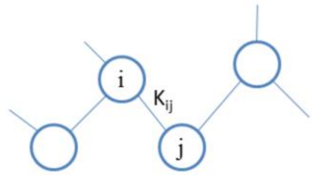
Equation of motion for coupled oscillator



$$F_{ix} = m_i \frac{d^2}{dt^2} x_i$$

$$= \sum_j \frac{d^2 \phi}{dx_i dx_j}(x_j - x_i) \equiv \sum_j k_{ij}(x_j - x_i)$$

$$\left.\begin{array}{l} K_{ij} = -k_{ij} \\ K_{ii} = \sum_j k_{ij} \end{array}\right\} \Rightarrow F_{ix} = -\sum_j K_{ij} x_j$$

φ: two-body potential
When a force proportional to displacement is taken into account, it is called harmonic approximation.

$$x_i = x_{0i} \exp(-i\omega t)$$

$$\Rightarrow F_{ix} = -m_i \omega^2 x_i$$

K: stiffness matrix

$$\sum_j K_{ij} x_j = m_i \omega^2 x_i \Rightarrow Kx = Mx\omega^2$$

Oscillating x is assumed as a solution.

$$V = \frac{1}{2} x^t K x = \frac{1}{2} x^t M x \omega^2$$

Simultaneous equations for all the particles.
→ An equation of matrix

V: Vibrational energy

Hessian method

$$M^{-1}Kx = x\omega^2$$

$$M = \begin{pmatrix} m_1 & & & & & & 0 \\ & m_1 & & & & & \\ & & m_1 & & & & \\ & & & \ddots & & & \\ & & & & m_N & & \\ & 0 & & & & m_N & \\ & & & & & & m_N \end{pmatrix}, \quad K = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & & & & \\ \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \cdots & & \cdots & \\ \frac{\partial^2 U}{\partial z_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \frac{\partial^2 U}{\partial z_1^2} & & & & \\ & \vdots & & \ddots & & & \\ & & & & \frac{\partial^2 U}{\partial x_N^2} & \frac{\partial^2 U}{\partial x_N \partial y_N} & \frac{\partial^2 U}{\partial x_N \partial z_N} \\ & \vdots & & & \frac{\partial^2 U}{\partial y_N \partial x_N} & \frac{\partial^2 U}{\partial y_N^2} & \frac{\partial^2 U}{\partial y_N \partial z_N} \\ & & & & \frac{\partial^2 U}{\partial z_N \partial x_N} & \frac{\partial^2 U}{\partial z_N \partial y_N} & \frac{\partial^2 U}{\partial z_N^2} \end{pmatrix}$$

$$M^{-1} = \begin{pmatrix} \mu_1 & & & & & & 0 \\ & \mu_1 & & & & & \\ & & \mu_1 & & & & \\ & & & \ddots & & & \\ & & & & \mu_N & & \\ & 0 & & & & \mu_N & \\ & & & & & & \mu_N \end{pmatrix}, \quad x = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix}$$

x is an eigenvector of $M^{-1}K$.
→ You have to find a set of x that diagonalizes $M^{-1}K$.

GF method

A variation of Hessian method, where the coordinate system is transformed so that the variables represents molecular parameters (such as bond length, bond angle, etc.).

$$\begin{cases} M^{-1}Kx = x\omega^2 \\ x' = U^t x \end{cases}$$

$$\Rightarrow U^t M^{-1} U U^t K U x' = U^t U x' \omega^2$$

$$\begin{cases} U^t M^{-1} U \equiv G \\ U^t K U \equiv F \end{cases}$$

$$\Rightarrow GFx' = x'\omega^2$$

U transforms the Cartesian coordinate into internal molecular coordinate.

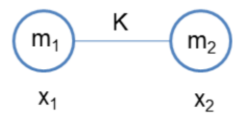
F is a set of parameters such as stretching, biting, etc., intuitionally understandable.

x' is an eigenvector of GF.

→ You have to find a set of *x'* that diagonalizes GF matrix.

Natural oscillation of a diatomic molecule

$$\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}\omega^2$$



Hesseian Method

$$\begin{pmatrix} \mu_1 K - \omega^2 & -\mu_1 K \\ -\mu_2 K & \mu_2 K - \omega^2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0$$

$when\ \omega^2 = 0$

$$x_1 = \frac{1}{\sqrt{2}},\ x_2 = \frac{1}{\sqrt{2}}$$

$when\ \omega^2 = (\mu_1 + \mu_2)K$

$$x_1 = \frac{\mu_1}{\sqrt{\mu_1^2 + \mu_2^2}},\ x_2 = -\frac{\mu_2}{\sqrt{\mu_1^2 + \mu_2^2}}$$

GF method

$$x' = U^t x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} x_1 + x_2 \\ x_1 - x_2 \end{pmatrix}$$

$$G = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} \mu_1 + \mu_2 & \mu_1 - \mu_2 \\ \mu_1 - \mu_2 & \mu_1 + \mu_2 \end{pmatrix}$$

$$F = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 2K \end{pmatrix}$$

$$GF = \begin{pmatrix} 0 & (\mu_1 - \mu_2)K \\ 0 & (\mu_1 + \mu_2)K \end{pmatrix}$$

$$\begin{pmatrix} -\omega^2 & (\mu_1 - \mu_2)K \\ 0 & (\mu_1 + \mu_2)K - \omega^2 \end{pmatrix}\begin{pmatrix} x_1' \\ x_2' \end{pmatrix} = 0$$

Mass-weighted Hessian method

$M^{-1}Kx = x\omega^2$

M^{-1}K is not a symmetric matrix.
→x's are not orthogonal to each other.
→ω is not necessarily real.

