} \mathbf{Q}_R \mathbf{Q}_L \]

\[ V^{\text{anh}}(\mathbf{Q}) = V_{\text{Morse}}(\mathbf{Q}) - \frac{1}{2} k \mathbf{Q}^2 \]

This enables us to use Harmonic-Oscillators for basis set but Morse simplification for the separate local oscillators.

We are going to expand \( V^{\text{anh}}(\mathbf{Q}) \) and keep only the \( \mathbf{Q}^3 \) and \( \mathbf{Q}^4 \) terms and treat them, respectively, by second-order and first-order perturbation theory, as we did for the simple Morse oscillator.

\[ \mathbf{H}^{\text{Local}} = \underbrace{\mathbf{h}^{(0)}_R + \mathbf{h}^{(0)}_L}_{\mathbf{h}^{(0)}} + \mathbf{h}^{(1)}_R + \mathbf{h}^{(1)}_L + \mathbf{H}^{(1)}_{RL} \]
2.3. \[ Q, P, H \rightarrow \hat{Q}, \hat{P}, \hat{H} \rightarrow a_R, a_R^\dagger, a_L, a_L^\dagger \]

\[ Q_i = \alpha_i^{-1/2} \hat{Q}_i \]

\[ P_i = \hbar \alpha_i^{1/2} \hat{P}_i \]

\[ H_{Local} = \hbar (2\pi c \omega_M) \hat{H}_{Local} \]

\[ \alpha_i = \frac{2\pi c \omega_i \mu_i}{\hbar} \]

\[ \omega_i = \frac{1}{2\pi c} \left[ k_i / \mu_i \right]^{1/2} \]

\[ \hat{Q}_R = 2^{-1/2} \left( a_R + a_R^\dagger \right) \text{ etc.} \]

\[ \hat{P}_R = 2^{-1/2} i \left( a_R^\dagger - a_R \right) \text{ etc.} \]

\[ H_{Local} = \hbar (2\pi c \omega_M) \left[ v_R v_L \langle v_R v_L \rangle \left\{ (v_R + 1/2) + (v_L + 1/2) + F \left[ (v_R + 1/2)^2 + (v_L + 1/2)^2 \right] \right\} \right. \]

\[ + |v_R \pm 1, v_L \mp 1 \rangle \langle v_R v_L | \left\{ \frac{D + C}{2} \left[ (v_R + 1/2 \pm 1/2)(v_L + 1/2 \mp 1/2) \right]^2 \right\} \]

\[ + |v_R \pm 1, v_L \pm 1 \rangle \langle v_R v_L | \left\{ \frac{D - C}{2} \left[ (v_R + 1/2 \pm 1/2)(v_L + 1/2 \pm 1/2) \right]^{1/2} \right\} \]

\[ F = - \frac{2^{-1/2} (\hbar a)}{4\pi (\mu D_e)^{1/2}} \text{ dimensionless (a, } D_e \text{ from Morse)} \]

\[ C = G_{rr} a \mu \]

\[ D = \frac{k_{RL}}{k_M} = \frac{k_{RL}}{2D_e a^2} \]

First 2 lines of \( H_{Local} \) are polyad, third line is out of polyad.
4. 

\[ \hat{H}_{\text{Local}}^{\text{eff}} = \left[ v_R v_L \right] \left[ \left( v_R + v_L + 1 \right) \left[ 1 - \frac{(D - C)^2}{8} \right] + \frac{F}{2} \left[ (v_R + v_L + 1)^2 + (v_R - v_L)^2 \right] \right] \]

\[ + \left[ v_R \pm 1, v_L \mp 1 \right] \left[ v_R v_L \right] \left[ \frac{D + C}{2} \left[ (v_R + 1/2 \pm 1/2)(v_L + 1/2 \mp 1/2) \right]^{1/2} \right] \]

\[ \frac{F}{2} (v_R - v_L)^2 \] tries to preserve local mode limit. The \( \frac{D+C}{2} \) coupling term tries to destroy the local mode limit.

**Polyad** \( P = v_R + v_L \)

Overall width of polyad: \( E^{(0)}_{(P/2,P/2)} - E^{(0)}_{(0,P)} = -\frac{F}{2} P^2 \quad (F < 0) \)

\( (0,P) \) and \( (P,0) \) are at low energy extreme because of anharmonicity: \( \omega(v + 1/2) - |x|(v + 1/2)^2 \).

Off-diagonal matrix elements are smallest between \( (0,P) \sim (1,P-1) \)

and \( (P,0) \sim (P-1,1) \)

\[ \hat{H}^{(1)}_{(0,P)(1,P-1)} = \left( \frac{D + C}{2} \right) P^{1/2} \]

Off diagonal matrix elements are largest between \( (P/2,P/2) \sim (P/2-1,P/2+1) \)

\[ \hat{H}^{(1)}_{(P/2,P/2)(P/2-1,P/2+1)} = \left( \frac{D + C}{2} \right) [(P/2)(P/2 + 1)]^{1/2} \]

larger by a factor of \( [(P/4) + 1/2]^{1/2} \).
5. General (minimal fit model)

\[
\mathbf{H}_{\text{Local}}^{\text{eff}}/\hbar c = |v_R v_L \rangle \langle v_R v_L | \left\{ \omega_R (v_R + 1/2) + \omega_L (v_L + 1/2) \\
+ x_R (v_R + 1/2)^2 + x_L (v_L + 1/2)^2 + x_{RL} (v_R + 1/2) (v_L + 1/2) \right\} \\
+ |v_R \pm 1, v_L \mp 1 \rangle \langle v_R v_L | \left\{ \left( H_{RL} / \hbar c \right) \left( (v_R + 1/2 \pm 1/2) (v_L + 1/2 \mp 1/2) \right)^{1/2} \right\}
\]

But, in the two identical 1:1 coupled Morse local oscillator picture

\[
\omega_R = \omega_L = \omega_M \left[ 1 - \frac{(D - C)^2}{8} \right] = \omega'
\]

\[
x_R = x_L = x_M = - \frac{a^2 \hbar}{4 \pi c \mu}
\]

\[
x_{RL} = 0
\]

\[
H_{RL} / \hbar c = \omega_M \left[ \frac{D + C}{2} \right]
\]