Normal ↔ Local Modes:
6-Parameter Models

Reading:	Chapter 9.4.12.5, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

ω_1, τ, ω_2 (measure populations) experiment

$$(abcd) \xleftarrow{\omega_2} (AB) \xleftarrow{\omega_1} g$$

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

could use $f_k = \dfrac{\overline{E}_{\mathrm{res},k}}{\overline{E}_{\mathrm{res}}}$ 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
$\mathbf{H}^{\mathrm{eff}}_{\mathrm{Local}}$. 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: $\mathbf{H}^{\mathrm{eff}}_{\mathrm{Normal}}$.

Two coupled identical harmonic oscillators: Classical Mechanics

$$\mathscr{H} = \mathscr{T}\left(P_R, P_L\right) + \mathscr{V}\left(Q_R, Q_L\right) \qquad \left(\mathrm{R} = \mathrm{Right},\ \mathrm{L} = \mathrm{Left}\right)$$

$$\mathscr{T} = \frac{1}{2}(P_R, P_L)\underset{\text{geometry and masses}}{\mathbf{G}}\begin{pmatrix} P_R \\ P_L \end{pmatrix}$$

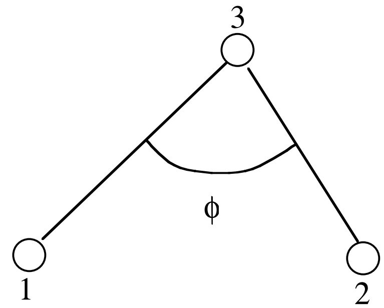
$$= \frac{1}{2}\left[G_{rr}\left(P_R^2 + P_L^2\right) + 2G_{rr'}P_R P_L\right]$$

$$\mathscr{V} = \frac{1}{2}(Q_R Q_L)\underset{\text{force constants}}{\mathbf{F}}\begin{pmatrix} Q_R \\ Q_L \end{pmatrix}$$

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

$$\mathscr{H} = \underbrace{\left[\frac{1}{2}G_{rr}P_R^2 + \frac{1}{2}F_{rr}Q_R^2\right]}_{\mathscr{H}_R^{(0)}} + \underbrace{\left[\frac{1}{2}G_{rr}P_L^2 + \frac{1}{2}F_{rr}Q_L^2\right]}_{\mathscr{H}_L^{(0)}}$$

$$+\underbrace{G_{rr'}P_R P_L}_{\text{kinetic coupling}} + \underbrace{F_{rr'}Q_R Q_L}_{\text{potential (anharmonic) coupling}}$$



$$F_{rr} = k$$
$$F_{rr'} = k_{RL}$$

$$G_{rr} = \frac{1}{m_1} + \frac{1}{m_3} = \frac{1}{m_2} + \frac{1}{m_3} = \frac{m_1 + m_3}{m_1 m_3} = \frac{1}{\mu}$$

$$G_{rr'} = \frac{1}{m_3}\cos\phi$$ (projection of velocity of ③ for ① — ③ stretch onto ③ — ② direction)

kinetic coupling gets small for large *m* or $\phi = \pi/2$

Each harmonic oscillator has a natural frequency, ω_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.

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

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

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!

$$\omega_s = \frac{1}{2\pi c}\left[\left(\frac{1}{\mu} + G_{rr'}\right)(k + k_{RL})\right]^{1/2}$$

$$\omega_a = \frac{1}{2\pi c}\left[\left(\frac{1}{\mu} - G_{rr'}\right)(k - k_{RL})\right]^{1/2}$$

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

$\omega_a = \omega_0 + \beta - \lambda$

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

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

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

usually + usually -

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

sign of λ 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.

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

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

If we use $f_{rr} = 2a^2 D_e$
$f_{rrr} = -6a^3 D_e$
$f_{rrrr} = 14a^4 D_e$

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:

$$E_{\text{Morse}}(v)/hc = E_0^{\text{Morse}}/hc + \omega_m(v + 1/2) + x_m(v + 1/2)^2$$

and an exact solution for the energy levels gives

$$E_0^{\text{Morse}} = 0$$
$$\omega_m = \frac{1}{2\pi c}\left(\frac{2a^2 D_e}{\mu}\right)^{1/2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$
$$x_m = -\frac{a^2 \hbar}{4\pi c \mu}$$

we get the exact same relationship between (D_e,a) and $\left(E_0^{\text{Morse}}, \omega_m, x_m\right)$ by perturbation theory (with a twist)

$$\mathbf{H}^{(0)} = \frac{1}{2} f_{rr}\mathbf{r}^2 + \frac{1}{2\mu}\mathbf{P}^2$$

$$E_v^{(1)} = \frac{1}{24} f_{rrrr}\langle v|\mathbf{r}^4|v\rangle$$

(quartic term treated to 1st order only!)

$$E_v^{(2)} = \left(\frac{f_{rrr}}{6}\right)^2 \frac{1}{\omega_m}\left[\frac{\langle v-1|\mathbf{r}^3|v\rangle - \langle v+1|\mathbf{r}^3|v\rangle}{1} + \frac{\langle v-3|\mathbf{r}^3|v\rangle - \langle v+3|\mathbf{r}^3|v\rangle}{3}\right]$$

