Polyads, a, a†, N

Readings:	Chapter 9.4.4 - 9.4.9, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

two level problem with complex $E_j^{(0)}$.

strong coupling limit $V^2 >> |\delta\varepsilon^2 + \delta\Gamma^2/4|$: if either $\delta\varepsilon = 0$ or $\delta\Gamma = 0$, the two quasi-eigenstates have the same width. Otherwise no major surprises.

weak coupling limit $V^2 << |\delta\varepsilon^2 - \delta\Gamma^2/4|$: if $\delta\varepsilon = 0$ 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_+, I_-, Γ_+, Γ_-, I_{QB}, Γ_{QB}, ω_{QB}, ϕ_{QB}) obtained from 6 dynamical parameters ($\delta\varepsilon$, $\delta\Gamma$, $\overline{\Gamma}$, V, I_A, I_B).

Today:

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

Polyatomic Molecule Vibration

$$\psi_{v_1 v_2 \ldots v_{3N-6}} = \psi_{\mathbf{V}} = \prod_{j=1}^{3N-6} \phi_{v_j} \qquad \text{product basis set}$$

$$\mathbf{H} = \underbrace{\sum_{j=1}^{3N-6} \mathbf{h}_j}_{\mathbf{H}^{(0)}} + \text{coupling terms} \quad \{\text{could also include diagonal anharmonicities}\}$$

$$E^{(0)} = \sum_j h\omega_j\left(v_j + 1/2\right)$$ (traditionally ω is in cm^{-1} units, $E = hc\omega\,(v + 1/2)$, and ω is not in radians/s)

coupling terms have the form

$$\underbrace{\underbrace{\sum_{i,j,k} k_{ijk}\mathbf{Q}_i\mathbf{Q}_j\mathbf{Q}_k}_{\textbf{cubic}} + \{\text{quartic}\}}_{\text{most important}} + \{\text{quintic}\} + \ldots$$

Enormous number of undeterminable anharmonic force constant terms.

matrix element scaling and selection rules

highest power term

scaling $\left\langle v_j + n \middle| \mathbf{Q}_j^a \middle| v_j \right\rangle = \left[\frac{\hbar}{2\pi c \mu_j \omega_j}\right]^{a/2} \left\{ v_j^{a/2} \right\}$ (and similarly for $\mathbf{P}_j^a$)

selection rule $n = a, a-2, \ldots -a$

force constant geometry

μ_j and ω_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 μ_j and a frequency factor analogous to ω_j.

<u>Polyads</u>

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

Fermi	$\omega_1 \approx 2\omega_2$	1 : 2	$\frac{k_{122}}{2}\mathbf{Q}_1\mathbf{Q}_2^2$
Darling-Dennison	$\omega_{\text{sym}} \approx \omega_{\text{antisym}}$	2 : 2 (why not 1 : 1 ?)	$\frac{k_{ssaa}}{4}\mathbf{Q}_s^2\mathbf{Q}_a^2$
3 modes	$\frac{k_{1,244}}{2}$	$\mathbf{Q}_1\mathbf{Q}_2\mathbf{Q}_4^2$	

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 = $2v_{\text{sym}} + 2v_{\text{anti}}$

$\mathbf{H}^{\text{polyad}}$	P	v_{sym}	v_{anti}
1×1	0	0	0
2×2	2	1	0
	2	0	1
3×3	4	2	0
	4	1	1
	4	0	2
4×4	6	3	0
	6	2	1
	6	1	2
	6	0	3

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.

$$\mathbf{a},\ \mathbf{a}^{\dagger},\ \mathbf{N}$$

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

Dimensionless Operators

generalize

$$\hat{\mathbf{Q}} = \left[\frac{2\pi c\mu\omega}{\hbar}\right]^{1/2}\mathbf{Q} \qquad\qquad \omega[\text{in cm}^{-1}] = \frac{1}{2\pi c}[k/\mu]^{1/2}$$

$$\hat{\mathbf{P}} = [\hbar 2\pi c \quad \omega]^{-1/2}\mathbf{P}$$

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

displays the equivalence of $\hat{\mathbf{Q}}^2$ and $\hat{\mathbf{P}}^2$.

