5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #25: Polyatomic Vibrations: Normal Mode Calculations

Pure rotation spectrum → A, B, C → some information about molecular shape
Vibrational spectrum:

Qualitative
GROUP THEORY

1. What point group?
2. How many vibrations of each symmetry species?
3. bend vs. stretch character for modes of each symmetry species
4. which modes are IR and Raman active?
5. band types (a–, b–, c–): rotational contours predicted.

Quantitative
NORMAL MODES

1. Derive force constants from spectrum and geometry.
2. Predict spectrum from geometry and force constants.
3. Isotope effects.
4. Pictures of normal modes in terms of internal coordinate displacements.
5. beyond normal modes.
   A. perturbations
   B. IVR

Wilson's **FG** matrix Method. Approximately 3 lectures. Not treated in Bernath, i.e., Bernath does what *ab initio* calculations do - eigenvalues of mass weighted Cartesian **f** matrix.

Lecture #1 (#25): Formal Derivation of **GF** matrix secular equation as condition for the existence of a transformation from Cartesian displacements to normal coordinates that permits **H** to be written as $\mathbf{H} = \frac{1}{2}\sum_k \dot{Q}_k^2 + \frac{1}{2}\sum_k \lambda_k Q_k^2$ (sum of separate harmonic oscillators)

Lecture #2 (#26): How do we actually obtain the **G** matrix? Eckart condition (a compromise): Vibration-rotation separation.

Lecture #3 (#27): Examples. Beyond the Harmonic Approximation.

Lots of matrices and transformations - introduce all of the actors now!

<u>COORDINATES</u>

3N CARTESIAN DISPLACEMENTS

$$\boldsymbol{\xi} \equiv \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_{3N} \end{pmatrix} = \begin{pmatrix} x_1 - x_1^e \\ y_1 - y_1^e \\ z_1 - z_1^e \\ \vdots \\ z_N - z_N^e \end{pmatrix}$$

<u>BODY</u>

3N MASS WEIGHTED CARTESIAN DISPLACEMENTS

$$\mathbf{q} = \mathbf{M}^{1/2}\xi = \begin{pmatrix} m_1^{1/2} & & & & & \\ & m_1^{1/2} & & & \mathbf{0} & \\ & & m_1^{1/2} & & & \\ & & & m_2^{1/2} & & \\ & \mathbf{0} & & & \ddots & \\ & & & & & m_N^{1/2} \end{pmatrix} \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_{3N} \end{pmatrix}$$

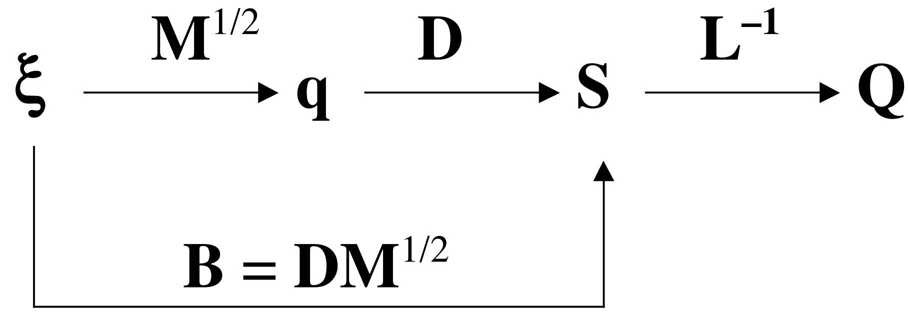
(groups of 3)

remove C. M. translation and rotation	3N–6 INTERNAL DISPLACEMENTS	$\mathbf{S} = \mathbf{Dq} = \mathbf{B}\boldsymbol{\xi}$

*** (to be defined later)*** see WILSON-DECIUS-CROSS
bond stretch, bend, torsion

3N–6 NORMAL DISPLACEMENTS	$\mathbf{Q} \equiv \mathbf{L}^{-1}\mathbf{S}$

today we will show formally the condition for the existence of **L**.



