Molecular Vibration

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Molecular Vibration

Molecules consists of many atoms can execute vibrational motions.

Treat the atoms as point particles moving around their equilibrium positions. Let $\vec{x} = (x_1, x_2, \cdots x_n)$ be the generalized coordinates the atoms in the molecule. For the small deviations, expand the potential energy V around the equilibrium position,

$$V\left(\vec{x}\right) = V\left(\vec{x_0}\right) + (x_i - x_{i0}) \left.\frac{\partial V}{\partial x_i}\right|_{x=x_0} + \frac{1}{2}\left(x_i - x_{i0}\right)\left(x_j - x_{j0}\right) \left.\frac{\partial^2 V}{\partial x_i \partial_j}\right|_{x=x_0} + \cdots$$

Here $\vec{x}_0$ is the equilibrium position, $\left.\frac{\partial V}{\partial x_i}\right|_{x=x_0}$. Write the potential energy as

$$V = V_0 + \frac{1}{2} u_{ij} q_i q_j$$

where

$$V_0 = V\left(\vec{x_0}\right), \qquad q_i = (x_i - x_{i0}), \qquad u_{ij} = \left.\frac{\partial^2 V}{\partial x_i \partial_j}\right|_{x=x_0}$$

Write the kinatic energy as

$$T = \frac{1}{2} M_{ij} \dot{q}_i \dot{q}_j, \qquad \text{where} \qquad M_{ij} = m_i \delta_{ij} \quad \text{(no sum over i)}$$

The Lagrangian is

$$L = T - V$$

From Euler-Lagrange equation,

$$M_{ij}\ddot{q}_j = -u_{ij}q_j$$

Normal mode solution, $q_i = \eta_i \exp(-i\omega t)$. Equation of motion gives

$$\omega^2 M_{ij}\eta_j = u_{ij}\eta_j \qquad (1)$$

Or in matrix notation,

$$\omega^2 M\eta = U\eta \qquad (2)$$

where

$$(M)_{ij} = M_{ij}, \qquad (U)_{ij} = u_{ij}, \qquad \eta = \begin{pmatrix} \eta_1 \\ \vdots \\ \eta_n \end{pmatrix}$$

Similar to the eigenvalue equation except for the presence of the mass matrix M. Non-trivial solution exists only if

$$\det |\omega^2 M - U| = 0$$

whose solutions give normal mode frequencies, $\omega^{(1)}, \omega^{(2)}, \cdots, \omega^{(n)}$. For each normal mode frequency, we get normal mode configuration, $\eta^{(1)}, \eta^{(2)}, \cdots, \eta^{(n)}$.

Orthogonality of normal modes

From

$$\omega^{(\alpha)2} M_{ij} \eta_j^{(\alpha)} = u_{ij} \eta_j^{(\alpha)}$$

$$\omega^{(\beta)2} M_{ij} \eta_j^{(\beta)} = u_{ij} \eta_j^{(\beta)}$$

we get

$$\left(\omega^{(\alpha)2} - \omega^{(\beta)2}\right) \eta^{(\beta)} M_{ij} \eta_j^{(\alpha)} = 0$$

Thus, normal modes are orthogonal with repect to M,

$$\eta^{(\beta)} M_{ij} \eta_j^{(\alpha)} = \delta_{\alpha\beta}$$

General solution

$$q = \sum_{i=1}^{n} c^{(i)} \eta^{(i)} \cos\left[\omega^{(i)} t + \phi^{(i)}\right]$$

Normal model coordinates

Define $R_{j\alpha} = \eta_j^{(\alpha)}$ then

$$\left(R^t M R\right)_{\alpha\beta} = R_{\alpha i}^T M_{ij} R_{j\beta} = \eta_i^{(\alpha)} M_{ij} \eta_j^{(\beta)} = \delta_{\alpha\beta}$$

$$\left(R^t u R\right)_{\alpha\beta} = R_{\alpha i}^T u_{ij} R_{j\beta} = \omega^{(\beta)2} \eta_i^{(\alpha)} M_{ij} \eta_j^{(\beta)} = \delta_{\alpha\beta} \omega^{(\beta)2}$$
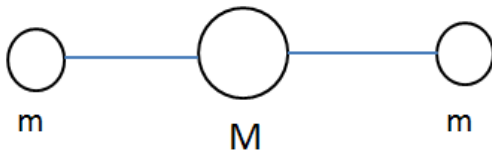
In new coordinates z defined by

