

# Vibration frequencies and force constants of water molecule -classical treatment

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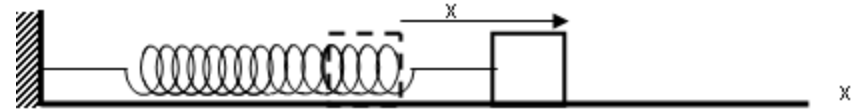
Suchi's Lab Group, 12/01/2009 (?)

References:

1. Wilson, Decius, and Cross, "Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra," McGraw Hill, NY (1955).
2. Cotton, "Chemical Applications of Group Theory," 3<sup>rd</sup> edition, John Wiley & Sons, NY (1990).
3. Landau and Lifshitz, "Quantum Mechanics : Non-relativistic Theory," Addison-Wesley , NY (1958).

# Classical Mechanics Background

- **Simple Harmonic Oscillator**



Kinetic energy,  $T = \frac{1}{2} m (dx/dt)^2$ ; Potential energy,  $V = \frac{1}{2} k x^2$ .

Equation of motion:  $m d^2x/dt^2 + k x = 0$ . (1)

Harmonic solution:  $x(t) = A e^{i\omega t}$  with  $A$  and  $\omega$  unknown. Plug into 1.

$$m(\omega^2 - k/m) A e^{i\omega t} = 0.$$

Either  $A = 0$  or  $\omega^2 - k/m = 0$ .

Since  $A \neq 0$ , we must have  $\omega = \sqrt{k/m}$ .

>>> So, if you know  $\omega$ , you can learn about force constant  $k$  and vice-versa.

>>> Frequency  $\omega$  for a molecular system is normally found by IR and/or Raman vibrational spectrum.

# Mass-weighted Cartesian Coordinates

## {q}

- Simple Harmonic Oscillator Revisited

Let  $q = x\sqrt{m}$  and let over dot represent d/dt.

Kinetic energy:  $T = \frac{1}{2}\dot{q}^2$ , often written as  $2T = \dot{q}^2$ .

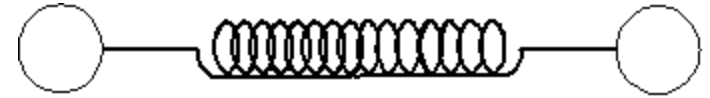
Potential energy:  $2V = \frac{k}{m}q^2$

Equation of motion:  $\ddot{q} + \frac{k}{m}q = 0$

>>> The angular frequency of oscillation:

$$\omega = \sqrt{\frac{k}{m}}$$

# Frequency of oscillation of a diatomic molecule (1)



Kinetic energy =  $\frac{1}{2} m_1 (dx_1/dt)^2 + \frac{1}{2} m_2 (dx_2/dt)^2$ ;

Potential energy =  $\frac{1}{2} k (x_1 - x_2)^2$ .

Equations of motion:

$$m_1 \frac{d^2 x_1}{dt^2} + k (x_1 - x_2) = 0. \quad (1a)$$

$$m_2 \frac{d^2 x_2}{dt^2} - k (x_1 - x_2) = 0. \quad (1b)$$

Seek harmonic solution:

$x_1(t) = A_1 e^{i\omega t}$ ,  $x_2(t) = A_2 e^{i\omega t}$ . Plug into (1).

• Simultaneous equations for  $A_1$  and  $A_2$ .

$$(-m_1 \omega^2 + k) A_1 - k A_2 = 0$$

$$-k A_1 + (-m_2 \omega^2 + k) A_2 = 0$$

# Diatomic molecule (2)



Write in matrix form:

$$\begin{bmatrix} (-m_1 \omega^2 + k) & -k \\ -k & (-m_2 \omega^2 + k) \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0$$

For nontrivial solution, the determinant of matrix must be

zero  $\rightarrow \omega^2 [m_1 m_2 \omega^2 - k (m_1 + m_2)] = 0$  [Secular Equation]

Two solutions for  $\omega$  :

$$\omega = 0 \quad [\text{Translation}] \quad [A_1 = A_2] \quad (2)$$

$$\text{and } \omega = \sqrt{k/\mu} \quad [\text{Vibration}] \quad [m_2 A_2 = m_1 A_1] \quad (3)$$

where  $\mu = m_1 m_2 / (m_1 + m_2)$ , the reduced mass.