B,**D** have 3N – 6 rows, 3N columns $\rightarrow$ to be defined later

F	$3N-6 \times 3N-6$ (not the same as **f**	FORCE CONSTANT MATRIX 3N × 3N force constant matrix)
G	$3N-6 \times 3N-6$	"GEOMETRY" MATRIX to be defined later

TODAY:

* $\mathbf{G} \equiv \mathbf{DD}^{\dagger}$
* $0 = \det[\mathbf{F} - \lambda\mathbf{G}^{-1}]$ is condition for the existence of non-trivial **L**, λ's are eigenvalues of **FG** or **GF** and $\nu_k \equiv \lambda_k^{1/2}/2\pi$ are the normal mode frequencies

Later, show how to derive **S** $\rightarrow$ **D** $\rightarrow$ **G** in order to do actual calculations!

We want to separate $\widehat{\mathbf{H}}^{\text{VIBR}}$ into sum over independent oscillators.

$$\widehat{\mathbf{H}} = \sum_{i=1}^{3N-6} \hat{\mathbf{h}}_i(Q_i) \text{ where } Q_i \text{ is a "normal coordinate"}$$

to do this we must be able to write $\hat{T} + V$ in separable forms

$$2T = \sum_{i=1}^{3N-6} \dot{Q}_i^2 \qquad \left(T_i = \frac{1}{2} m_i v_i^2\right)$$

$$2V = \sum_{i=1}^{3N-6} \lambda_i Q_i^2 \qquad \text{truncated at harmonic terms} \quad \left(V_i = \frac{1}{2} k_i q_i^2\right)$$

If we can do this, then

$$\psi^0_{\underset{\sim}{V}} = \prod_{i=1}^{3N-6} \phi_{v_i}(Q_i) \qquad E^0_{\underset{\sim}{V}} = \sum_{i=1}^{3N-6} (v_i + 1/2) \underbrace{\frac{1}{2\pi}\lambda_i^{1/2}}_{\omega_i}$$

which is a complete set of zero-order functions with which we can solve the exact (full $V(\underset{\sim}{Q})$) vibrational problem.

<u>Some useful notation</u>

An arbitrary displacement vector $|q\rangle \equiv \begin{pmatrix} q_1 \\ \vdots \\ q_{3N} \end{pmatrix}$

$$\langle q| \equiv (|q\rangle)^{\dagger} = \begin{bmatrix} q_1^* & \ldots & q_{3N}^* \end{bmatrix} \qquad \text{q's are real}$$

A unit vector pointing in the i-th direction.

$$|i\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} \leftarrow \boxed{\text{i-th row}}$$

$$\langle i|q\rangle \equiv q_i$$ a number, the value of the i-th displacement coordinate in $|q\rangle$

A matrix element (an implicit double summation).

$$\text{e.g.} \qquad \langle S \,|\, F \,|\, S\rangle \equiv \sum_{i,j} S_i^* F_{ij} S_j \quad \text{a number}$$

PLAN OF ATTACK

1. assume we know **B** or **D** (derive it next time), this speciefies the $\boldsymbol{\xi} \to \mathbf{S}$ transformation
2. define **S** in terms of $\boldsymbol{\xi}$
3. define **F** by expressing **V** in terms of **S**
4. define **G** by expressing **T** in terms of $\dot{\mathbf{S}}$
5. obtain secular equation from $\mathcal{L} = T(\dot{\mathbf{S}}) - V(\mathbf{S})$

   and $0 = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{S}_i}\right) - \frac{\partial \mathcal{L}}{\partial S_i}$ Lagrange Equation of Motion
6. set up **GF** secular equation
7. solve for λ_i (eigenvalues) and **L** (eigenvectors)

<u>Mass Weighted</u> Cartesian displacement Coordinates

$$q_i = m_i^{1/2}\xi_i$$

$$|q\rangle = \mathbf{M}^{1/2}|\xi\rangle$$

$$\begin{pmatrix} q_1 \\ \vdots \\ q_{3N} \end{pmatrix} = \begin{pmatrix} m_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & m_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & m_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & m_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & m_N \end{pmatrix}^{1/2} \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_{3N} \end{pmatrix}$$

<u>Internal</u> (bond stretch, inter-bond angles, dihedral or torsional angles…) coordinates

$$|S\rangle \equiv \mathbf{B}|\xi\rangle \qquad \text{or} \qquad |S\rangle = \mathbf{D}|q\rangle$$

$$S_t = \langle t|S\rangle = \langle t|B|\xi\rangle = \sum_{i=1}^{3N} B_{ti}\xi_i$$

the t-th internal coordinate is expressed as a weighted sum of Cartesian displacements.

