

5.04, Principles of Inorganic Chemistry II
 MIT Department of Chemistry
Lecture 33: Normal Coordinate Analysis

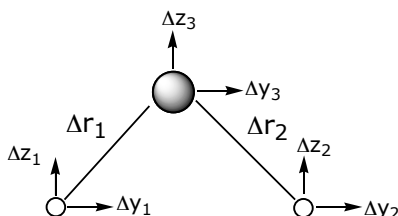
Normal coordinates are obtained from the solution of the eigenvalue problem,

$$|\underline{G} \underline{F} - \underline{E} \lambda| = 0 \quad \leftarrow \text{solution of Schrödinger's equation in terms of internal coordinates}$$

(T \leftarrow) geometry \swarrow
 force constant (\rightarrow V) \searrow

where \underline{G} is the matrix representation for kinetic energy, \underline{F} is the matrix representation for the potential energy and \underline{E} is the unit matrix. λ is the eigenvalue and equal to $4\pi^2c^2\bar{\nu}^2$. The unit matrix is needed to eliminate cross terms in the secular determinant... this is required since normal modes of vibration are completely independent from each other (and hence their KE and PE can not depend on each other).

The KE and PE may be expressed in terms of the internal coordinates. For our H₂O example, these are the Δr_1 , Δr_2 and $\Delta\theta$ basis:



By choosing this basis, translational and rotational coordinates are eliminated from the outset. Defining the force constants as follows:

$$f_{11} = f_{22} = \text{stretching} \square$$

$$f_{12} = f_{21} = \text{stretching-stretching} \square$$

$$f_{13} = f_{31} = f_{23} = f_{32} = \text{stretching-bending} \square$$

$$f_{33} = \text{bending} \square$$

The $\underline{PE}(v)$ is defined by an F-matrix:

$$2V = f_{11}(\Delta r_1)^2 + f_{22}(\Delta r_2)^2 + f_{23}r^2(\Delta\alpha)^2 + f_{12}(\Delta r_1)(\Delta r_2) + f_{21}(\Delta r_1)(\Delta r_2) + f_{13}(\Delta r_1)(\Delta\alpha)r + f_{31}(\Delta r_1)(\Delta\alpha)r + f_{23}(\Delta r_2)(\Delta\alpha)r + f_{32}(\Delta r_2)(\Delta\alpha)r$$

where $r = r_1 = r_2$, which is the equilibrium distance (needed to make terms dimensionally similar)

In matrix notation,

where appropriate substitutions have been made
(i.e. $f_{11} = f_{22}$; $f_{13} = f_{31}$; $f_{23} = f_{32}$)

$$2V = \begin{bmatrix} \Delta r_1 & \Delta r_2 & \Delta\alpha \end{bmatrix} \begin{bmatrix} f_{11} & f_{12} & rf_{13} \\ f_{12} & f_{11} & rf_{13} \\ rf_{13} & rf_{13} & r^2f_{33} \end{bmatrix} \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta\alpha \end{bmatrix} = \underline{R}^T \cdot \underline{F} \cdot \underline{R}$$

This type of potential is called a Generalized Valence Force (GVF) field, including all force constants. For large molecules, there is insufficient experimental data that allows for the determination of all force constants. For this case, other force fields have been defined (e.g. Urey - Bradley)

The $\underline{KE}(T)$ is defined by a \underline{G} -matrix,

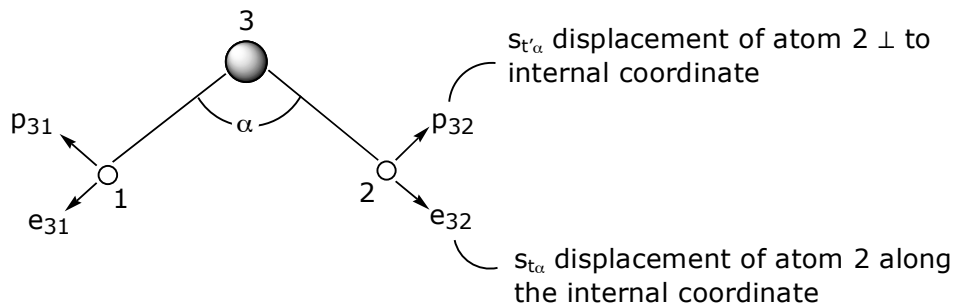
$$2T = \dot{\underline{R}} \cdot \underline{G}^{-1} \cdot \dot{\underline{R}}$$

where $\dot{\underline{R}}$ is the time derivative of the internal coordinates... the \underline{G} matrix is therefore a matrix of mass - weighted vector displacements of the atoms with elements

$$G_{tt'} = \sum_{\alpha} \mu_{\alpha} \bar{s}_{t\alpha} \bar{s}_{t'\alpha}$$

where $\bar{s}_{t\alpha}$ is oriented in the direction in which atom is moving along internal coordinate s_t over a unit distance. Thus, the time derivative taken twice of atom α , of reduced mass μ_{α} , displacing a distance s_t yields the KE.

