5.73 Lecture #17 – Perturbation Theory IV

Vibrations of Polyatomic Molecules
H is ∞ dimension
How do we arrange and "read" it?
How do we truncate it? **H**⟶**H**$^{\text{eff}}$
Near Degeneracies – accidental or "intentional"
molecular dynamics is uniquely sensitive to "resonances"
unique sensitivity to inter- and intra-molecular interactions
*IVR – Intramolecular Vibrational Redistribution
*x-k relationships
*Polyads
Two frequently occurring polyad cases 2:1 and 2:2 resonances
Van Vleck Transformation for inter-polyad interactions
Isomerization

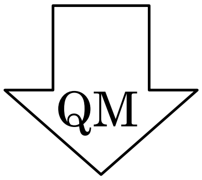
LOCAL MODES

Not just for small molecules in gas phase

Mark Johnson for H-bonding in H_2O clusters.

molecule with N atoms: 3N-6 normal modes

What is a Normal Mode?
synchronized dance of all N atoms
Classical Mechanics
Wilson Decius and Cross "Molecular Vibrations"



$$\omega_e = [k/\mu]^{1/2}$$

↓

μ is generalized

$$\begin{pmatrix}
E_1^{(0)} & & & & & \\
& E_2^{(0)} & & & & \\
& & \ddots & & & \\
& & & E_n^{(0)} & H_{12}^{(1)} & & \\
& & & H_{12} & E_{n+1}^{(0)} & & \\
& & & & & \ddots & \\
& & & & & & E_\infty^{(0)}
\end{pmatrix}$$

$$\text{usually} \left| \frac{H_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \right| \ll 1$$

but we will see 2 things:

matrix elements of $\mathbf{x}^k$ grow as constant ⊗ $n^{k/2}$ and contribute to energy levels as n^{k-1}

density of states increases so some get very small

We need to deal with anharmonic interactions, which become increasingly important E ↑

N-Atom Polyatomic Molecules

[use **BOLD CAPITAL** letters to symbolize many vibrational modes]

3N–6 normal modes

What is a normal mode?

$$V(\mathbf{Q})^{(0)} = \sum_{i=1}^{3N-6} \frac{1}{2} k_i Q_i^2$$

$$E^{(0)}_{\{n_i\}} = \sum_{i=1}^{3N-6} \hbar\omega_i (n_i + 1/2)$$

synchronized dance of *all* atoms

↓

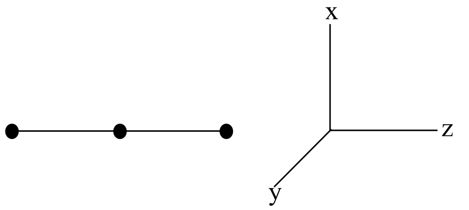
what happens if one dancer has a sprained ankle?

↓

everyone for themself! (i.e., "local modes")

transitions $\mu(\mathbf{Q}) = \mu_0 + \underbrace{\frac{d\mu}{dQ_i}}_{\text{change of } Q_i \text{ causes change of } \mu} \mathbf{Q}_i$

CO_2 is symmetric $\mu_0 = 0$



mode 1	symmetric stretch	$\frac{d\mu}{dQ_1} = 0$	$\Delta\mathbf{V} = 0$
mode 2	band (⊥) type	$\frac{d\mu}{dQ_2} \neq 0$	$\Delta n_2 = \pm 1$
mode 3	anti-symmetric stretch (‖) type	$\frac{d\mu}{dQ_3} \neq 0$	$\Delta n_3 = \pm 1$

Expect simple spectra, exclusively $\Delta n_2 = 1$ or $\Delta n_3 = 1$

NOT BOTH $\Delta n_2 = 1$ and $\Delta n_3 = 1$ simultaneously

Expect energy initially deposited in specific $(n_1, n_2, n_3)^0$ basis state to stay in that state. "Mode Specific Chemistry": an unfulfilled dream

Expectations are violated because of anharmonic interaction terms.

$$V^{(1)}(\mathbf{Q}) = \sum_{i=1} \{\text{cubic terms}\} + \{\text{quartic terms}\}$$

$$\text{cubic} \quad \left\{ \begin{aligned} &\frac{1}{6}k_{111}Q_1^3 + \frac{1}{6}k_{222}Q_2^3 + \frac{1}{6}k_{333}Q_3^3 \\ &\frac{1}{2}k_{112}Q_1^2Q_2 + \frac{1}{2}k_{113}Q_1^2Q_3 + \frac{1}{2}k_{123}Q_1Q_2Q_3 \end{aligned} \right.$$

$$\text{quartic} \quad \frac{1}{24}k_{1111}Q_1^4 \quad \text{etc.}$$

Each of these terms has explicitly known quantum number dependent selection rules and magnitude scaling rules.