(if we displace all atoms by $\{\xi_i\}$, we can calculate all of the resulting internal coordinate displacements $\{S_t\}$)

Since there are only <u>3N–6</u> independent internal coordinates, **B** and **D** must be 3N–6 (columns) × 3N (rows) (non-square) matrices.

<u>Normal</u> coordinates

$$|S\rangle \equiv \mathbf{L}|Q\rangle \qquad \text{or} \qquad |Q\rangle = \mathbf{L}^{-1}|S\rangle$$

L is $3N - 6 \times 3N - 6$ square matrix

Potential Energy — natural to express in terms of internal coordinates.

power series expansion

$$V(S_1,\ldots S_{3N-6}) \equiv V(\{S\}) = V(\{0\}) + \sum_t \left(\frac{\partial V}{\partial S_t}\right)_0 S_t + \frac{1}{2}\sum_{t,t'} \left(\frac{\partial^2 V}{\partial S_t \partial S_{t'}}\right)_0 S_t S_{t'}$$ + **neglected** higher terms

* choose zero of energy at equilibrium: $\{S_e\} = \{0\}$ $V(\{0\}) \equiv 0$
* recognize that, at equilibrium (minimum of V)

$$\left(\frac{\partial V}{\partial S_t}\right)_0 = 0 \text{ for all t}$$ (all first derivatives are zero at equilibrium)

*so only the $\left(\frac{\partial^2 V}{\partial S_t \partial S_t'}\right)_0 \equiv F_{tt'}$ (second derivative) terms are retained. **F** is real and symmetric

$$V(\{S\}) = \frac{1}{2}\sum_{t,t'} F_{tt'} S_t S_{t'}$$

or, in matrix form

$$\boxed{V(\{S\}) = \frac{1}{2}\langle S|\mathbf{F}|S\rangle}$$

$$V(\{\xi\}) = \frac{1}{2}\langle \xi|\mathbf{B}^\dagger \mathbf{F}\mathbf{B}|\xi\rangle$$

how is this related to Bernath's mass weighted **f**?

what do we know about the signs of F_{tt}? $F_{tt'}$?

barrier?
saddle?

There is no problem about adding higher order terms to V({S}) later, after we have defined the normal mode basis set (but this is still Classical Mechanics).

Kinetic Energy — natural to express in terms of Cartesian displacement velocities and then to transform to other more useful coordinates.

$$2T = \langle \dot{\xi}|\mathbf{M}|\dot{\xi}\rangle \qquad T = \sum_i \frac{1}{2} m v_i^2$$

$$|\dot{\xi}\rangle = \mathbf{M}^{-1/2}|\dot{q}\rangle$$ (**M** is independent of time)

$$2T = \left\langle \dot{q}\left|(\mathbf{M}^{-1/2})^\dagger \mathbf{M}\mathbf{M}^{-1/2}\right|\dot{q}\right\rangle = \langle \dot{q}|\dot{q}\rangle = \sum_{i=1}^{3N-6} \dot{q}_i^* \dot{q}_i$$

$\dot{q}_i$ are real

$|\dot{q}\rangle = \mathbf{D}^{-1}|\dot{S}\rangle$ because **D** is independent of time and $\mathbf{D}|q\rangle = |S\rangle$