for H₂O, the θ -matrix is,



The internal coordinates Δr_1 , Δr_2 and $\Delta\alpha$ in terms of above vector displacements are:

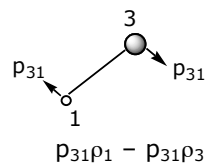
$$\Delta r_1 = e_{31}\rho_1 - e_{31}\rho_3$$

$$\Delta r_2 = e_{32}\rho_2 - e_{32}\rho_3$$

$$\Delta\alpha = [\rho_{31}\rho_1 + \rho_{32}\rho_2 - (\rho_{31} + \rho_{32})\rho_3] / r$$

unit displacement vectors

indicates motion of atom 3 (O) in opposite direction to atom 1 (H)



Thus

$$\begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta r_3 \end{bmatrix} = \begin{bmatrix} e_{31} & 0 & -e_{31} \\ 0 & e_{32} & -e_{32} \\ \frac{\rho_{31}}{r} & \frac{\rho_{32}}{r} & -\frac{(\rho_{31} + \rho_{32})}{r} \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix}$$

the \underline{S} -matrix

Must maintain the center of gravity in molecule during vector displacements... this criterion defines the G-matrix

$$\underline{G} = \underline{S} \cdot \underline{M}^{-1} \cdot \underline{S}^T$$

inverse masses of atoms

Therefore,

$$\underline{G} = \begin{bmatrix} \mathbf{e}_{31} & 0 & -\mathbf{e}_{31} \\ 0 & \mathbf{e}_{32} & -\mathbf{e}_{32} \\ p_{31}/r & p_{32}/r & -(p_{31} + p_{32})/r \end{bmatrix} \begin{bmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \end{bmatrix} \begin{bmatrix} \mathbf{e}_{31} & 0 & p_{31}/r \\ 0 & \mathbf{e}_{32} & p_{32}/r \\ -\mathbf{e}_{31} & -\mathbf{e}_{32} & -(p_{31} + p_{32})/r \end{bmatrix}$$

multiplying out,

$$\dot{\underline{G}} = \begin{bmatrix} (\mu_3 + \mu_1)\mathbf{e}_{31} \cdot \mathbf{e}_{31} & \mu_3 \mathbf{e}_{31} \cdot \mathbf{e}_{32} & \frac{\mu_1}{r} \mathbf{e}_{31} \cdot p_{31} + \frac{\mu_3}{r} \mathbf{e}_{32} \cdot (p_{31} + p_{32}) \\ & (\mu_3 + \mu_1)\mathbf{e}_{32} \cdot \mathbf{e}_{32} & \frac{\mu_1}{r} \mathbf{e}_{32} \cdot p_{32} + \frac{\mu_3}{r} \mathbf{e}_{32} \cdot (p_{31} + p_{32}) \\ & & \frac{\mu_1}{r^2} p_{31} \cdot p_{31} + \frac{\mu_1}{r^2} p_{32} \cdot p_{32} + \frac{\mu_3}{r} (p_{31} + p_{32})^2 \end{bmatrix}$$

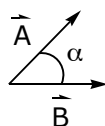
a symmetric matrix

But the following relations hold

$$\mathbf{e}_{31} \cdot \mathbf{e}_{31} = \mathbf{e}_{32} \cdot \mathbf{e}_{32} = p_{32} \cdot p_{32} = p_{31} \cdot p_{31} = 1 \quad \text{unit displacements}$$

$$\mathbf{e}_{31} \cdot \mathbf{e}_{32} = \cos \alpha$$

$$\mathbf{e}_{31} \cdot p_{31} = \mathbf{e}_{32} \cdot p_{32} = 0$$



$$\vec{A} \cdot \vec{B} = AB \cos \alpha$$

$$\mathbf{e}_{31} \cdot p_{31} = \mathbf{e}_{32} \cdot p_{32} = \cos(\alpha + 90) = -\sin \alpha \quad \cos(a+b) = \cos a \cdot \cos b - \sin a \cdot \sin b$$

$$(p_{31} + p_{32})^2 = 2(1 - \cos \alpha)$$

Substituting these vector products into the above matrix gives

$$\underline{G} = \begin{bmatrix} \mu_3 + \mu_1 & \mu_3 \cos \alpha & -\frac{\mu_3}{r} \sin \alpha \\ & \mu_3 + \mu_1 & -\frac{\mu_3}{r} \sin \alpha \\ & & \frac{2\mu_1}{r^2} + \frac{2\mu_3}{r^2} (1 - \cos \alpha) \end{bmatrix}$$

μ_1 and μ_3 are the reciprocal masses of H and O, respectively.