$$x_j = R_{j\alpha} z_\alpha$$

the kinetic and potential energies are all diagonal

$$T = \frac{1}{2} \dot{x}_i M_{ij} \dot{x}_j = \frac{1}{2} \dot{z}_\alpha \dot{z}_\alpha, \qquad V = \frac{1}{2} x_i u_{ij} x_j = \frac{1}{2} \omega^{(\alpha)2} z_\alpha^2$$

Thus in terms of z_α, the normal mode coordinates, the oscillators decouple.

Example 1: Linear triatomic molecule

$$T = \frac{1}{2} \left[m\dot{x}_1^2 + M\dot{x}_2^2 + m\dot{x}_3^2 \right]$$

$$V = \frac{k}{2} \left[(x_1 - x_2)^2 + (x_2 - x_3)^2 \right]$$

The mass matrix and potential matrix are

$$M = \begin{pmatrix} m & & \\ & M & \\ & & m \end{pmatrix}, \qquad u = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

Normal mode frequencies

$$\begin{vmatrix} k - m\omega^2 & -k & 0 \\ -k & 2k - m\omega^2 & -k \\ 0 & -k & k - m\omega^2 \end{vmatrix} = 0$$

or

$$\omega^2 \left(k - m\omega^2 \right) \left[mM\omega^2 - km \left(2m + M \right) \right] = 0$$

1. $\omega = 0$, translational mode

$$\eta^{(1)} = \frac{1}{\sqrt{2m + M}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

2. $\omega = \sqrt{\frac{k}{m}}$, spring frequency

$$\eta^{(2)} = \frac{1}{\sqrt{2m}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

3. $\omega = \sqrt{\frac{k}{M} \left(2 + \frac{M}{m} \right)}$

$$\eta^{(3)} = \frac{1}{\sqrt{2m \left(1 + 2\frac{m}{M} \right)}} \begin{pmatrix} 1 \\ -2\left(\frac{m}{M} \right) \\ 1 \end{pmatrix}$$

Symmetries and Normal modes

This system is symmetric under, $x_1 \leftrightarrow x_3$, which can be represented by,

$$\sigma = \begin{pmatrix} & & 1 \\ & 1 & \\ 1 & & \end{pmatrix}$$

The eigenvectors are

$$v_1 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \qquad v_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad \text{with eigenvalue } 1$$

$$v_3 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \qquad \text{with eigenvalue } -1$$

By inspection, v_3 is a normal mode. Zero mode of translation is $v_1 + v_2$, the remaining mode can be obtained by orthogonality.

Example: 4-chain

$$T = \frac{m}{2} \left[\overset{\cdot}{x_1}^2 + \overset{\cdot}{x_2}^2 + \overset{\cdot}{x_3}^2 + \overset{\cdot}{x_4}^2 \right]$$

$$V = \frac{k}{2} \left[(x_1 - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x_4)^2 \right] = \frac{1}{2} \left(x_i u_{ij} x_j \right)$$

where

$$u = k \begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 1 \end{pmatrix}$$

The translational zero mode is,

$$\eta^{(1)} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Symmetric under $x_1 \leftrightarrow x_4$, $x_3 \leftrightarrow x_4$, represented by the matrix

$$\sigma = \begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix}$$

The eigenvectors are

$$\eta^{(1)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, \qquad \eta^{(2)} = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \qquad \text{with eigenvalue 1}$$

and

$$\eta^{(3)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix}, \qquad \eta^{(4)} = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \qquad \text{with eigenvalue } -1$$

