Lecture #28: Polyatomic Vibrations IV: Symmetry

What is a normal mode?

all atoms undergoing oscillation at the same frequency and phase and with amplitudes determined by the eigenvectors of the GF matrix.

\[ |Q\rangle = L^{-1} |S\rangle \quad \widetilde{s}_{t\alpha} = |s_{t\alpha}(t)\rangle |\hat{e}_{S_{t\alpha}}\]

we built in specific relative lengths of displacements

\[ |s_{t\alpha}(t)\rangle \cos(\lambda t + \delta) \]

e.g. \( Q_j = \sum_i L^{-1}_{ji} S_i \)

If we represent \( S_i \) by a set of \( s_{i\alpha} \) vectors of prescribed lengths and directions, then \( L^{-1} \) tells us how to weight and add the vectors at each atom associated with the various internal displacements

e.g. \( H_2O \) (page 4 of \( H_2O \) example in 4/24/96 notes)

\( Q_1 = 0.685 (S_2 - S_1) \)

\( Q_2 = 0.695 (S_1 + S_2) + 0.037S_3 \)

\( Q_3 = 0.655S_3 \)

\( S_1 = \)

\( S_2 = \)

\( S_3 = \)
names of normal modes
from pictures or from equations?

Note that each of the pictures involves some change of bond angle. So which mode is the “bend”?

Q₁ involves dominantly a compression of one bond and an expansion of the other equivalent one;
Q₂ involves dominantly two equivalent bonds expanding and contracting in phase;
Q₃ pure internal bend.

equations: \[ S_1 \pm S_2 \] “symmetric” “antisymmetric”

mixed character — no \( S_3 \) in \( Q_1 \)
some \( S_3 \) character in \( Q_2 \)
Why no \( (S_1 + S_2) \) character in \( Q_3 \)? Actually, there is some, but very small.
Why are there mixtures of internal coordinates in the normal coordinates?

Some are due solely to symmetry. Others are due to the structure of the $F$ and $G$ matrices. The detailed character of the modes depends on ratios of off diagonal matrix elements of $GF$ to differences between diagonal values, just as for $H$ (even though $GF$ is not symmetric).

Best to see the cause of mixed character normal modes by going to symmetrized internal coordinates.

Let $|\tilde{S}\rangle = U|S\rangle$

$$U = \begin{pmatrix} 2^{-1/2} & 2^{-1/2} & 0 \\ 2^{-1/2} & -2^{-1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\langle S|F|S\rangle = \langle S|U^*F^*U^*U|S\rangle = \langle \tilde{S}|\tilde{F}|\tilde{S}\rangle$$
similarly  
\[ \mathbf{F} = \mathbf{UFU}^{\dagger} \]
\[ \mathbf{G} = \mathbf{UGU}^{\dagger} \]

\[
\mathbf{F} = \begin{pmatrix}
8.454 \text{ md} / \text{Å} & -0.100 \text{ md} / \text{Å} & 0.224 \text{ md} \\
-0.100 \text{ md} / \text{Å} & 8.454 \text{ md} / \text{Å} & 0.244 \text{ md} \\
0.224 \text{ md} & 0.224 \text{ md} & 0.697 \text{ md} \cdot \text{Å}
\end{pmatrix}
\]

(md = millidyne, dyne is the cgs unit of force, now illegal.)

Note that each term in expansion of determinant |\( \mathbf{F} \)| has same units: \( \text{md}^3/\text{Å} \) even though individual terms in \( \mathbf{F} \) do not.

An easy way for humans, not computers, to compute new \( \mathbf{F} \) matrix is term by term rather than multiplying out.

\[
\tilde{\mathbf{F}}_{11} = 2^{-1/2} \left \langle (S_1 + S_2) | \mathbf{F} | (S_1 + S_2) \right \rangle 2^{-1/2}
\]
\[
= \frac{1}{2} \left[ F_{11} + F_{22} + 2F_{12} \right] = 8.454 \text{ md} / \text{Å} - 0.200 \text{ md} / \text{Å}
\]
\[
= 8.254 \text{ md} / \text{Å}
\]

\[
\tilde{\mathbf{F}}_{12} = \frac{1}{2} \left \langle (S_1 - S_2) | \mathbf{F} | (S_1 + S_2) \right \rangle = \frac{1}{2} \left[ F_{11} - F_{22} + F_{12} - F_{21} \right] = 0
\]

etc.

\[
\tilde{\mathbf{F}} = \begin{pmatrix}
8.254 \text{ md} / \text{Å} & 0 & 0.317 \text{ md} \\
0 & 8.654 \text{ md} / \text{Å} & 0 \\
0.317 \text{ md} & 0 & 0.697 \text{ md} \cdot \text{Å}
\end{pmatrix}
\]
rearrange

\[
\tilde{F} = \begin{pmatrix}
8.254 \text{md/Å} & 0.317 \text{md} & 0 \\
\text{sym} & 0.697 \text{md·Å} & 0 \\
0 & 0 & 8.654 \text{md/Å}
\end{pmatrix}
\]

Similarly for

\[
\tilde{G} = \begin{pmatrix}
1.054 \text{amu}^{-1} & -0.015 \text{amu}^{-1} & -0.063 \text{amu}^{-1} \text{Å}^{-1} \\
-0.015 \text{amu}^{-1} & 1.054 \text{amu}^{-1} & -0.063 \text{amu}^{-1} \text{Å}^{-1} \\
-0.063 \text{amu}^{-1} & -0.063 \text{amu}^{-1} \text{Å}^{-1} & 2.336 \text{amu}^{-1} \text{Å}^{-2}
\end{pmatrix}
\]

and, in re-arranged form

\[
\tilde{G} = \begin{pmatrix}
1.039 \text{amu}^{-1} & -0.089 \text{amu}^{-1} \text{Å}^{-1} & 0 \\
\text{sym} & 2.336 \text{amu}^{-1} \text{Å}^{-2} & 0 \\
0 & 0 & 1.069 \text{amu}^{-1}
\end{pmatrix}
\]

Notice that both \( \tilde{F} \) and \( \tilde{G} \) are block diagonalized.