# Small vibrations in Classical Mech

## General Treatment (slide 1)

Let us use mass-weighted coordinates  $\{q_1, q_2, q_3, \dots, q_{3N}\}$ .

Kinetic energy:  $2T = \sum_{i=1}^{3N} \dot{q}_i^2$

Potential energy:  $2V = \sum_{i=1}^{3N} \sum_{j=1}^{3N} f_{ij} q_i q_j$

Equations of motion:  $\ddot{q}_i + \sum_{j=1}^{3N} f_{ij} q_j = 0 \quad (i=1, \dots, 3N)$

Harmonic solutions:  $q_i = A_i e^{-i\omega t} \quad (i=1, \dots, 3N; \quad A_i \text{ complex})$

Simultaneous equations:  $\sum_{j=1}^{3N} (f_{ij} - \omega^2 \delta_{ij}) A_j = 0 \quad (i=1, \dots, 3N)$

- Gives normal modes of vibration, translation and rotation

# Small vibrations (slide 2)

- Simultaneous equations for Amplitudes  $\{A_i\}$

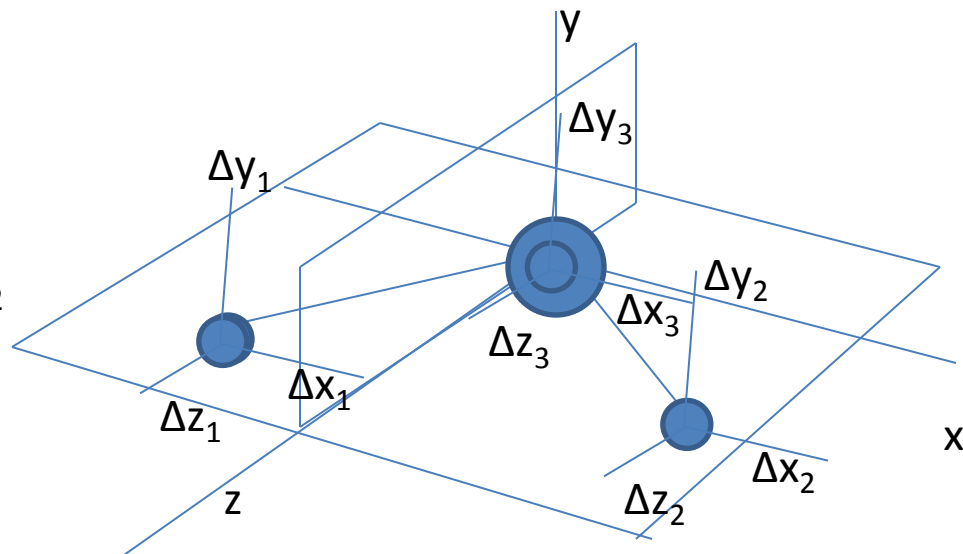
$$\sum_{j=1}^{3N} (f_{ij} - \omega^2 \delta_{ij}) A_j = 0 \quad (i=1, \dots, 3N)$$

- Eigenvalue/Eigenvector problem
- $3N$  eigenvalues are normal mode frequencies, 3 of which correspond to translation and 3 or 2 to rotation:  $\omega_k$  ( $k=1, 2, \dots, 3N$ ).
- $3N$  eigenvectors  $Q_k$  corresponds to the normal coordinates expressed in terms of the  $\{q\}$  coordinates:  $Q_k = \text{Sum}[A_{ik} q_i, i=1, \dots, 3N]$  if properly normalized.
- $2T = \sum (dQ_k/dt)^2$  and  $2V = \sum [\omega_k^2 Q_k^2]$ .  
 >>> Every problem turns into sum of simple harmonic oscillations for each normal mode. Quantum states labeled with occupation number  $n_k$  of each mode  $\omega_k$  and energies are simply  $(n_k + 1/2) \hbar \omega_k$ .