Seems like a nightmare! But actually it is quite the opposite.

Most of the anharmonic terms connect basis states that are energetically remote from each other. These interactions can be dealt with by 2nd order Perturbation Theory.

A few interaction terms connect near degenerate basis states. These dominate the dynamics and give rise to "polyads"

- ✸ must be diagonalized
- ✸ can lead to local modes
- ✸ can enable isomerization

broken picture of level splittings and transition intensities

Let’s look at a simple example that illustrates all of the steps.

There are two special cases.

Fermi Resonance	$\omega_1 \approx 2\omega_2$	2:1
Darling-Dennison	$2\omega_1 \approx 2\omega_3$	2:2

Symmetric stretch and anti-symmetric stretch usually have similar frequency, but one is symmetric and the other is anti-symmetric.

$Q_1 \otimes Q_1$ is symmetric

Q_3 is anti-symmetric

$Q_3 \otimes Q_3$ is symmetric

→[these 2:2 anharmonic terms lead to “local stretchers”]

$\boxed{\text{wave my arms}}$

Fermi Resonance involves a cubic anharmonic term.

$$k_{133}Q_1Q_3^2$$

put this into $\mathbf{a},\mathbf{a}^\dagger$ form

$$\mathrm{Q}_1 = \left(\frac{\hbar}{2m_1\omega_1}\right)^{1/2}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)$$

$$\mathrm{Q}_3 = \left(\frac{\hbar}{2m_3\omega_3}\right)^{1/2}\left(\mathbf{a}_3 + \mathbf{a}_3^\dagger\right)$$

Let $m_1 = m_3$ (this is a bit of a fraud because the mass factors are not quite so simple)

$$k_{133}Q_1Q_3^2 = \left[\frac{\hbar}{2m}\right]^{3/2}\left[\omega_1\omega_3^2\right]^{-1/2}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)\left(\mathbf{a}_3 + \mathbf{a}_3^\dagger\right)^2$$

Operator algebra: intermode $\left[\mathbf{a}_i,\mathbf{a}_j\right]=\left[\mathbf{a}_i,\mathbf{a}_j^\dagger\right]=0$

$$\left(\mathbf{a}_1+\mathbf{a}_1^\dagger\right)\left(\mathbf{a}_3+\mathbf{a}_3^\dagger\right)=\mathbf{a}_1\left[\mathbf{a}_3^2+\mathbf{a}_3^{\dagger 2}+\left(2N_3+1\right)\right]$$
$$+\mathbf{a}_1^\dagger\left[\mathbf{a}_3^2+\mathbf{a}_3^{\dagger 2}+\left(2N_3+1\right)\right]$$

6 terms $\qquad H_{n_1,n_3;n_1',n_3'}\equiv\left\langle n_1,n_3\right|\mathbf{H}^{(1)}\left|n_1',n_3'\right\rangle$

operator	n_1-n_1'	n_3-n_3'	$\mathbf{H}^{(1)}_{n_1,n_3;n_1',n_3'}$	$\Delta E=E_{n_1,n_3}-E_{n_1',n_3'}$ $=\hbar\left[\left(n_1-n_1'\right)\omega_1+\left(n_3-n_3'\right)\omega_3\right]$
$\mathbf{a}_1,\mathbf{a}_3^2$	-1	-2	$(n_1+1)^{1/2}[(n_3+2)(n_3+1)]^{1/2}$	$\hbar[-\omega_1-2\omega_3]$
$\mathbf{a}_1,\mathbf{a}_3^{\dagger 2}$	-1	$+2$	$(n_1+1)^{1/2}[n(n-1)]^{1/2}$	$\boxed{\hbar[-\omega_1+2\omega_3]}$
$\mathbf{a}_1(2\mathbf{N}_3+1)$	-1	0	$(n_1+1)^{1/2}[(2n_3+1)]^{1/2}$	$\hbar[-\omega_1]$
$\mathbf{a}_1^\dagger,\mathbf{a}_3^2$	$+1$	-2	$(n_1)^{1/2}[(n_3+2)(n_3+1)]^{1/2}$	$\boxed{\hbar[\omega_1-2\omega_3]}$
$\mathbf{a}_1^\dagger,\mathbf{a}_3^{\dagger 2}$	$+1$	$+2$	$(n_1)^{1/2}[n(n-1)]^{1/2}$	$\hbar[\omega_1+2\omega_3]$
$\mathbf{a}_1^\dagger\left(2\mathbf{N}_3+1\right)$	$+1$	0	$(n_1)^{1/2}[2n_3+1]^{1/2}$	$\hbar[\omega_1]$

The two $\boxed{\text{circled terms}}$ involve near degeneracy.

