

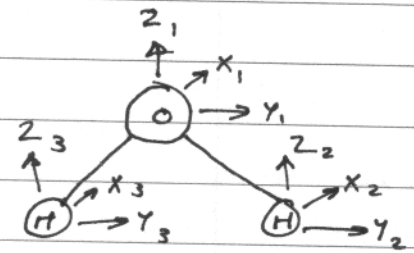
Classical Treatment of Normal Modes in Polyatomic Molecules

Our target is to express the classical Hamiltonian ($H = T + V$) for normal modes of a given molecule.

N atoms have $3N$ coordinates (or degrees of freedom)

$$x_1, y_1, z_1, x_2, y_2, \dots, x_N, y_N, z_N$$

Easier notation is to make $z_{3i} = x_i$ to have



$$z_{31}, z_{32}, z_{33}, z_{34}, z_{35}, \dots, z_{3N-2}, z_{3N-1}, z_{3N}$$

Potential and kinetic energy fields will be then functions of those $3N$ coordinates.

$$T = T(z_1, z_2, \dots, z_{3N})$$

$$V = V(z_1, z_2, \dots, z_{3N})$$

KE

For each atom $T_i = \frac{1}{2} m_i v_i^2$

$$v = \frac{dx}{dt} = \frac{dz_i}{dt} = \dot{z}_i$$

Thus, total kinetic energy is:

$$T = \frac{1}{2} \sum_i m_i \dot{z}_i^2$$

PE

The potential energy is expanded as Taylor's series (similar to diatomic):

$$V = V_0 + \sum_i^{3N} \left(\frac{\partial V}{\partial z_i} \right)_0 \xi_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial z_i \partial z_j} \right)_0 \xi_i \xi_j + \frac{1}{3!} \sum_{i,j,k} \left(\frac{\partial^3 V}{\partial z_i \partial z_j \partial z_k} \right)_0 \xi_i \xi_j \xi_k + \dots$$

Anharmonicity first term

f_i is zero at minima

f_{ij} f_{ijk}

f_{ij} is the force constant

$$2V = \sum_{i,j}^{3N} f_{ij} \xi_i \xi_j + \text{Higher order anharmonicity terms}$$

Polyatomic motion is treated using the "Lagrange's equation" which is equivalent to Newton's 2nd law of motion ($\sum \vec{F}_i = m_i a_i$)

Lagrangian (L) is given by:

$$L = T(\dot{z}_i) - V(z_i)$$

Lagrange's equation is:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{z}_i} \right)_{z_i} - \left(\frac{\partial L}{\partial z_i} \right)_{\dot{z}_i} = 0$$

Proof

For one-dimensional motion of a particle, Lagrangian is given by:

$$L = T - V \\ = \frac{1}{2} m \dot{x}^2 - V(x)$$

The Lagrange's equation is:

$$\frac{d}{dt} \frac{\partial}{\partial \dot{x}} \left(\frac{1}{2} m \dot{x}^2 - V \right) - \frac{\partial}{\partial x} \left(\frac{1}{2} m \dot{x}^2 - V \right) = 0$$

$$\frac{d}{dt} m \dot{x} + \frac{\partial V}{\partial x} = 0$$

$$-\frac{\partial V}{\partial x} = \frac{d}{dt} m \dot{x} = m \ddot{x} = ma = F$$

but for one-dimensional motion: $F = -\frac{\partial V}{\partial x}$

Thus, Lagrange's equation is equivalent to 2nd law.

$$F = ma = -\frac{\partial V}{\partial x} = \dot{p}$$

Then, Lagrange's equation can be applied to the vibration of polyatomic molecules.

$$L = T - V = \frac{1}{2} \sum_i^{3N} m_i \dot{\xi}_i^2 - \frac{1}{2} \sum_{i,j}^{3N} f_{ij} \xi_i \xi_j$$

→ Mass-weighted Cartesian coordinate (q_i)

$$\begin{aligned} \text{Let: } q_1 &= m_1^{1/2} (x_1 - x_{1eq}) \\ q_2 &= m_1^{1/2} (y_1 - y_{1eq}) \\ q_3 &= m_1^{1/2} (z_1 - z_{1eq}) \\ q_4 &= m_2^{1/2} (x_2 - x_{2eq}) \\ &\vdots \\ q_{3N} &= m_N^{1/2} (z_N - z_{Neq}) \end{aligned}$$

q_i is proportional to the displacement from the equilibrium value

ξ_i 's are to be transformed into q_i 's.