This is a symmetry effect \( \rightarrow \) Group Theory.
(torsions in \( \overbrace{\text{sym}} \) would have been a separate block in symmetry coordinates)

What would cause the coupling between \( \tilde{S}_1 \) and \( \tilde{S}_3 \) to get larger or smaller? [VR]

Look at \( \tilde{G}_{13} \) and \( \tilde{F}_{13} \).
\[
\tilde{G}_{13} = -2^{-1/2} \left( r_{32}^e \right)^{-1} \sin \theta^e \frac{1}{m^3} \quad \text{with respect to } \begin{vmatrix} \tilde{G}_{11} - \tilde{G}_{33} \end{vmatrix}
\]

with respect to \begin{vmatrix} \tilde{F}_{11} - \tilde{F}_{33} \end{vmatrix}

mass & geometry effects

\[
\tilde{F}_{13}
\]

bend and stretch have very different \( F_{ii} \) but
two stretches or two bends have
more similar ones
Physical basis for “bend” vs. “stretch” as dominant
class character in a normal mode, even though there is no
symmetry reason that stretches and bends should
not mix strongly.

Alternate approach to vibrational analysis.

See Bernath pages 220-225.

Work in mass weighted Cartesian displacement representation rather than internal coordinates.
Convenient for electronic structure calculations. No insight. No transferability.
\( 3N \times 3N f \) matrix
\( f \) is symmetric
\( \mathbf{ee} = \mathbf{A} \quad \text{eigenvalues of } f \text{ matrix} \)
(6 are zero)
\( \mathbf{e} = \mathbf{e}^{-1} \text{ unitary } \rightarrow \quad |Q\rangle = \mathbf{e}|q\rangle \)

Once we obtain \( \{\lambda_i\} \) and \( \mathbf{e} \) can get to \( |S\rangle \) and \( F \) representations if desired.

Now for quantum mechanics and treatment beyond harmonic level.

We know what individual atom motions are involved in each \( Q \). Set up matrix representation of
\( H(P,Q) \).
\[ H = \sum_{n=1}^{3N-6} h_n^0 (Q_n, P_n) + V' (Q_1, \ldots Q_{3N-6}) \]

\[ h_n^0 = h \omega_n \begin{pmatrix} 1/2 & & & & \\ & 3/2 & & & \\ & & \ddots & & \\ & & & 0 & \\ & & & & v_n + 1/2 \end{pmatrix} \]

\[ V = \sum_{ijk} F_{ijk} Q_i Q_j Q_k + \sum_{ijkl} F_{ijkl} Q_i Q_j Q_k Q_l \]

Matrix elements

\[ H_{v_1 \ldots v_{3N-6}, v'_1 \ldots v'_{3N-6}} \]

Infinite matrix

How to truncate?

How to organize?

* in order of increasing energy
* polyads

**What is a polyad?**

2 mode frequencies are near integer multiples of each other, e.g. 2 : 1.

2 : 1 polyad

\[ \omega_1 \approx 2 \omega_2 \]

etc.
hexad ——— (0,10) ——— (1,8) ——— (2,6) ——— (3,4) ——— (4,2) ——— (5,0)

... triad ——— (0,4) ——— (1,2) ——— (2,0)

——— (0,3) ——— (1,1) 

dyad ——— (0,2) ——— (1,0) 

——— (0,1) 

——— (v_1,v_2) = (0,0)

# of levels in polyad increase monotonically, but all matrix elements are related to 1st example.

\[
H_{0,2;1,0} \propto F_{122} (2 \cdot 1)^{1/2} (1) = 2^{1/2} F_{122}
\]

\[
H_{nm;n+1 m-2} \propto F_{122} (m \cdot m - 1)^{1/2} (n + 1)^{1/2} = H_{02;10} \left[ \frac{m(m-1)(n+1)}{2} \right]^{1/2}
\]

“superpolyad” — two interlocking polyads, as in acetylene \( \omega_1 : \omega_2 : \omega_3 : \omega_4 : \omega_5 = 5 : 3 : 5 : 1 : 1 \)

Darling-Dennison  \( Q_1^2 Q_3^2 \)  
2345  \( Q_2 Q_4 Q_5 \)

Resonance Vectors

Basis Vectors \((v_1, v_2, v_3, v_4, \ell_4, v_5, \ell_5)\) 7 dimensional vector

each harmonic oscillator product state represented by a 7 dimensional vector

each coupling term represented by a vector that describes its selection rules.

\[
Q_1^2 Q_3^2 \ (2 0 \ -2 0 0 0 0)
\]

\[
\left| Q_1^2 Q_3^2 \rightangle
\]

\(\psi_1\) \(\psi_2\)

Find conserved quantum numbers by listing all relevant resonance vectors, then find directions \(\perp\) to all of those.

In HCCH \( n_{\text{res}}, n, \ell \) are the conserved quantities: “polyad quantum numbers”.

Tells you which block of \( H \) to diagonalize.