5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #26: Polyatomic Vibrations II: s-Vectors, G-matrix, and Eckart Condition

Last time: ξ, q, S, Q

$$\mathbf{Q} = \mathbf{L}^{-1}\,\mathbf{D}\underbrace{\mathbf{M}^{1/2}\xi}_{\mathbf{q}}$$
$$\underbrace{\qquad\qquad}_{\mathbf{S}}$$

$2T = \langle \dot{S}|G^{-1}|\dot{S}\rangle$ $\quad \mathbf{G}^{-1} \equiv (\mathbf{D}^{-1})^{\dagger}\mathbf{D}^{-1}$ $\quad$ (because $|\dot{q}\rangle = \mathbf{D}^{-1}|\dot{S}\rangle$ and $\mathbf{D}|q\rangle = |S\rangle$)

$2V = \langle S|F|S\rangle$ $\quad F_{ij} \equiv \left(\dfrac{\partial^2 V}{\partial S_i \partial S_j}\right)_0$

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

$$\frac{d}{dT}\left(\frac{\partial \mathcal{L}}{\partial \dot{S}_j}\right) - \frac{\partial \mathcal{L}}{\partial S_j} = 0 \Rightarrow \left|\mathbf{F} - \lambda \mathbf{G}^{-1}\right| = 0$$ ← secular equation

assuming that $S_j(t) = A_j \cos(\lambda^{1/2} t + \varepsilon)$ all j = 1, 2, … 3N–6

i.e. that all internal coordinates oscillate at *same* frequency and relative phase (but with different amplitudes)

$$\nu = \frac{\lambda^{1/2}}{2\pi}$$

3N–6 possible different values of λ obtained from (3N – 6) × (3N – 6) secular equation.

TODAY: Finish discussion of * secular equation
* forms of various transformations
* descriptions of each normal coordinate

$\underset{\sim}{\mathbf{s}}$-Vectors
* definition and properties
* imposition of translational and rotational constraints
* derivation of **G** from $\underset{\sim}{\mathbf{s}}$-Vectors

NEXT TIME - SOME EXAMPLES OF $\underset{\sim}{\mathbf{s}}$-VECTOR CALCULATIONS

Last time, we derived $0 = |\mathbf{F} - \lambda\mathbf{G}^{-1}|$

left multiply by $|\mathbf{G}|$

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

must diagonalize **GF** to get 3N – 6 eigenvalues $\{\lambda_k\}$

Similarity (not unitary) transformation

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

(Although **G** and **F** are both <u>real</u> and <u>symmetric</u>, **GF** is not symmetric, so the diagonalizing transformation is not unitary: $\mathbf{L}^{-1} \neq \mathbf{L}^{\dagger}$)

For example, the product of two real and symmetric matrices

$$\begin{pmatrix} a & b \\ b & -a \end{pmatrix}\begin{pmatrix} c & d \\ d & -c \end{pmatrix}\begin{pmatrix} ac+bd & ad-bc \\ bc-ad & bd+ac \end{pmatrix}$$

is a matrix that is not symmetric.

What do we already know about **L** from prior requirements that **T** and **V** must be put into separable forms?

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

We had, previously
$$2\mathbf{T} = \langle \dot{q}|\dot{q}\rangle = \langle \dot{S}|(\mathbf{D}^{-1})^{\dagger}\mathbf{D}^{-1}|\dot{S}\rangle = \langle \dot{S}|\mathbf{G}^{-1}|\dot{S}\rangle \qquad \left[\mathbf{G}^{-1} \equiv (\mathbf{D}^{-1})^{\dagger}\mathbf{D}^{-1}\right]$$
$$= \langle \dot{Q}|\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{L}|\dot{Q}\rangle$$

So $\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{L} = \mathbb{1}$ is required
thus $\boxed{\mathbf{L}^{-1} = \mathbf{L}^{\dagger}\mathbf{G}^{-1}}$ is needed to keep **T** in separable form.