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

But it is more useful to express $\hat{\mathbf{Q}}$ and $\hat{\mathbf{P}}$ in terms of something even more fundamental: $\mathbf{a}$, $\mathbf{a}^\dagger$, $\mathbf{N}$

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

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

$$\hat{\mathbf{Q}} = 2^{-1/2}\left[\mathbf{a}^\dagger + \mathbf{a}\right]$$

$$\hat{\mathbf{P}} = 2^{-1/2}i\left[\mathbf{a}^\dagger - \mathbf{a}\right]$$

$$\mathbf{N} = \mathbf{a}^\dagger\mathbf{a}$$

$$\left\langle v+1\middle|\mathbf{a}^\dagger\middle|v\right\rangle = [v+1]^{1/2}$$

$$\left\langle v\middle|\mathbf{a}\middle|v+1\right\rangle = [v+1]^{1/2}$$

$$\left\langle v\middle|\mathbf{N}\middle|v\right\rangle = \left\langle v\middle|\mathbf{a}^\dagger\mathbf{a}\middle|v\right\rangle = v$$

$$\mathbf{H}^{(0)} = \sum_{j=1}^{3N-6} \hbar 2\pi c\omega_j\left(\mathbf{a}_j^\dagger\mathbf{a}_j + 1/2\right) \qquad \text{OR} \qquad \left(\mathbf{a}_j^\dagger\mathbf{a}_j + \mathbf{a}_j\mathbf{a}_j^\dagger\right)$$

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

$$k_{i\ldots ij\ldots j}\mathbf{Q}_i^n\mathbf{Q}_j^m = k_{i\ldots ij\ldots j}\left(2^{-1/2}\right)^{n+m}\left[\mathbf{a}_i^\dagger + \mathbf{a}_i\right]^n\left[\mathbf{a}_j^\dagger + \mathbf{a}_j\right]^m$$

Commutation rules

$$\left[\mathbf{a}_i,\mathbf{a}_i^\dagger\right] = 1$$

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

Setting up an $\mathbf{H}^{\text{eff}}$ — We have two choices:

1st choice

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

$$\mathbf{H}^{(1)} = V(\mathbf{Q}) - \underbrace{\sum_j \left(k_j/2\right)\frac{1}{2}\left(\mathbf{a}_j + \mathbf{a}_j^\dagger\right)^2}_{\text{already included in } \mathbf{H}^{(0)}}$$

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

2nd choice

$$\begin{aligned}\mathbf{H}^{(0)} = &\sum_j \hbar 2\pi c\omega_j \left(\mathbf{a}_j^\dagger \mathbf{a}_j + 1/2\right) \\ &+ \sum_{j\le k} x_{jk}\left(\mathbf{a}_j^\dagger \mathbf{a}_j + 1/2\right)\left(\mathbf{a}_k^\dagger \mathbf{a}_k + 1/2\right) \\ &+ \sum_{j,k,\ell} y_{jk\ell}\left(\mathbf{a}_j^\dagger \mathbf{a}_j + 1/2\right)\left(\mathbf{a}_k^\dagger \mathbf{a}_k + 1/2\right)\left(\mathbf{a}_\ell^\dagger \mathbf{a}_\ell + 1/2\right)\end{aligned}$$

[terms from a Dunham expansion converted to $\mathbf{a}^\dagger$,$\mathbf{a}$ form]

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

e.g. $$\frac{1}{4}k_{ssaa}\mathbf{Q}_s^2\mathbf{Q}_a^2 = \frac{1}{16}k_{ssaa}\left(\mathbf{a}_s^\dagger + \mathbf{a}_s\right)^2\left(\mathbf{a}_a^\dagger + \mathbf{a}_a\right)^2$$

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 $\mathbf{H}$ because $\mathbf{H}^{(1)}$ 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-degeneragte perturbation theory to convert anharmonic terms in $V(\mathbf{Q})$ (k's) into anharmonic terms in $E(\mathbf{V})$ (x's) [x-k relationships: Ian Mills].

matrix elements of

$$\frac{1}{2}k_{1,22}\mathbf{Q}_1\mathbf{Q}_2^2 = \frac{1}{2}2^{-3/2}\left[\frac{\hbar}{2\pi c\mu_1\omega_1}\right]^{1/2}\left[\frac{\hbar}{2\pi c\mu_2\omega_2}\right]k_{1,22}\left(\mathbf{a}_1^\dagger + \mathbf{a}_1\right)\left(\mathbf{a}_2^\dagger + \mathbf{a}_2\right)^2$$

$$\mathbf{H}_{v_1,v_2;v_1-1,v_2+2}/hc = k'_{1,22}\left\langle v_1 v_2\, \mathbf{a}_1^\dagger \mathbf{a}_2^2\, v_1 - 1, v_2 + 2\right\rangle$$

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

$$\left\langle v_1 v_2\middle|\mathbf{a}_1^\dagger \mathbf{a}_2^2\middle|v_1 - 1, v_2 + 2\right\rangle = \left[(v_2+2)(v_2+1)(v_1)\right]^{1/2}$$

$$\mathbf{H}_{v_1,v_2;v_1+1,v_2-2}/hc = k'_{1,22}\left\langle v_1 v_2\middle|\mathbf{a}_1 \mathbf{a}_2^{\dagger 2}\middle|v_1 + 1, v_2 - 2\right\rangle$$
$$= k'_{1,22}\left[(v_1+1)(v_2)(v_2-1)\right]^{1/2}.$$

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).

