Polyads, a, a†, N


Last time:

- Two level problem with complex $E_j^{(0)}$.
- **Strong coupling limit** $V^2 \gg |\delta \epsilon^2 + \delta \Gamma^2/4|$: if either $\delta \epsilon = 0$ or $\delta \Gamma = 0$, the two quasi-eigenstates have the same width. Otherwise no major surprises.
- **Weak coupling limit** $V^2 \ll |\delta \epsilon^2 - \delta \Gamma^2/4|$: if $\delta \epsilon = 0$ we get no level repulsion and no level-width sharing. Big surprise!

Quantum beats between two decaying quasi-eigenstates. $I(t)$ expressed in terms of 8 parameters ($I_\pm$, $I_\pm$, $\Gamma_\pm$, $\Gamma_\pm$, $\omega_{QB}$, $\phi_{QB}$) obtained from 6 dynamical parameters ($\delta \epsilon$, $\delta \Gamma$, $\Gamma^2$, $V$, $I_A$, $I_B$).

Today:

- Begin study of vibrational dynamics, leading eventually to replacement of the quantum mechanical $H^{\text{eff}}$ by a classical mechanical $\mathcal{H}^{\text{eff}}$. Tricks to get $\langle A \rangle$ without use of $\text{Trace}(A\rho(t))$.

Polyatomic Molecule Vibration

\[
\psi_{v_1v_2\ldots v_{3N-6}} = \psi_{\nu} = \prod_{j=1}^{3N-6} \phi_{v_j} \quad \text{product basis set}
\]

\[
H = \sum_{j=1}^{3N-6} h_j + \text{coupling terms}
\]

\[
E_j^{(0)} = \sum_j h\omega_j (v_j + 1/2) \quad \text{(traditionally $\omega$ is in cm}^{-1}\text{ units, } E = h\omega (v + 1/2), \text{ and } \omega \text{ is not in radians/s)}
\]

coupling terms have the form

\[
\sum_{i,j,k} k_{ijk} Q_i Q_j Q_k + \{\text{quartic}\} + \{\text{quintic}\} + \ldots
\]

most important

Enormous number of undeterminable anharmonic force constant terms.
matrix element scaling and selection rules

\[
\langle v_j + n | Q^a_j | v_j \rangle = \left[ \frac{\hbar}{2\pi c \mu_j \omega_j} \right]^{a/2} \left\{ v_j^{a/2} \right\}^2 \tag{highest power term} 
\]

and similarly for \( P^a_j \)

selection rule \( n = a, a - 2, \ldots -a \)

\( \mu_j \) and \( \omega_j \) must be generalized from single oscillator (diatomic molecule) form via a Wilson \( F, G \) matrix treatment, but there is always a mass factor analogous to \( \mu_j \) and a frequency factor analogous to \( \omega_j \).

**Polyads**

Often, there are approximate integer multiple ratios between harmonic frequencies.

<table>
<thead>
<tr>
<th>Fermi</th>
<th>( \omega_1 \approx 2\omega_2 )</th>
<th>1 : 2</th>
<th>( \frac{k_{122}}{2} Q_1 Q_2^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darling-Dennison</td>
<td>( \omega_{sym} \approx \omega_{antisym} )</td>
<td>2 : 2</td>
<td>( k_{ssaa} \frac{Q_1^2 Q_2^2}{4} )</td>
</tr>
<tr>
<td>3 modes</td>
<td>( \frac{k_{1244}}{2} Q_1 Q_2 Q_4^2 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

comma is used to separate modes that receive from those that donate

large and increasing numbers of quasi-degenerate basis states all interacting increasingly strongly

e.g. Darling-Dennison

\[
P = 2v_{sym} + 2v_{anti}
\]

<table>
<thead>
<tr>
<th>( P )</th>
<th>( v_{sym} )</th>
<th>( v_{anti} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 × 1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2 × 2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
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<td></td>
<td>4</td>
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<td></td>
<td>6</td>
<td>3</td>
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<td>6</td>
<td>2</td>
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<td></td>
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<td>1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>
Polyad: a small piece of state space in which dynamics is

* fast
* predictable
* scalable
* visualizable

We need an algebra that will make all of this more transparent.

\[ a, a^+, N \]

Eventually we will find that we can use this algebra to go from Quantum Mechanical \( H^{\text{eff}} \) to Classical Mechanical \( \mathcal{H}^{\text{eff}} \).

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**Dimensionless Operators**

\[
\hat{Q} = \left[ \frac{2\pi c \mu \omega}{\hbar} \right]^{1/2} Q
\]

\[
\hat{P} = \left[ \frac{\hbar 2\pi c}{\omega} \right]^{1/2} P
\]

\[
\hat{H}^{(0)} = \left[ \frac{1}{2\pi \hbar c \omega} \right] H^{(0)} = \frac{1}{2} \left[ \hat{Q}^2 + \hat{P}^2 \right]
\]

displays the equivalence of \( \hat{Q}^2 \) and \( \hat{P}^2 \).