So $\quad 2\mathbf{T} = \langle \dot{q}|\dot{q}\rangle = \left\langle \dot{S}\left|(\mathbf{D}^{-1})^\dagger \mathbf{D}^{-1}\right|\dot{S}\right\rangle$

let $\mathbf{G}^{-1} \equiv (\mathbf{D}^{-1})^\dagger \mathbf{D}^{-1}$

$\boxed{2\mathbf{T} = \langle \dot{S} | \mathbf{G}^{-1} | \dot{S} \rangle}$ What would **T** be in $\dot{q}$ basis?

evidently **G** = **DD**† because $\mathbf{G}\mathbf{G}^{-1} = \mathbf{D}\mathbf{D}^{\dagger}(\mathbf{D}^{-1})^{\dagger}\mathbf{D}^{-1} = \mathbb{1}$ $\left[\mathbf{G} = (\mathbf{G}^{-1})^{-1} = ((\mathbf{D}^{-1})^{\dagger}\mathbf{D}^{-1})^{-1} = \mathbf{D}\mathbf{D}^{\dagger}\right]$

also $\mathbf{G}^{\dagger} = (\mathbf{D}\mathbf{D}^{\dagger})^{\dagger} = \mathbf{D}^{\dagger\dagger}\mathbf{D}^{\dagger} = \mathbf{D}\mathbf{D}^{\dagger} = \mathbf{G}$ so **G** must be real and symmetric

Now we are ready for secular equation.

$$\mathcal{L}\left(\{S\},\{\dot{S}\}\right) = T(\{\dot{S}\}) - V(\{S\})$$

Lagrange Equation of motion: $\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{S}_i}\right) = \frac{\partial \mathcal{L}}{\partial S_i}$ (like ma = F)

$2\mathbf{T} = \langle \dot{S} | \mathbf{G}^{-1} | \dot{S} \rangle = \sum_{i,j} (G^{-1})_{i,j}\dot{S}_i\dot{S}_j$ convenient for $\frac{\partial}{\partial \dot{S}_i}$

$2V = \langle S | \mathbf{F} | S \rangle = \sum_{i,j} F_{i,j}S_iS_j$ convenient for $\frac{\partial}{\partial S_i}$

$$\mathcal{L} = T - V = \frac{1}{2}\sum_{ij}\left[(G^{-1})_{ij}\dot{S}_i\dot{S}_j - F_{ij}S_iS_j\right]$$

$$0 = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{S}_i}\right) - \frac{\partial \mathcal{L}}{\partial S_i} = \frac{1}{2}\sum_{j}\left[(G^{-1})_{ij}\ddot{S}_j + F_{ij}S_j\right] \qquad \text{for } i = 1, 2, \ldots 3N\text{–}6$$

3N – 6 simultaneous coupled differential equations of the form $\ddot{x} = ax$ (harmonic oscillator)

> Amplitude for j–th displacement in normal mode of frequency $\lambda^{1/2}/2\pi$. Same λ for all 3N – 6 internal displacements $\{S_j\}$.

$$S_j = A_j \cos\left(\lambda^{1/2}t + \varepsilon\right) \qquad j = 1, 2, \ldots 3N - 6$$

try $\ddot{S}_j = -\lambda S_j$

(see whether 3N – 6 independent harmonic oscillations can yield 3N – 6 independent and non-trivial normal modes, Q_j)

plugging into RHS of equation of motion

$$0 = \frac{1}{2}\sum_{j=1}^{3N-6} S_j\left[-\lambda(G^{-1})_{ij} + F_{ij}\right] \qquad i = 1,2,\ldots 3N-6$$

$$0 = \frac{1}{2}\cos(\lambda^{1/2}t+\varepsilon)\sum_{j=1}^{3N-6} A_j\left[F_{ij} - \lambda G^{-1}_{ij}\right] \qquad i = 1,2,\ldots 3N-6$$

set of 3N–6 linear, homogeneous equations in 3N–6 unknowns (the A_j's). Nontrivial solution (A's ≠ 0) only when determinant of coefficients is = 0.