$\omega_1 \approx \omega_3 \approx 2\omega_2$

ω_1 is symmetric stretch:	totally symmetric
ω_3 is antisymmetric stretch:	anti-symmetric (need even number of quanta to be totally symmetric)
ω_2 is bend:	totally symmetric (a further level of complexity could be a doubly degenerate bending mode)

Resonance #1

$$\frac{1}{4}k_{1133}\mathbf{Q}_1^2\mathbf{Q}_3^2 = k'_{11,33}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)^2\left(\mathbf{a}_3 + \mathbf{a}_3^\dagger\right)^2$$

Resonance #2

$$\frac{1}{2}k_{122}\mathbf{Q}_1\mathbf{Q}_2^2 = k'_{1,22}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)\left(\mathbf{a}_2 + \mathbf{a}_2^\dagger\right)^2$$

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

$$k_{1,22} = \frac{1}{2}k_{122}2^{-3/2}\left(\frac{\hbar}{2\pi c\mu_1\omega_1}\right)^{1/2}\left(\frac{\hbar}{2\pi c\mu_2\omega_2}\right)\frac{1}{hc}$$

Polyad number is $P = 2v_1 + 2v_3 + v_2$. There are connected manifolds of resonances.

$$
\begin{array}{ccccc}
(0,2n,0) & & & & \\
\vdots & (0,2n-4,2) & & & \\
\vdots & \vdots & (0,2n-8,4) & & \\
\vdots & \vdots & \vdots & & \\
\vdots & \vdots & \vdots & & \\
(n-2,4,0) & (n-4,4,2) & (n-6,4,4) & & \\
(n-1,2,0) & (n-3,2,2) & (n-5,2,4) & & \\
(n,0,0) & (n-2,0,2) & (n-4,0,4) & \cdots & (0,0,n)
\end{array}
$$

Number of states in polyad:

$\underline{N}$	$\underline{\text{\# states}}$	
0	1	$(0,0,0)$
1	1	$(0,1,0)$
2	2	$(1,0,0),(0,2,0)$
3	2	$(1,1,0)(0,3,0)$
4	4	$(2,0,0),(1,2,0),(0,4,0),(0,0,2)$
…	…	
12	16	
…	…	
24	49	

The polyad conserving resonance operators are

$$\mathbf{\Omega}_1 = k'_{11,33}\ \mathbf{a}_1^2 \mathbf{a}_3^{\dagger 2} \qquad \Delta v_1 = -2,\ \Delta v_3 = +2$$

$$\mathbf{\Omega}_1^\dagger = k'_{11,33}\ \mathbf{a}_1^{\dagger 2} \mathbf{a}_3^{\dagger 2} \qquad \Delta v_1 = +2,\ \Delta v_3 = -2$$

$$\mathbf{\Omega}_2 = k'_{1,22}\ \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} \qquad \Delta v_1 = -1,\ \Delta v_2 = +2$$

$$\mathbf{\Omega}_2^\dagger = k'_{1,22}\ \mathbf{a}_1^\dagger \mathbf{a}_2^2 \qquad \Delta v_1 = +1,\ \Delta v_2 = -2$$

You know how to set up the matrices for each polyad

$$\begin{aligned}\mathbf{H}/hc = \{&\omega_1(\mathbf{N}_1 + 1/2) + \omega_2(\mathbf{N}_2 + 1/2) + \omega_3(\mathbf{N}_3 + 1/2)\\ &+ x_{11}(\mathbf{N}_1 + 1/2)^2 + x_{22}(\mathbf{N}_2 + 1/2)^2 + x_{33}(\mathbf{N}_3 + 1/2)^2\\ &+ x_{12}(\mathbf{N}_1 + 1/2)(\mathbf{N}_2 + 1/2) + x_{13}(\mathbf{N}_1 + 1/2)(\mathbf{N}_3 + 1/2) + x_{23}(\mathbf{N}_2 + 1/2)(\mathbf{N}_3 + 1/2)\}\\ &+ [\mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger + \mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger]\\ &\qquad \{\ \}\ \text{diagonal}\\ &\qquad [\ ]\ \text{non-diagonal}\end{aligned}$$

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.