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

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

So $\boxed{\mathbf{L}^{\dagger}\mathbf{F}\mathbf{L} = \mathbf{\Lambda}}$ is required to keep **V** in separable form.
(**L** is not unitary, we already know that $\mathbf{L}^{-1} = \mathbf{L}^{\dagger}\mathbf{G}^{-1} \neq \mathbf{L}^{\dagger}$, so
* the λ's are not eigenvalues of **F**
* $\mathbf{L}^{\dagger}\mathbf{F}\mathbf{L}$ is not a similarity transformation)

putting it all together — the secular equation requires

$\mathbf{L}^{-1}\mathbf{GFL} = \mathbf{\Lambda}$ (The λ_i are eigenvalues of **GF**, not of **F**)
↓ (multiply on left by $\mathbf{L}^{-1} = \mathbf{L}^{\dagger}\mathbf{G}^{-1}$)
$\mathbf{L}^{\dagger}\mathbf{G}^{-1}\mathbf{GFL} = \mathbf{\Lambda}$
$\mathbf{L}^{\dagger}\mathbf{FL} = \mathbf{\Lambda}$ is self-consistent

Now we are ready to ask
* where do we get **G**?
* can we determine **F** from spectrum?
* how do we define 3N–6 independent internal coordinates subject to the two constraints of:
  NO center of mass translation
  NO Rotation about center of mass?

F-matrix $(3N–6) \times (3N–6)$ symmetric

these are $\left[\frac{(3N-6)\times(3N-7)}{2 \leftarrow \text{symmetric}}\right]$ linearly independent off-diagonal elements

3N – 6 diagonal elements

$\frac{(3N–6) \times (3N–5)}{2}$ independent elements

	# elements	# modes
N = 3	6	3
4	21	6
5	45	9
6	78	12

Too many, even for isotopes!

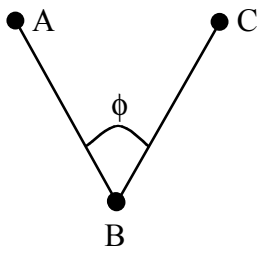
Must use tricks (group theory), insight (set non-adjacent F's = 0), *ab initio* calculations, borrowing from similar groups in other molecules, and isotopic substitution to determine a complete set of F_{ij}'s, even at only the harmonic (quadratic) level!

Imagine how many cubic and quartic force constants might be needed!

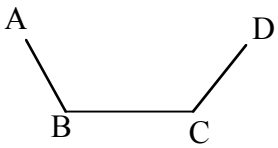
Internal Coordinates

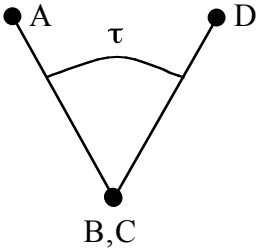
Stretch Δr_{AB}

Bend $\Delta\phi_{ABC}$



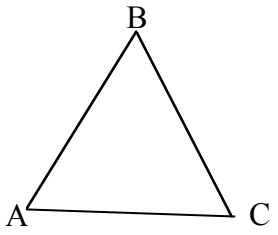
Torsion (dihedral angle τ)





angle between ABC and BCD planes

* how to select 3N–6 independent internal coordinates



e.g. can't have Δr_{AB}, $\Delta\phi_{ABC}$
Δr_{BC}, $\Delta\phi_{BCA}$
Δr_{CA}, $\Delta\phi_{CAB}$

how to limit to only 3 S's?

group theory (projection operators) will be helpful.

Actually no problem if we define **F** and **G** matrices that have extra rows and columns. Get normal modes with zero frequency.

* How to impose constraints?

no center of mass translation
no rotation about center of mass
} algebraic and trigonometric nightmare?

turns out that all cases have been worked out and tabulated — imposing these constraints is an essential part of the process of generating the **G** matrix!

G-matrix – elements are tabulated in Wilson, Decius, and Cross pages 303-306 in concise but obscure notation and diagrams.