They require diagonalization of a near-degenerate block.

All of the other terms can be dealt with by 2nd order non-degenerate Perturbation Theory.

OK, we are interested in all of the terms where $\omega_1 - 2\omega_3 \approx 0$.

$$P = \underset{\substack{\downarrow \\ \text{2 points} \\ \text{for } \omega_1 = 2\omega}}{2n_1} + \underset{\substack{\downarrow \\ \text{1 point} \\ \text{for } \omega_3 = \omega}}{n_2}$$

Polyad #	total membership of states	
P = 0	(0, 0)	1
P = 1	(0, 1)	1
P = 2	(1, 0), (0, 2)	2
P = 3	(1, 1), (0, 3)	2
P = 4	(2, 0), (1, 2), (0, 4)	3
P = 5	(2, 1), (1, 3), (0, 5)	3
P = 6	(3, 0), (2, 2), (1, 4), (0, 6)	4

We have degenerate groups of levels where all within-group matrix elements scale larger with n_1, n_3 and within-group membership increases. Worse and worse!!!!! Or is it?

This amounts to increasingly strong interactions among larger groups of states. But it is consistent with a mode. **NOT ERGODIC!!!**

This is a dominant feature of both spectrum and dynamics.

$\mathbf{k}_{133}$ can either make the bend softer or stiffer as the stretch increases.

We can rewrite everything so far in terms of P.

$$\begin{aligned}\frac{E_p^{(0)}}{\hbar\omega} &= 2\left(n_1 + 1/2\right) + \left(n_3 + 1/2\right) \\ &= 2n_1 + n_3 + 3/2 = P + 3/2\end{aligned}$$

even-P: states are $\left(n_1 = \frac{P}{2}, n_3 = 0\right), \left(n_1 = \frac{P}{2} - 1, n_3 = 2\right), \ldots (0, P)$

there are $\frac{P+2}{2}$ states in polyad

odd-P: states are $\left(n_1 = \frac{P-1}{2} - 1, n_3 = 1\right), \left(n_1 = \frac{P-3}{2}, n_3 = 3\right), \ldots (0, P)$

there are $\frac{P+1}{2}$ states in polyad

$$\left(\frac{\mathbf{H}^{(1)}}{\hbar^{3/2}m^{-3/2}\omega_1^{-1/2}\omega_3^{-1}k_{122}2^{-3/2}}\right) = \underbrace{\mathbf{a}_1\mathbf{a}_3^{\dagger 2}+\mathbf{a}_1^{\dagger}\mathbf{a}_3^{2}}_{\Delta P = 0} + \underbrace{\underbrace{\mathbf{a}_1\mathbf{a}_3^{2}+\mathbf{a}_1^{\dagger}\mathbf{a}_3^{\dagger 2}}_{-4 \qquad -4}\;\underbrace{\mathbf{a}_1^{\dagger}\left(N_2+1\right)+\mathbf{a}\left(N_2+1\right)}_{-2 \qquad -2}}_{\text{between polyads}}$$

This is a recipe for adding <u>interpolyad interactions</u> via 2nd order Perturbation Theory.

The 133 Polyad itself:

$$\frac{\mathbf{H}_P^{(0)}}{\hbar\omega} = \begin{pmatrix} P+3/2 & 0 & 0 & 0 \\ 0 & P+3/2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & P+3/2 \end{pmatrix}$$

$$\begin{array}{llccccc}
 & \dfrac{\mathbf{H}_P^{(1)}}{\text{stuff}} = & \dfrac{P}{2},0 & \dfrac{P}{2}-1,2 & \dfrac{P}{2}-2,4 & \cdots & 0,P \\
\text{even } P & \dfrac{P}{2},0 & 0 & \left[\left(\dfrac{P}{2}\right)(2-1)\right] & & & \\
 & \dfrac{P}{2}-1,2 & \text{sym} & 0 & \left[\left(\dfrac{P}{2}-1\right)(3\cdot 4)\right]^{1/2} & & \\
 & \dfrac{P}{2}-2,4 & & \text{sym} & 0 & & \\
 & \vdots & & & & & \left[(1)(P)(P-1)\right]^{1/2} \\
 & 0,P & & & & \text{sym} & 0
\end{array}$$