Matrix elements of \( \hat{Q}, \hat{P}, \) and \( \hat{H}^{(0)} \) are simple functions of integers.

\[ \omega [\text{in cm}^{-1}] = \frac{1}{2\pi c} [k/\mu]^{1/2} \]
But it is more useful to express $\hat{Q}$ and $\hat{P}$ in terms of something even more fundamental: $a, a^\dagger, N$

$$a^\dagger = 2^{-1/2} [\hat{Q} - i\hat{P}]$$
$$a = 2^{-1/2} [\hat{Q} + i\hat{P}]$$
$$\hat{Q} = 2^{-1/2} [a^\dagger + a]$$
$$\hat{P} = 2^{-1/2} i[a^\dagger - a]$$

$$N = a^\dagger a$$

$$\langle v + 1 | a^\dagger | v \rangle = [v + 1]^{1/2}$$
$$\langle v | a | v + 1 \rangle = [v + 1]^{1/2}$$
$$\langle v | N | v \rangle = \langle v | a^\dagger a | v \rangle = v$$

$$H^{(0)} = \sum_{j=1}^{3N-6} \hbar 2\pi c \omega_j (a^\dagger a_j + 1/2)$$

$$H^{(1)}$$ anharmonic coupling terms, e. g.

$$k_{i...ij...j} Q_i^n Q_j^m = k_{i...ij...j} (2^{-1/2})^{n+m} [a_i^\dagger + a_i]^n [a_j^\dagger + a_j]^m$$

Commutation rules

$$[a_i, a_i^\dagger] = 1$$

$$[a_i, a_j] = [a_i, a_j^\dagger] = 0$$
Setting up an $H^{\text{eff}}$ — We have two choices:

1st choice

$$
H^{(0)} = \sum_j \hbar 2\pi c \omega_j \left( a_j^\dagger a_j + 1/2 \right)
$$

$$
H^{(1)} = V(Q) - \sum_j \left( k_j / 2 \right) \frac{1}{2} \left( a_j + a_j^\dagger \right)^2
$$

already included in $H^{(0)}$

Possibly use hybrid perturbation theory and DVR methods to evaluate matrix elements of $V(Q)$.

2nd choice

$$
H^{(0)} = \sum_j \hbar 2\pi c \omega_j \left( a_j^\dagger a_j + 1/2 \right)
$$

$$
+ \sum_{j \leq k} x_{jk} \left( a_j^\dagger a_j + 1/2 \right) \left( a_k^\dagger a_k + 1/2 \right)
$$

$$
+ \sum_{j,k,\ell} y_{jk\ell} \left( a_j^\dagger a_j + 1/2 \right) \left( a_k^\dagger a_k + 1/2 \right) \left( a_\ell^\dagger a_\ell + 1/2 \right)
$$

[terms from a Dunham expansion converted to $a^\dagger a$ form]

$H^{(1)}$ = specific anharmonic resonance terms that require diagonalization of a polyad block

e.g. $\frac{1}{4} k_{ssaa} Q_s^2 Q_a^2 = \frac{1}{16} k_{ssaa} \left( a_s^\dagger + a_s \right)^2 \left( a_a^\dagger + a_a \right)^2$

The second choice is vastly preferable because:

1. it is in the form of a traditional fit model;
2. it does not require diagonalization of the full $H$ because $H^{(1)}$ is block diagonalized into polyads (actually need to perform a Van Vleck transformation to fold out-of-polyad matrix elements of the selected anharmonic resonances into the quasi-degenerate polyad blocks);
3. it does not require extensive use of non-degenerate perturbation theory to convert anharmonic terms in $V(Q)$ ($k$'s) into anharmonic terms in $E(V)$ ($x$'s) [$x$-$k$ relationships: Ian Mills].
matrix elements of

\[
\frac{1}{2} k_{1,22} Q_1 Q_2^2 = \frac{1}{2} 2^{-3/2} \left[ \frac{\hbar}{2\pi c \mu_1 \omega_1} \right]^{1/2} \left[ \frac{\hbar}{2\pi c \mu_2 \omega_2} \right]^{1/2} k_{1,22} (a_1^+ + a_1)(a_2^+ + a_2)^2
\]

\[
H_{v_1,v_2,v_1-1,v_2+2}/\hbar c = k'_{1,22} \langle v_1 v_2 a_1^+ a_2^2 v_1 - 1, v_2 + 2 \rangle
\]

\[
k'_{1,22} = \frac{1}{2} 2^{-3/2} \left[ \frac{\hbar}{2\pi c \mu_1 \omega_1} \right]^{1/2} \left[ \frac{\hbar}{2\pi c \mu_2 \omega_2} \right]^{1/2} \frac{1}{\hbar c} k_{1,22}
\]

\[
\langle v_1 v_2 | a_1 a_2^2 | v_1 - 1, v_2 + 2 \rangle = [(v_2 + 2)(v_2 + 1)(v_1)]^{1/2}
\]

\[
H_{v_1,v_2,v_1+1,v_2-2}/\hbar c = k'_{1,22} \langle v_1 v_2 | a_1 a_2^+ | v_1 + 1, v_2 - 2 \rangle
\]

\[
= k'_{1,22} [(v_1 + 1)(v_2 - 1)]^{1/2}.
\]