By inspection,

$$u\eta^{(2)} = 2k\eta^{(2)}$$

Thus $\eta^{(2)}$ is a normal mode with $\omega^2 = \frac{2k}{m}$. Now in space $\eta^{(3)}$, and $\eta^{(4)}$,
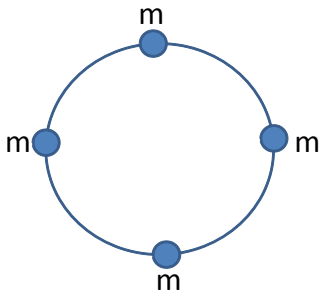
$$u\eta^{(3)} = k\left(\eta^{(3)} - \eta^{(4)}\right)$$

$$u\eta^{(4)} = k\left(-\eta^{(3)} + 3\eta^{(4)}\right)$$

or

$$u' = k\begin{pmatrix} 1 & -1 \\ -1 & 3 \end{pmatrix}$$

Diagonalize this martrix: eigenvalues are $k\left(2 \pm \sqrt{2}\right)$ and eigenvectors are $\eta^{(3)} - \left(1 + \sqrt{2}\right)\eta^{(4)}$, and $\left(1 + \sqrt{2}\right)\eta^{(3)} + \eta^{(4)}$.

Example: 4-ring

The potential energy is,

$$u = k \begin{pmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{pmatrix}$$

Clearly the zero mode is

$$\eta^{(1)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Symmetry: $x_1 \leftrightarrow x_3$, $x_2 \leftrightarrow x_4$. The latter one can be represented by

$$\sigma_y = \left(\begin{array}{cccc} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{array} \right)$$

The eigenvectors are

$$\eta^{(1)} = \frac{1}{2} \left(\begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \end{array} \right), \qquad \eta^{(2)} = \frac{1}{2} \left(\begin{array}{c} 1 \\ -1 \\ 1 \\ -1 \end{array} \right), \qquad \lambda = 1$$

$$\eta^{(3)} = \frac{1}{2} \left(\begin{array}{c} 1 \\ 1 \\ -1 \\ -1 \end{array} \right), \qquad \eta^{(4)} = \frac{1}{2} \left(\begin{array}{c} 1 \\ -1 \\ -1 \\ 1 \end{array} \right), \qquad \lambda = -1$$

It can be checked that these are all nomal modes.

Symmetry and Molecule Vibration

For a molecule with symmetry G, both the kinetic and potential energies are invariant under the group transformation T,

$$[T, M] = 0, \qquad [T, U] = 0$$

Then from eigenvalue equation in Eq(2) we get

$$TU\eta = U(T\eta) = T\omega^2 M\eta = \omega^2 M(T\eta)$$

$\implies \eta$ and $T\eta$ have the same frequency ω. Run transformation T over the whole group and select a linear independent set, $\phi_1, \phi_2, \cdots \phi_r$,
this will form a basis for the transformation $T_i \in G$.
As discussed before, coordinates $\overrightarrow{x} = (x_1, x_2, \cdots x_n)$, will give a reducible representation of group G,

$$T_i x_a = x_b X_{ba}(T_i), \qquad \text{and} \qquad X(T_j) X(T_i) = X(T_j T_i)$$

Want to find out how coordinate vector, $\overrightarrow{x} = (x_1, x_2, \cdots x_n)$, reduces in terms of irrep to get degenercies and structure of normal modes,

$$X = \sum_i k_i D^{(i)}$$

where $D^{(i)}$ are the irrep and k_i is the # of time each irrep $D^{(i)}$ appears in this reduction and can be calculated in terms of the characters

of the representations,

$$k_i = \frac{1}{g} \sum_i n_P \chi_p^{(i)*} \chi_p^{(X)}$$

we only need the trace of each group element. Thus $\chi_p^{(X)}$ comes from those atoms which are unmoved by transformation of the
symmetry group G. For a proper rotation of angle θ, $R(\theta)$, a unmoved atom will contribute $(1 + 2\cos\theta)$ to the trace and the total trace is

$$\chi^{(X)}(R(\theta)) = N_{R(\theta)}(1 + 2\cos\theta)$$

where $N_{R(\theta)}$ is # of atoms not moved by $R(\theta)$. Similarly, for an improper rotation of angle θ, $S(\theta)$,, the trace is,

$$\chi^{(X)}(S(\theta)) = N_{S(\theta)}(-1 + 2\cos\theta)$$

where $N_{S(\theta)}$ is # of atoms not moved by the rotation $S(\theta)$. However, there are always 6 zero modes, 3 for translation and 3 for rotation. We need to remove these zero modes to get the real vibrational mode. We can used center of mass coordinates $\vec{R}$ to describe these motions. So under proper rotation, and improper rotation we have,

$$\chi_{trans}^{(X)}(R(\theta)) = (1 + 2\cos\theta), \qquad \chi_{trans}^{(X)}(S(\theta)) = (-1 + 2\cos\theta)$$