Derived by "**s**-vector method"

$$S_t = \sum_{\substack{\alpha \\ \text{atoms}}} \underset{\sim}{S}_{t\alpha} \bullet \vec{\rho}_\alpha$$

$\vec{\rho}_\alpha$ specifies an arbitrary translation of atom α (not mass-weighted)

$$G_{tt'} = \sum_\alpha \frac{1}{m_\alpha} \underset{\sim}{S}_{t\alpha} \bullet \underset{\sim}{S}_{t'\alpha}$$

(to be derived later in this lecture)

$\underset{\sim}{\mathbf{s}}$-vectors

recall $|s\rangle \equiv \mathbf{B}|\xi\rangle$ $\qquad S_t = \sum_i B_{ti}\xi_i$

power series expansion of S for small displacements from equilibrium — retain only leading term

$$S_t = \sum_i \left(\frac{\partial S_t}{\partial \xi_i}\right)_0 \xi_i$$ plus neglected higher terms

$\left(\frac{\partial S_t}{\partial \xi_i}\right)_0 = B_{ti}$

now rewrite S_t as sum over atoms rather than over individual ξ_i.

$$S_t = \sum_{\alpha=1}^{N} \left[\left(\frac{\partial S_t}{\partial \xi_x^\alpha}\right)_0 \xi_x^\alpha + \left(\frac{\partial S_t}{\partial \xi_y^\alpha}\right)_0 \xi_y^\alpha + \left(\frac{\partial S_t}{\partial \xi_z^\alpha}\right)_0 \xi_z^\alpha \right]$$

but we should recognize that this is expressed compactly in terms of the gradient of **S**.

$$S_t = \sum_{\alpha=1}^{N} \left(\underset{\sim}{\nabla}_\alpha S_t\right) \cdot \vec{\rho}_\alpha$$

Arbitrary displacement of atom α

$$\nabla_\alpha S_t = \frac{\partial S_t}{\partial \xi_x^\alpha}\hat{x} + \frac{\partial S_t}{\partial \xi_y^\alpha}\hat{y} + \frac{\partial S_t}{\partial \xi_z^\alpha}\hat{z}$$

$$\vec{\rho}_\alpha = \xi_x^\alpha \hat{x} + \xi_y^\alpha \hat{y} + \xi_z^\alpha \hat{z}$$

Note that choice of $\vec{\rho}_\alpha$ parallel to $\underset{\sim}{\nabla}_\alpha S_t$ gives largest change in S_t.

$\left(\underset{\sim}{\nabla}_\alpha S_t\right) \equiv \underset{\sim}{\mathbf{s}}_{t\alpha}$

Thus $\underset{\sim}{\mathbf{s}}_{t\alpha}$ is vector pointing in the direction in which a displacement of atom α gives the LARGEST increase in S_t.

$\left|\underset{\sim}{s}_{t\alpha}\right| = s_{t\alpha}$

The actual increase in S_t that results from UNIT DISPLACEMENT of atom α in direction that increases S_t most rapidly.

These $\underset{\sim}{\mathbf{s}}$ vectors are derivable by vector analysis for all conceivable topological situations and are tabulated by WILSON, DECIUS, AND CROSS pages 55-61.

This will tell us how to build in translation and rotation constraints!

$$S_t \equiv \sum_\alpha \underset{\sim}{s}_{t\alpha} \cdot \vec{\rho}_\alpha$$

1. Rigid translation of molecule prohibited by ensuring that rigid translation (all $\vec{\rho}_1 = \vec{\rho}_2 = \ldots \vec{\rho}_N = \vec{\varepsilon}$) has zero projection on each S_t.

want $0 = S_t = \sum_\alpha \underset{\sim}{s}_{t\alpha} \cdot \vec{\rho}_\alpha = \vec{\varepsilon} \cdot \sum_\alpha \underset{\sim}{s}_{t\alpha}$

satisfied if $\boxed{\sum_\alpha \underset{\sim}{s}_{t\alpha} = 0}$ 3 constraints, one each for x, y, and z.

2. Rotation prohibited? A much more difficult problem.

How do we define a body fixed coordinate system if the atoms are not a rigid framework? This question is at the heart of the distinction between vibration and rotation.

We must specify how the body fixed coordinate system is defined at all times, based on the observable instantaneous positions of all atoms in a laboratory fixed coordinate system with its origin at the center of mass.