Yet, ξ_i 's of the potential energy term are already dependent on the displacement w.r.t. equilibrium positions.

$$L = \frac{1}{2} \sum_i^{3N} \dot{q}_i^2 - \frac{1}{2} \sum_{i,j}^{3N} f_{ij} q_i q_j$$

Applying Lagrangian equation of motion gives:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) - \left(\frac{\partial L}{\partial q_i} \right) = 0 \quad i = 1, 2, \dots, 3N$$

$$\textcircled{A} \quad \ddot{q}_i + \sum_j^{3N} f_{ij} q_j = 0 \quad i = 1, 2, \dots, 3N$$

There are $3N$ equations for each i .

Solution of these equations is of the form:

$$\textcircled{B} \quad q_i = A_i \cos(\lambda^{1/2} t + \delta)$$

A_i : constant related to amplitude of motion.

λ : \sim \sim to frequency.

δ : \sim \sim to shift of phase.

Substituting B in A gives:

$$-\lambda A_i \cos(\lambda^{1/2} t + \delta) + \sum_j f_{ij} A_j \cos(\lambda^{1/2} t + \delta) = 0$$

$$-\lambda A_i + \sum_j f_{ij} A_j = 0 \quad i = 1, 2, \dots, 3N.$$

or

$$\sum_j f_{ij} A_j - \lambda A_i = 0$$

$$\sum_{i \neq j} f_{ij} A_j + f_{ii} A_i - \lambda A_i = 0$$

$$\sum_{i \neq j} f_{ij} A_j + (f_{ii} - \lambda) A_i = 0 \quad i = 1, 2, \dots, 3N$$

We then have a set of $3N$ simultaneous equations

Example: For $N=3 \rightarrow 3N=9$ equations:

$$(f_{11} - \lambda)A_1 + f_{12}A_2 + f_{13}A_3 + \dots + f_{19}A_9 = 0$$

$$f_{21}A_1 + (f_{22} - \lambda)A_2 + f_{23}A_3 + \dots + f_{29}A_9 = 0$$

⋮

$$f_{91}A_1 + f_{92}A_2 + f_{93}A_3 + \dots + (f_{99} - \lambda)A_9 = 0$$

Trivial (meaningless) solutions are:

$$A_1 = A_2 = A_3 = \dots = A_{3N} = 0$$

Other non-trivial solutions:

$$\begin{vmatrix} (f_{11} - \lambda) & f_{12} & f_{13} & \dots & f_{1,3N} \\ f_{12} & (f_{22} - \lambda) & f_{23} & \dots & f_{2,3N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ f_{3N,1} & f_{3N,2} & f_{3N,3} & \dots & (f_{3N,3N} - \lambda) \end{vmatrix} = 0$$

Each f_{ij} or f_{ii} is a kind of force constant.

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \quad \text{off-diagonal elements}$$

$$f_{ii} = \left(\frac{\partial^2 V}{\partial q_i^2} \right)_0 \quad \text{Diagonal elements that are associated to bond strengths.}$$

The above determinant is often written in the form of secular equation:

$$|f_{ij} - \lambda \delta_{ij}| = 0 \quad \delta_{ij} \text{ is called "Kronecker delta"}$$

$$\delta_{ij} = 1 \text{ for } i=j \\ = 0 \text{ for } i \neq j$$

There are $3N$ solutions for the secular equation with $3N$ values of λ .

Each solution shows how q_i varies with time. Such a coordinate q_i is known as "normal mode coordinate".

Among the $3N$ solutions of λ , it is found that:

- ① Five λ eigenvalues are zero for linear molecules.
- ② Six λ \sim \sim \sim \sim nonlinear \sim .
- ③ $\lambda = 4\pi^2 \nu^2$ for the rest of vibration. (non-rotational or non-translational).

① and ② are just coordinates, ③ are called normal modes.

* Normal mode approximation is very useful but is not completely valid. Normal mode approximation assumes no coupling taking place between each of the normal mode coordinates. In reality, there are a great deal of coupling between these modes.

This is because we utilized the harmonic oscillator model in this treatment. The anharmonicity terms

in the potential energy expansion are then said to ~~be~~
couple the normal modes.