For the rotational modes, we can describe it in terms of total angular momentum, an axial vector

$$\chi_{rot}^{(X)}(R(\theta)) = (1 + 2\cos\theta), \qquad \chi_{rot}^{(X)}(S(\theta)) = (-1 + 2\cos\theta)$$

Substract these zero modes, we get pure vibrational modes,

$$\chi_{vib}^{(X)}\left(R\left(\theta\right)\right) = \left(N_{S(\theta)} - 2\right)\left(-1 + 2\cos\theta\right)$$

$$\chi_{vib}^{(X)}\left(S\left(\theta\right)\right) = N_{S(\theta)}\left(-1 + 2\cos\theta\right)$$

As a illustration, we will study the water molecule H_2O, which has C_{2v} symmetry. The vibrational characters are

$$
\begin{aligned}
E\ (proper, \theta = 0, N_E = 3) & \quad \chi_{vib}(E) = 3 \\
C_2\ (proper, \theta = \pi, N_{C_2} = 1) & \quad \chi_{vib}(C_2) = 1 \\
\sigma_v\ (improper, \theta = 0, N_{\sigma_v} = 3) & \quad \chi_{vib}(\sigma_v) = 3 \\
\sigma'_v\ \left(improper, \theta = 0, N_{\sigma'_v} = 1\right) & \quad \chi_{vib}(\sigma'_v) = 1
\end{aligned}
$$

We can use the character table for C_{2v} to see how the vibrational modes reduced in terms of irrep of C_{2v}.

C_{2v}	E	C_2	σ_v	σ'_v
$A_1\ (z)$	1	1	1	1
$A_2\ (R_z)$	1	1	-1	-1
$B_1\ (x)$	1	-1	1	-1
$B_2\ (y)$	1	-1	-1	1
χ_{vib}	3	1	3	1

We take σ_v to be the reflection in the plane of the molecule and σ'_v to be reflection in the perpendicular plane bisecting the HOH bond angle. The C_2 axis is z and y axis. We see that the reduction is perpendicular to the plane of the molecule.
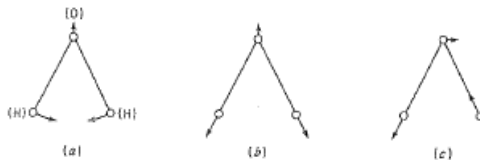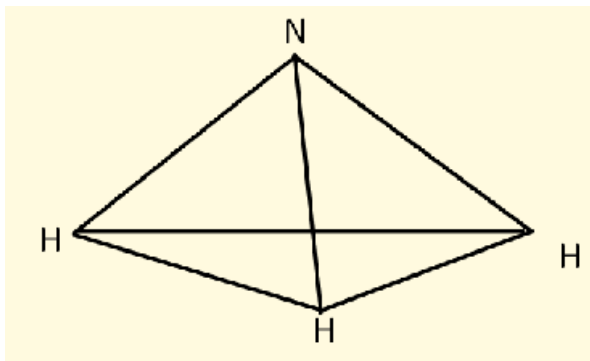
$$
\chi_{vib} = 2A_1 + B_1
$$

Fig. 7-8. *Normal modes of water molecule.* (a)-(b) Symmetry A_1; (c) symmetry B_1

Thus the vibrational modes are given by 2 A_1 modes which are invariant under C_{2v} and 1 B_1 mode which is invariant under C_2 rotation and change sign under σ_v.

Another example : NH_3 molecule

This molecule has D_3 symmetry. The characters for vibrational modes are

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
χ_{vib}	6	0	2

We see that the reduction of vibrational modes are

$$\chi_{vib} = 2A_1 + 2E$$

Thus there are 2 non-degenerate and 2 doubly degenerate modes.