Inter-Block Interactions

$$\begin{pmatrix} \boxed{P1} & & \boxed{P1 \sim P2} \\ & \ddots & \\ & & \boxed{P2} \end{pmatrix}$$

Van Vleck Transformation [HLB-RWF, pages 237-243]

Second-Order corrections along diagonal

$$E_1^{(0)} + \frac{\mathbf{H}_{ij}^{(1)2}}{E_i^{(0)} - E_1^{(0)}}$$

Off diagonal

$$\mathbf{H}_{ab}^{(1)} + \sum_{\alpha} \frac{\mathbf{H}_{a\alpha}^{(1)}\mathbf{H}_{\alpha b}^{(1)}}{\frac{E_a^{(0)} + E_b^{(0)}}{2} - E_\alpha^{(0)}}$$

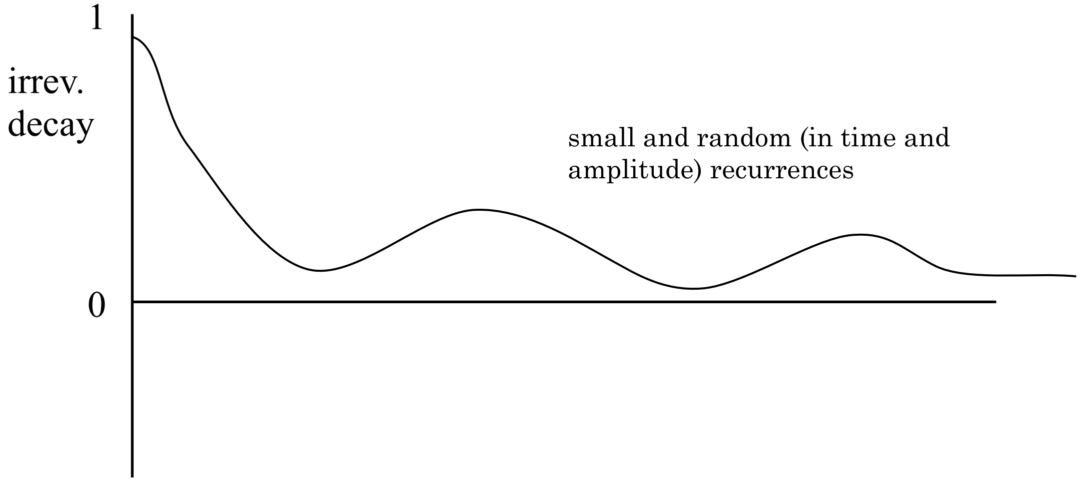
Intramolecular Vibrational Redistribution (IVR)

The Pluck: $\Psi(\mathbf{Q},0) = \phi_{\{\mathrm{V}\}}^{(0)}$

$\phi_{\{\mathrm{V}\}}^{(0)}$ expressed as a sum of $a_{\{\mathrm{V}\}}\psi_{\{\mathrm{V}\}}$

$$\Psi\left(\mathbf{Q},t\right) = \sum_{\{\mathrm{V}\}} a_{\{\mathrm{V}\}} e^{-iE_{\{\mathrm{V}\}}t/\hbar}$$

"Survival Probability": $P = \left|\int \Psi^*(\mathbf{Q},0)^* \Psi(\mathbf{Q},t) d\mathbf{Q}\right|^2$



how fast?
minor recurrences?

“x-k” relationships

$$E_{\{\mathbf{v}\}} = \hbar \sum_{\{\mathbf{v}\}} \omega_i \left(n_i + 1/2\right) - \sum_{\{\mathbf{v}\},\{\mathbf{v}^1\}} x_{ij} \left(n_i + 1/2\right)\left(n_j + 1/2\right)$$

$$\left\{x_{ij}\right\} \leftrightarrow k_{iij}, k_{iiij}, k_{iiiij}$$

from Perturbation Theory

Polyads – a model of what is supposed to happen far above where normal modes are well known to be a bad approximation.

↗

a “broken pattern” that extrapolates well ⟶ a “pattern of broken patterns”

But at high E, some normal modes are replaced by local modes.

⇓ a frequent path to isomerization

trans-cis in S_1 acetylene [*Science* **350**, 1338 (2015)]
acetylene-vinylidene in S_0 acetylene [*Science* **358**, 336 (2017)]

5.73 Quantum Mechanics I
Fall 2018