We have several choices of how to do this. A key criterion is avoiding large, high frequency angular accelerations in the lab frame (centrifugal and Coriolis fictitious forces in the BODY frame).

One way is to insist that the body frame is the instantaneous inertial axis system (inertial tensor is kept diagonal). This is bad because this frame would wobble at vibrational frequencies. Enormous fictitious forces! Strong vibration-rotation couplings. [If $\underset{\sim}{I}$ is instantaneously non-diagonal, terms of the form $J_\alpha I^{-1}_{\alpha\beta} J_\beta$ might average to zero over a vibrational period (no effect on $\mathbf{H}^{ROT}$) but could still cause nonzero matrix elements between vibrational states.]

The ECKART condition minimizes "vibrational angular momentum" (except for degenerate vibrations).

$$\sum_{\alpha=1}^{N} \vec{R}^e_\alpha \times \underset{\sim}{s}_{t\alpha} = 0$$

ECKART CONDITION
(3 components of vector equation — 3 more constraints)

$\vec{R}^e_\alpha$ is the equilibrium coordinate of atom α in the LAB-FIXED coordinate system with origin at the center of mass.

This is designed to minimize rigid body rotation. Let's see how.

A rigid body rotation by $d\vec{\Omega}$

$$\vec{\rho}_\alpha (d\vec{\Omega}) = \vec{R}_\alpha \times d\vec{\Omega}$$

$\vec{R}_\alpha$ is location of atom α (before applying $d\vec{\Omega}$)

How does this project onto S_t?

$$0 \stackrel{?}{=} S_t\left(d\vec{\Omega}\right) = \sum_\alpha \underset{\sim}{s}_{t\alpha} \cdot \left(\vec{R}_\alpha \times d\vec{\Omega}\right)$$

$$= \sum_\alpha \left(\underset{\sim}{s}_{t\alpha} \times \vec{R}_\alpha\right) \cdot d\vec{\Omega}$$

uses rule for vector triple product

$$= d\vec{\Omega} \cdot \underbrace{\sum_\alpha \underset{\sim}{s}_{t\alpha} \times \vec{R}_\alpha}_{=0 \text{ if } \vec{R}_\alpha \approx \vec{R}_\alpha^e \text{ by Eckart condition}}$$

so, for small displacements from equilibrium, the Eckart condition ensures that $d\vec{\Omega}$ has zero projection onto all internal coordinates. An approximation. Bad for floppy molecules. See WILSON, DECIUS, AND CROSS, pages 273-277.

Six constraints:

$$\sum_{\alpha=1}^{N} \underset{\sim}{s}_{t\alpha} = 0$$

$$\sum_{\alpha=1}^{N} \vec{R}_\alpha^e \times \underset{\sim}{s}_{t\alpha} = 0$$

We still have not derived the $\underset{\sim}{s}_{t\alpha}$'s! Before doing that, let's show how **G** is related to the $\underset{\sim}{s}_{t\alpha}$'s.

$$G \equiv BM^{-1}B^\dagger = DD^\dagger$$

$$G_{tt'} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ti} B^*_{t'i} = \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \underset{\sim}{S}_{t\alpha} \cdot \underset{\sim}{S}_{t'\alpha}$$

$B_{ti} = \left(\frac{\partial S_t}{\partial \xi_i}\right)_0$, $B^*_{t'i} = \left(\frac{\partial S_{t'}}{\partial \xi_i}\right)_0$

$$\underset{\sim}{s}_{t\alpha} = \nabla^e_\alpha S_t = \frac{\partial S_t}{\partial \xi^\alpha_x}\hat{x} + \frac{\partial S_t}{\partial \xi^\alpha_y}\hat{y} + \frac{\partial S_t}{\partial \xi^\alpha_z}\hat{z}$$

This definition of $G_{tt'}$ is convenient because

* depends on locally defined $\underset{\sim}{s}_{t\alpha}$ — easy to derive from the $\underset{\sim}{s}_{t\alpha}$ defined with respect to bond directions and angles;
* each S_t involves motions of a small number of involved atoms.
* There are a limited number of topological cases for internal displacements. They have all been analyzed. Wilson, Decius, and Cross, pages 303-306.