Suppose we have a polyad involving three vibrational normal modes connected by two anharmonic resonances (we are going to use this model for several lectures).

\[
\omega_1 = \omega_3 = 2\omega_2
\]

\[
\omega_1 \text{ is symmetric stretch: totally symmetric}
\]

\[
\omega_3 \text{ is antisymmetric stretch: anti-symmetric (need even number of quanta to be totally symmetric)}
\]

\[
\omega_2 \text{ is bend: totally symmetric (a further level of complexity could be a doubly degenerate bending mode)}
\]

Resonance #1

\[
\frac{1}{4} k_{1133} Q_1^2 Q_3^2 = k'_{11,33} (a_1 + a_1^+) (a_3 + a_3^+)^2
\]

Resonance #2

\[
\frac{1}{2} k_{122} Q_1 Q_2^2 = k'_{12,22} (a_1 + a_1^+) (a_2 + a_2^+)^2
\]

\[
k'_{11,33} = \frac{1}{4} k_{1133} \left( \frac{\hbar}{2\pi c \mu_1 \omega_1} \right) \left( \frac{\hbar}{2\pi c \mu_3 \omega_3} \right) \frac{1}{\hbar c}
\]

\[
k'_{12,22} = \frac{1}{2} k_{122} 2^{-3/2} \left( \frac{\hbar}{2\pi c \mu_1 \omega_1} \right)^{1/2} \left( \frac{\hbar}{2\pi c \mu_2 \omega_2} \right) \frac{1}{\hbar c}
\]

Polyad number is \( P = 2v_1 + 2v_3 + v_2 \). There are connected manifolds of resonances.
\[(0,2n,0) \rightarrow (0,2n-4,2) \rightarrow \cdots \rightarrow (0,2n-8,4) \rightarrow \cdots \rightarrow (n-2,4,0) \rightarrow (n-4,4,2) \rightarrow (n-6,4,4) \\]
\[(n-1,2,0) \rightarrow (n-3,2,2) \rightarrow (n-5,2,4) \\]
\[(n,0,0) \rightarrow (n-2,0,2) \rightarrow (n-4,0,4) \rightarrow \cdots \rightarrow (0,0,n) \]

Number of states in polyad:

<table>
<thead>
<tr>
<th>(N)</th>
<th># states</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 ((0,0,0))</td>
</tr>
<tr>
<td>1</td>
<td>1 ((0,1,0))</td>
</tr>
<tr>
<td>2</td>
<td>2 ((1,0,0),(0,2,0))</td>
</tr>
<tr>
<td>3</td>
<td>2 ((1,1,0)(0,3,0))</td>
</tr>
<tr>
<td>4</td>
<td>4 ((2,0,0),(1,2,0),(0,4,0),(0,0,2))</td>
</tr>
<tr>
<td>(\cdots)</td>
<td>(\cdots)</td>
</tr>
<tr>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>(\cdots)</td>
<td>(\cdots)</td>
</tr>
<tr>
<td>24</td>
<td>49</td>
</tr>
</tbody>
</table>
The polyad conserving resonance operators are

\[ \Omega_1 = k'_1 a_1^2 a_3^{\dagger 2} \]

\[ \Delta \nu_1 = -2, \quad \Delta \nu_3 = +2 \]

\[ \Omega_1^{\dagger} = k'_1 a_1^{\dagger 2} a_3^{\dagger 2} \]

\[ \Delta \nu_1 = +2, \quad \Delta \nu_3 = -2 \]

\[ \Omega_2 = k'_2 a_1 a_2^{\dagger 2} \]

\[ \Delta \nu_1 = -1, \quad \Delta \nu_2 = +2 \]

\[ \Omega_2^{\dagger} = k'_2 a_1^{\dagger} a_2^{\dagger 2} \]

\[ \Delta \nu_1 = +1, \quad \Delta \nu_2 = -2 \]

You know how to set up the matrices for each polyad

\[ H/hc = \{ \omega_1(N_1 + 1/2) + \omega_2(N_2 + 1/2) + \omega_3(N_3 + 1/2) \]

\[ + x_{11}(N_1 + 1/2)^2 + x_{22}(N_2 + 1/2)^2 + x_{33}(N_3 + 1/2)^2 \]

\[ + x_{12}(N_1 + 1/2)(N_2 + 1/2) + x_{13}(N_1 + 1/2)(N_3 + 1/2) + x_{23}(N_2 + 1/2)(N_3 + 1/2) \} \]

\[ + \left[ \Omega_1 + \Omega_1^{\dagger} + \Omega_2 + \Omega_2^{\dagger} \right] \]

\[ \{ \} \text{ diagonal} \]

\[ [ ] \text{ non-diagonal} \]

We are now equipped to look at dynamics in state space (intrapolyad dynamics), dynamics in \( Q, P \) space (interpolyad dynamics), and dynamics of the resonance and transfer rate operators. Next time. Also final exam.