**\*Solution of more complicated molecules immensely helped by an application of the. Group Theory We will do H<sub>2</sub>O next.**

# Symmetry of H<sub>2</sub>O

- Place molecule in xz-plane.
- Four symmetry operations
  - Do nothing: E
  - Rotate 180° about z-axis: C<sub>2</sub>
  - Reflect in xz-plane: σ<sub>v</sub>(xz)
  - Reflect in yz-plane: σ<sub>v</sub>(yz)



- The character table: Four 1-dimensional irreps A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>.

C <sub>2v</sub>	E	C <sub>2</sub>	σ <sub>v</sub> (xz)	σ <sub>v</sub> (yz)	Basis
A <sub>1</sub>	1	1	1	1	z
A <sub>2</sub>	1	1	-1	-1	R <sub>z</sub>
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>
B <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>

A and B reps distinguished by action of C<sub>2</sub>

# Full Representation in the basis of the nine Cartesian displacements

(Read:  $\Delta X_1$  for X1, etc.)

Displacement	E	C2	$\sigma(xz)$	$\sigma(yz)$
X1	X1	-X2	X1	-X2
Y1	Y1	-Y2	-Y1	Y2
Z1	Z1	Z2	Z1	Z2
X2	X2	-X1	X2	-X1
Y2	Y2	-Y1	-Y2	Y1
Z2	Z2	Z1	Z2	Z1
X3	X3	-X3	X3	-X3
Y3	Y3	-Y3	-Y3	Y3
Z3	Z3	Z3	Z3	Z3
Characters	9	-1	3	1

# Reducing full rep into irreps

- By inspection or by using Great Orthogonality theorem:

$$\Gamma = 3 A_1 + A_2 + 3 B_1 + 2 B_2$$

- Look into the table to identify translation and rotation from the list.
  - Translation basis are x, y, z: B1, B2, A1
  - Rotation basis are Rx, Ry, Rz: B2, B1, A2
- The remainder reps in  $\Gamma$  are purely vibs:

$$\Gamma_{\text{vib}} = 2 A_1 + B_1.$$

# Build basis for $A_1$ and $B_1$ from internal coordinates

- How do displacements  $\Delta\phi$ ,  $\Delta r_{31}$ , and  $\Delta r_{32}$  transform under operations of the group of  $H_2O$ ?

	E	C2	$\sigma(xz)$	$\sigma(yz)$
$\Delta\phi$	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$
$\Delta r_{31}$	$\Delta r_{31}$	$\Delta r_{32}$	$\Delta r_{31}$	$\Delta r_{32}$
$\Delta r_{32}$	$\Delta r_{32}$	$\Delta r_{31}$	$\Delta r_{32}$	$\Delta r_{31}$

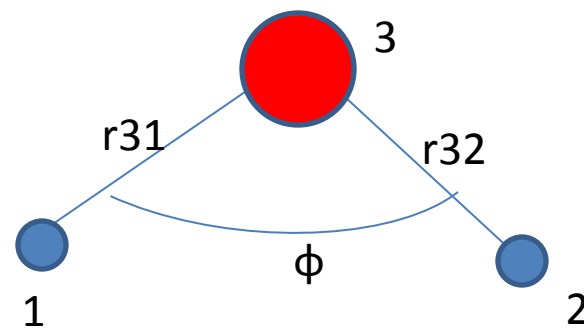
$\Delta\phi$  transforms as  $A_1$ .