The \underline{F} and \underline{G} matrices are not diagonalized in the internal coordinates... this has already been determined - these are the symmetry coordinates. Expressed as a matrix representation,

$$\begin{bmatrix} s_1(a_1) \\ s_3(a_1) \\ s_2(b_2) \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 2 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{bmatrix} \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta \alpha \end{bmatrix}$$

↑ this is a $\underline{\mu}$ matrix

The symmetry coordinate matrix (the $\underline{\mu}$ matrix) provides the similarity transform for \underline{F} and \underline{G}

$$\underline{F}_{\text{sym}} = \underline{\mu}^{-1} \cdot \underline{F} \cdot \underline{\mu}$$

$$\underline{G}_{\text{sym}} = \underline{\mu}^{-1} \cdot \underline{G} \cdot \underline{\mu}$$

Performing the operation,

$$\underline{F}_{\text{sym}} = \left[\begin{array}{cc|c} f_{11} + f_{12} & r\sqrt{2}f_{13} & 0 \\ r\sqrt{2}f_{13} & r^2f_{33} & 0 \\ \hline 0 & 0 & f_{11} - f_{22} \end{array} \right]$$

$$\underline{G}_{\text{sym}} = \left[\begin{array}{cc|c} \mu_3(1 + \cos \alpha) + \mu_1 & -\frac{\sqrt{2}}{r} \mu_3 \sin \alpha & 0 \\ -\frac{\sqrt{2}}{r} \mu_3 \sin \alpha & \frac{2\mu_1}{r^2} + \frac{2\mu_3}{r^2} (1 - \cos \alpha) & 0 \\ \hline 0 & 0 & \mu_3(1 - \cos \alpha) + \mu_1 \end{array} \right]$$

Have a 2 x 2 determinant for the a_1 coordinates (which needs to be solved for eigenvalue) and a 1 x 1 determinant for b_1 .

For the b_2 term,

$$|G_{33}F_{33} - E\lambda_3| = 0$$

$$\therefore \lambda_3 = G_{33}F_{33} = [\mu_3(1 - \cos \alpha) + \mu_1] [f_{11} - f_{22}]$$

for the a_1 terms,

$$|GF - E\lambda| = \begin{vmatrix} G_{11}F_{11} + G_{12}F_{12} - \lambda & G_{11}F_{12} + G_{12}F_{22} \\ G_{21}F_{11} + G_{22}F_{21} & G_{21}F_{12} + G_{22}F_{22} - \lambda \end{vmatrix} = 0$$

$$\lambda^2 - (G_{11}F_{11} + G_{22}F_{22} + 2G_{12}F_{12})\lambda + (G_{11}G_{22} - G_{12}^2)(F_{11}F_{12} - F_{12}^2) = 0$$

for H_2O ,

$$\mu_1 = \mu_H = \frac{1}{1.008} = 0.99206$$

$$\mu_3 = \mu_O = \frac{1}{15.995} = 0.06252$$

$$r = 0.96 \text{ \AA}$$

$$\alpha = 105^\circ$$

Assume a set of force constants (determined from experiment)

$$f_{11} = 8.4280, f_{12} = -0.1050, f_{13} = 0.2625, f_{33} = 0.7680$$

Numerically solving the above eigenvalue equations,

$$\lambda_+ = 8.61475 \rightarrow \bar{\nu}_1 = 3824 \text{ cm}^{-1} \quad \nu_1(\text{exp}) = 3825 \text{ cm}^{-1}$$

$$\lambda_- = 1.60914 \rightarrow \bar{\nu}_2 = 1653 \text{ cm}^{-1} \quad \nu_2(\text{exp}) = 1654 \text{ cm}^{-1}$$

$$\lambda_3 = 9.13681 \rightarrow \bar{\nu}_3 = 3938 \text{ cm}^{-1} \quad \nu_3(\text{exp}) = 3936 \text{ cm}^{-1}$$

$$\lambda = 4\pi^2 c^2 \bar{\nu}^2$$