$0 = \det|\mathbf{F} - \lambda\mathbf{G}^{-1}|$

multiply thru by $|\mathbf{G}|$ on left $\qquad \det(\mathbf{AB}) = (\det \mathbf{A})(\det \mathbf{B})$

$0 = |\mathbf{GF} - \lambda\mathbb{1}|$

must diagonalize **GF** to get eigenvalues $\{\lambda_k\}$

$$\mathbf{L}^{-1}\mathbf{GFL} = \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \lambda_{3N-6} \end{pmatrix}$$

We diagonalize **GF** to obtain eigenvalues and eigenvectors that define **S**.

each internal displacement

$$S_j = A_{jk}\cos\left(\lambda_k^{1/2}t + \varepsilon_k\right)$$

all S's oscillate harmonically at same frequency and phase for k-th normal mode

amplitude in k-th normal mode (obtained from one of the 3N – 6 eigenvalues of **GF**).

obtained as one of the eigenvalues of **GF**.

$$\nu_k \equiv \frac{\lambda_k^{1/2}}{2\pi}$$

eigenvectors of transformation that diagonalizes **GF** give **L** (**L** is not the same thing as $\mathcal{L}$), which we use to obtain $|Q\rangle$.

$$|S\rangle = \mathbf{L}|Q\rangle$$

amplitude of the j-th internal coordinate displacement associated with the k-th eigenvalue of **GF**.

$$S_j = \sum_k N_k A_{jk} Q_k \equiv \sum_{k=1}^{3N-6} L_{jk} Q_k$$

j-th internal coordinate
k-th normal mode

normalization factor

how much of each normal displacement?

L defines the similarity transformation that diagonalizes **GF**

$$\mathbf{L}^{-1}\mathbf{GFL} = \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \lambda_{3N-6} \end{pmatrix}.$$

What properties must **L** have to put both **T** and **V** into separable forms?

Want $2T = \langle \dot{Q}|\dot{Q}\rangle = \sum_k \dot{Q}_k^2$ where $|\dot{Q}\rangle = \mathbf{L}^{-1}|\dot{S}\rangle$ $\left(|\dot{S}\rangle = \mathbf{L}|\dot{Q}\rangle\right)$

had $2T = \langle \dot{S}|\mathbf{G}^{-1}|\dot{S}\rangle = \langle \dot{Q}|\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{L}|\dot{Q}\rangle$

so $\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{L} = \mathbb{1}$ is required for **T** to be in separable form.

This is equivalent to $\boxed{\mathbf{L}^{\dagger}\mathbf{G}^{-1} = \mathbf{L}^{-1}}$

Want $2V = \langle Q|\mathbf{\Lambda}|Q\rangle = \sum \lambda_k Q_k^2$

had $2V = \langle S|\mathbf{F}|S\rangle = \langle Q|\mathbf{L}^{\dagger}\mathbf{FL}|Q\rangle$.

λ's are eigenvalues of **GF**.
F is real and symmetric but $\mathbf{L}^{\dagger} \neq \mathbf{L}^{-1}$ so $\mathbf{L}^{\dagger}\mathbf{FL}$ is not a similarity transformation.

This is equivalent to $\boxed{\mathbf{L}^{\dagger}\mathbf{FL} = \mathbf{\Lambda}}$ (this must be shown to be compatible with $\mathbf{L}^{\dagger}\mathbf{G}^{-1} = \mathbf{L}^{-1}$).

WANT $\mathbf{L}^{-1}\mathbf{G}\,\mathbf{FL} = \mathbf{\Lambda}$ (replace $\mathbf{L}^{-1}$ by $\mathbf{L}^{\dagger}\mathbf{G}^{-1}$)

$\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{GFL} = \mathbf{L}^{\dagger}\mathbf{FL} = \mathbf{\Lambda}$ SELF CONSISTENT!

[Caution: $\mathbf{L}^{-1}\mathbf{FGL} \neq \mathbf{\Lambda}$ even though eigenvalues of **FG** and **GF** are identical!] We have shown that the eigenvalues and eigenvectors of **GF** give $|S\rangle$ and that the relationship between $|S\rangle$ and $|Q\rangle$ is given by **L**, which diagonalizes **GF**: $\mathbf{L}^{-1}\mathbf{GFL} = \mathbf{\Lambda}$.