$\Delta r_{31}$  and  $\Delta r_{32}$  go into each other

- they are not basis for  $C_{2v}$

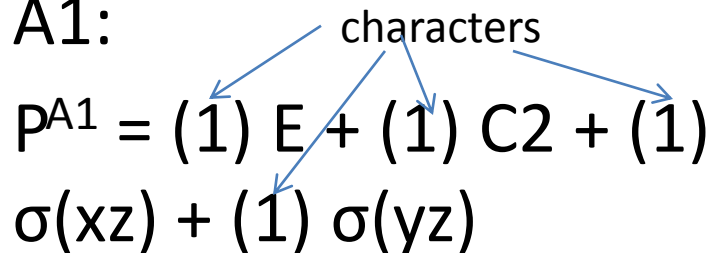
- use projection operator method

- Internal coordinates



# Projection operators for A1 and B1

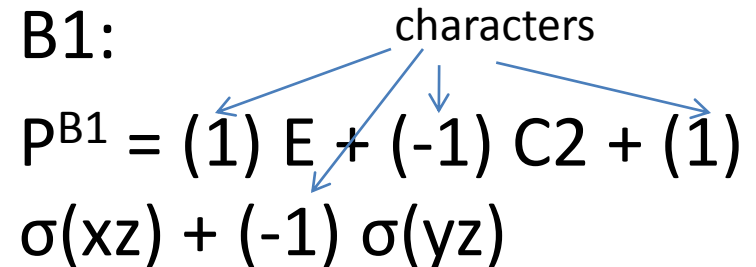
- Projection operator for A1:


$$P^{A1} = (1) E + (1) C2 + (1) \sigma(xz) + (1) \sigma(yz)$$

- Act on  $r_{13}$ .
- The result up to a constant:

$$P^{A1} r_{31} \rightarrow (r_{31} + r_{32})$$

- Projection operator for B1:


$$P^{B1} = (1) E + (-1) C2 + (1) \sigma(xz) + (-1) \sigma(yz)$$

- Act on  $r_{13}$ .
- The result up to a constant:

$$P^{B1} r_{31} \rightarrow (r_{31} - r_{32})$$

# Symmetry coordinates and internal coordinates

## Internal coordinates

$$\mathbf{s} = \{ s_1 = r_{31}, s_2 = r_{32}, s_3 = \phi \}$$

## Symmetry coordinates

$$\mathbf{S} = \{ S_1 = \phi, \\ S_2 = (1/\sqrt{2}) [r_{31} + r_{32}], \\ S_3 = (1/\sqrt{2}) [r_{31} - r_{32}] \}$$

## Transformation between coordinates

$$\mathbf{S} = \mathbf{U} \mathbf{s} \quad \leftrightarrow \quad \mathbf{s} = \mathbf{U}^{-1} \mathbf{S}$$

$$\mathbf{U} = \begin{bmatrix} 0 & 0 & 1 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \end{bmatrix}$$

$$\mathbf{U}^{-1} = \begin{bmatrix} 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 1 & 0 & 0 \end{bmatrix}$$

# Potpourri of Coordinates

1. Cartesian:  $\{X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3\}$   
Good for generating the full representation
2. Mass-weighted Cartesian coordinates:  $\{q_1, q_2, q_3, q_4, q_5, q_6, q_7, q_8, q_9\}$   
Good for simplifying equations
3. Normal Coordinates  $\{Q_1, Q_2, Q_3, Q_4, Q_5, Q_6, Q_7, Q_8, Q_9\}$   
Good for quantizing
4. Internal :  $\mathbf{s} \{s_1 = r_{31}, s_2 = r_{32}, s_3 = \phi\}$   
Good for writing potential energy
5. Symmetry coordinates:  $\mathbf{S} \{S_1, S_2, S_3\}$   
Good for implementing simplification in calculations arising as a result of point group symmetry

# Potential energy in internal coordinates (f matrix)

- Potential energy most directly written using the internal coordinates  $\{s\}$ .
- $2V = \sum_{(ab)} f_{ab} s_a s_b$  ( $\leftrightarrow$  linear restoring force)
- Here  $f_{ab}$  are nine force constants or “spring constants”.
- Why nine?
  - Change in one, say  $\phi$ , can cause change in others, namely  $r_{31}$  and  $r_{32}$ .
  - Use symmetry here to reduce number of unique components of  $f_{ab}$ .

# f matrix for H<sub>2</sub>O

## Only 4 unique force constants

- $f = \begin{bmatrix} f_1 & f_3 & f_4 \\ f_3 & f_1 & f_4 \\ f_4 & f_4 & f_2 \end{bmatrix}$

- Here:

$f_1$  = force constant for O-H stretch

$f_2$  = force constant for H-O-H bend

$f_3$  = force constant between two stretches

$f_4$  = force constant between a stretch and the bend.