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
* $\mathbf{H}^{\text{eff}}$ contains antagonistic terms that preserve and destroy limiting behavior
* the roles are reversed for $\mathbf{H}^{\text{eff}}_{\text{Local}}$ and $\mathbf{H}^{\text{eff}}_{\text{Normal}}$

See Section 9.4.12.3 of HLB-RWF
Extremely complicated algebra

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

1.
$$\mathbf{H}^{\text{Local}} = \left[\overbrace{\frac{1}{2\mu}\mathbf{P}_R^2 + \frac{1}{2\mu}\mathbf{Q}_R^2}^{\mathbf{h}_R^{(0)}} + \overbrace{V^{anh}(\mathbf{Q}_R)}^{\mathbf{h}_R^{(1)}}\right]$$
$$+\left[\frac{1}{2\mu}\mathbf{P}_L^2 + \frac{1}{2\mu}\mathbf{Q}_L^2 + V^{anh}(\mathbf{Q}_L)\right]$$
$$\underbrace{+G_{rr'}\mathbf{P}_R\mathbf{P}_L + k_{RL}\mathbf{Q}_R\mathbf{Q}_L}_{\mathbf{H}_{RL}^{(1)}}$$
$$V^{anh}(\mathbf{Q}) = V_{\text{Morse}}(\mathbf{Q}) - \frac{1}{2}k\mathbf{Q}^2$$

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

We are going to expand $V^{anh}(\mathbf{Q})$ 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.

$$\mathbf{H}^{\text{Local}} = \underbrace{\mathbf{h}_R^{(0)} + \mathbf{h}_L^{(0)}}_{\mathbf{H}^{(0)}} + \mathbf{h}_R^{(1)} + \mathbf{h}_L^{(1)} + \mathbf{H}_{RL}^{(1)}$$

2,3. $\mathbf{Q},\mathbf{P},\mathbf{H} \to \hat{\mathbf{Q}},\hat{\mathbf{P}},\hat{\mathbf{H}} \to \mathbf{a}_R,\mathbf{a}_R^\dagger,\mathbf{a}_L,\mathbf{a}_L^\dagger$

$$\mathbf{Q}_i = \alpha_i^{-1/2}\hat{\mathbf{Q}}_i$$

$$\mathbf{P}_i = \hbar\alpha_i^{1/2}\hat{\mathbf{P}}_i$$

$$\mathbf{H}^{\text{Local}} = \hbar(2\pi c\omega_M)\hat{\mathbf{H}}^{\text{Local}}$$

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

note inconsistency between ω_M in **H** and ω_i in α

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

$$\hat{\mathbf{Q}}_R = 2^{-1/2}\left(\mathbf{a}_R + \mathbf{a}_R^\dagger\right) \text{ etc.}$$

$$\hat{\mathbf{P}}_R = 2^{-1/2}i\left(\mathbf{a}_R^\dagger - \mathbf{a}_R\right) \text{ etc.}$$

$$\begin{aligned}\mathbf{H}^{\text{Local}} = \hbar(2\pi c\omega_M)\Big[|v_R v_L\rangle\langle v_R v_L|\Big]&\Big\{(v_R+1/2)+(v_L+1/2)+F\left[(v_R+1/2)^2+(v_L+1/2)^2\right]\Big\}\\ &+|v_R\pm1,v_L\mp1\rangle\langle v_R v_L|\left\{\frac{D+C}{2}\left[(v_R+1/2\pm1/2)(v_L+1/2\mp1/2)\right]^2\right\}\\ &+|v_R\pm1,v_L\pm1\rangle\langle v_R v_L|\left\{\frac{D-C}{2}\left[(v_R+1/2\pm1/2)(v_L+1/2\pm1/2)\right]^{1/2}\right\}\end{aligned}$$

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

$$\left.\begin{aligned}C &= G_{rr'}\mu\\ D &= \frac{k_{RL}}{k_M} = \frac{k_{RL}}{2D_e a^2}\end{aligned}\right\}\text{dimensionless}$$

First 2 lines of $\mathbf{H}^{\text{Local}}$ are polyad, third line is out of polyad.

4.

$$\hat{\mathbf{H}}^{\text{eff}}_{\text{Local}} = \left|v_R v_L\right\rangle\left\langle v_R v_L\right|\left\{(v_R + v_L + 1)\left[1 - \frac{(D-C)^2}{8}\right] + \frac{F}{2}\left[(v_R + v_L + 1)^2 + \overbrace{(v_R - v_L)^2}^{\text{Lifts Degeneracy}}\right]\right\}$$

$$+\underbrace{\left|v_R \pm 1, v_L \mp 1\right\rangle\left\langle v_R v_L\right|}_{\text{coupling within polyad}}\left\{\frac{D+C}{2}\left[(v_r + 1/2 \pm 1/2)(v_L + 1/2 \mp 1/2)\right]^{1/2}\right\}$$

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

Polyad $\qquad P = v_R + v_L$

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

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

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

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

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

larger by a factor of $[(P/4) + 1/2]^{1/2}$.

5. General (minimal fit model)

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

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

$$\omega_R=\omega_L=\omega_M\left[1-\frac{(D-C)^2}{8}\right]=\omega'$$
$$x_R=x_L=x_M=-\frac{a^2\hbar}{4\pi c\mu}$$
$$x_{RL}=0$$
$$H_{RL}/hc=\omega_M\left[\frac{D+C}{2}\right]$$