- How can we determine force constants from experiment?

Ans: the same way you determine force constant dynamically for a simple harmonic oscillator. Which is?

# Potential energy in symmetry coordinates $\{\mathbf{S}\}$

- Using  $\mathbf{s} = \mathbf{U}^{-1} \mathbf{S}$  to write the potential energy

$$\begin{aligned} \text{as } 2V &= \sum_{(ab)} f_{ab} s_a s_b \\ &= \sum_{(ab)} F_{ab} S_a S_b \end{aligned}$$

$$\text{where } F = \mathbf{U} \mathbf{f} \mathbf{U}^{-1} = \begin{bmatrix} f_2 & f_4 \sqrt{2} & 0 \\ f_4 \sqrt{2} & f_1 + f_3 & 0 \\ 0 & 0 & f_1 - f_3 \end{bmatrix}$$

# Kinetic energy (slide 1)

- Kinetic energy in mass-weighted coordinates  $\{q\}$ : 
$$2T = \begin{bmatrix} \dot{q}_1 \\ \vdots \\ \dot{q}_n \end{bmatrix}^T \begin{bmatrix} 1 & & \\ & \dots & \\ & & 1 \end{bmatrix} \begin{bmatrix} \dot{q}_1 \\ \vdots \\ \dot{q}_n \end{bmatrix} = \dot{q}_1^2 + \dots + \dot{q}_n^2$$
- In terms of momenta  $\{p\}$ :  $2T = \dot{p}_1^2 + \dots + \dot{p}_n^2$  ( $p_i = \partial T / \partial \dot{q}_i$ )
- Compact notation:  $2T = p^T p$  (1)

- Let  $\{s\}$  stand for internal coordinates. Recall that they are built out of  $\{q\}$  linearly.

$$s = Dq \quad (\text{compact notation})$$

- Coordinates and conjugate momenta:

<i>Coords</i>	$\leftrightarrow$	<i>Momenta</i>
$q$	$\leftrightarrow$	$p$
$s$	$\leftrightarrow$	$P$
$S$	$\leftrightarrow$	$\Pi$

# Kinetic energy (slide 1)

- Momenta  $\{p\}$  in terms of momenta  $\{P\}$  for internal coordinates:

$$p_a = \frac{\partial T}{\partial \dot{q}_a} = \sum_{\alpha} \frac{\partial T}{\partial \dot{s}_{\alpha}} \frac{\partial \dot{s}_{\alpha}}{\partial \dot{q}_a} = \sum_{\alpha} P_{\alpha} D_{\alpha a} \Rightarrow p^T = P^T D \text{ (compact)}$$

- Use in Eq. (1)
- Kinetic energy in terms of internal coords

$$2T = P^T (DD^T) P \equiv P^T (g) P$$

- Wilson's  $g$  matrix:  $g = DD^T$

# Kinetic Energy (slide 2)

- The symmetry coords  $\{S\}$  are related to internal coords  $\{s\}$  by linear trf:  $S = U s$
- Kinetic energy in terms of symmetry coords

$$p_a = \frac{\partial T}{\partial \dot{q}_a} = \sum_{\alpha} \sum_{\beta} \frac{\partial T}{\partial \dot{S}_{\alpha}} \frac{\partial \dot{S}_{\alpha}}{\partial \dot{s}_{\beta}} \frac{\partial \dot{s}_{\beta}}{\partial \dot{q}_a} = \sum_{\alpha} \Pi_{\alpha} U_{\alpha\beta} D_{\beta a} \Rightarrow p^T = \Pi^T U D \text{ (compact)}$$

$$2T = \Pi^T (U D D^T U^T) \Pi = \Pi^T (U g U^{-1}) \Pi \equiv \Pi^T G \Pi$$

- Wilson's G matrix:  $G = U g U^{-1}$

# Secular equation in symmetry coordinates (slide 1)

- Recall secular equations

- Simple Harmonic Oscillator

$$m\omega^2 - k = 0 \Rightarrow \omega^2 - m^{-1}k = 0$$

- Diatomic molecule – vibration part

$$\frac{m_1 m_2}{m_1 + m_2} \omega^2 - k = 0 \Rightarrow \omega^2 - \mu^{-1}k = 0 \quad (\text{for internal coordinate } x_1 - x_2)$$

- More general:  $2T = P^T g P$  and  $2V = s^T f s$  giving secular equation:

$$\det \left\| \omega^2 I - g^{-1} f \right\| = 0$$

- where  $I$  is identity matrix,  $f$  is the f-matrix consisting of force constants and  $g$  is the g-matrix consisting of inverse masses:

$$f_{ab} = \frac{\partial^2 V}{\partial s_a \partial s_b}, \quad (g)^{-1}_{ab} = \frac{\partial^2 T}{\partial \dot{s}_a \partial \dot{s}_b}$$

based on internal coordinates  $\{x_a\}$ .

# Secular Equation in symmetry coordinates (slide 2)

- Internal coordinates:

$$\det \left\| \omega^2 I - g f \right\| = 0$$

- Symmetry coordinates:

$$\det \left\| \omega^2 I - GF \right\| = 0$$

# Wilson's g matrix for H<sub>2</sub>O

## [internal coords]

- Not block diagonal in these coords
- Tables of g-matrix for commonly encountered atomic arrangements ( $m = m_{\text{H}}$ ,  $M = m_{\text{O}}$ ).

$$g = \begin{bmatrix} \frac{1}{m} + \frac{1}{M} & \frac{\cos \phi}{M} & -\frac{\sin \phi}{Mr_2^2} \\ \frac{\cos \phi}{M} & \frac{1}{m} + \frac{1}{M} & -\frac{\sin \phi}{Mr_1^2} \\ -\frac{\sin \phi}{Mr_2^2} & -\frac{\sin \phi}{Mr_1^2} & \frac{1}{mr_1^2} + \frac{1}{mr_2^2} + \frac{1}{M} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} - \frac{2 \cos \phi}{r_1 r_2} \right) \end{bmatrix}$$

# Wilson's G matrix for H<sub>2</sub>O

[symmetry coords] – Note Block Diagonal Form

$$\bullet \quad G = U g U^{-1} = \begin{bmatrix} 2 \left\{ \frac{\mu_H + \mu_O (-\cos \phi)}{r^2} \right\} & -\frac{\sqrt{2} \mu_O \sin \phi}{r} & 0 \\ -\frac{\sqrt{2} \mu_O \sin \phi}{r} & \mu_H + \mu_O (+\cos \phi) & 0 \\ 0 & 0 & \mu_H + \mu_O (-\cos \phi) \end{bmatrix}$$

$$= \begin{bmatrix} 2.33 & -0.09 & 0 \\ -0.09 & 1.04 & 0 \\ 0 & 0 & 1.07 \end{bmatrix}$$

Here:

$\mu_H = 1/m_H$ ;  $\mu_O = 1/m_O$ ;  
 $r = \text{equilib. bond length.}$

# Force constants and frequencies

- Use secular equation  $\det[\omega^2 I - GF]=0$  (block-diagonal).
- $A_1$ : Given freq solve for force constants:

$$\text{Det} \begin{bmatrix} 2.33f_2 - 0.13f_4 - \omega^2 & -0.09f_2 + 1.47f_4 \\ -0.09(f_1 + f_3) + 3.30f_4 & 1.04(f_1 + f_3) - 0.13f_4 - \omega^2 \end{bmatrix} = 0.$$

- $B_1$ :  $1.07(f_1 - f_3) = \omega^2$ .
- Three equations and seven unknowns:  $f_1, f_2, f_3, f_4, \omega_1, \omega_2$  and  $\omega_3$ .
- Additional experimental inputs, such as change in frequencies for different isotopes with presumably same force constant often gives information to solve for the force constants and/or frequencies.

NEXT PRESENTATION: QUANTUM MECHANICAL TREATMENT OF VIBRATION