$M^{-1/2}KM^{-1/2}M^{1/2}x = M^{1/2}x\omega^2$

When we multiply M$^{1/2}$ on the both hands of the equation.

$$M^{1/2} = \begin{pmatrix} \sqrt{m_1} & & & & & & 0 \\ & \sqrt{m_1} & & & & & \\ & & \sqrt{m_1} & & & & \\ & & & \ddots & & & \\ & & & & \sqrt{m_N} & & \\ & 0 & & & & \sqrt{m_N} & \\ & & & & & & \sqrt{m_N} \end{pmatrix}$$

M is a diagonal matrix.
→$M^{1/2}$ is easily obtained.

$$\left.\begin{matrix} M^{-1/2}KM^{-1/2} \equiv D \\ M^{1/2}x \equiv w \end{matrix}\right\} \Rightarrow Dw = w\omega^2 \qquad D_{ij} = \sqrt{\mu_i}\sqrt{\mu_j}K_{ij}$$

D is symmetrical matrix.
→so-called dynamical matrix

Natural oscillation of a diatomic molecule

$$\begin{pmatrix} \mu_1 K & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} w_1 \\ w_2 \end{pmatrix}\omega^2$$

$$\begin{pmatrix} \mu_1 K-\omega^2 & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K-\omega^2 \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = 0$$

$when \quad \omega^2 = 0$

$$w_1 = \sqrt{\frac{\mu_2}{\mu_1+\mu_2}},\ w_2 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}}$$

$when \quad \omega^2 = (\mu_1+\mu_2)K$

$$w_1 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}},\ w_2 = -\sqrt{\frac{\mu_2}{\mu_1+\mu_2}}$$

Compared with GFmethod

$$GFx' = x'\omega^2$$

$$G^{1/2}FG^{1/2}G^{-1/2}x'$$

$$\begin{cases} G^{1/2}FG^{1/2} \equiv D' \\ G^{-1/2}x' \equiv w' \end{cases}$$

$$\Rightarrow D'w' = w'\omega^2$$

$$\begin{cases} w' = G^{-1/2}x' \\ \quad = U^tM^{1/2}UU^tM^{-1/2}w = U^tw \\ D' = G^{1/2}FG^{1/2} \\ \quad = U^tM^{-1/2}UU^tKUU^tM^{-1/2}U \\ \quad = U^tDU \end{cases}$$

Symmetrize GF matrix
→*D* and *D*’ are transformed to each other using U.

Natural oscillation of a diatomic molecule (cont.)

mass-weighted coordinate (orthonormalized)

$$\hat{\mathbf{W}} = \frac{1}{\sqrt{\mu_1+\mu_2}}\begin{pmatrix}\sqrt{\mu_2} & \sqrt{\mu_1}\\ \sqrt{\mu_1} & -\sqrt{\mu_2}\end{pmatrix}$$

Cartesian coordinate

$$\mathbf{X} = \mathbf{M}^{-1/2}\hat{\mathbf{W}} = \frac{1}{\sqrt{\mu_1+\mu_2}}\begin{pmatrix}\sqrt{\mu_1\mu_2} & \mu_1\\ \sqrt{\mu_1\mu_2} & -\mu_2\end{pmatrix}$$

Cartesian coordinate (normalized)

$$\hat{\mathbf{X}} = \frac{1}{\sqrt{2(\mu_1^2+\mu_2^2)}}\begin{pmatrix}\sqrt{\mu_1^2+\mu_2^2} & \sqrt{2}\mu_1\\ \sqrt{\mu_1^2+\mu_2^2} & -\sqrt{2}\mu_2\end{pmatrix}$$

modal mass matrix

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{M}\hat{\mathbf{X}} = \begin{pmatrix}\dfrac{\mu_1+\mu_2}{2\mu_1\mu_2} & 0\\ 0 & \dfrac{\mu_1+\mu_2}{\mu_1^2+\mu_2^2}\end{pmatrix} \equiv \begin{pmatrix} m_{\mathrm{T}} & 0\\ 0 & m_{\mathrm{V}}\end{pmatrix}$$

modal stiffness matrix

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{K}\hat{\mathbf{X}} = \begin{pmatrix}0 & 0\\ 0 & \dfrac{(\mu_1+\mu_2)^2}{\mu_1^2+\mu_2^2}K\end{pmatrix} \equiv \begin{pmatrix} K_{\mathrm{T}} & 0\\ 0 & K_{\mathrm{V}}\end{pmatrix}$$

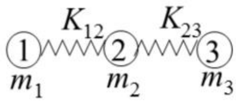
angular frequency

$$\omega_{\mathrm{T}} = \sqrt{\frac{K_{\mathrm{T}}}{m_{\mathrm{T}}}}\ ,\quad \omega_{\mathrm{V}} = \sqrt{\frac{K_{\mathrm{V}}}{m_{\mathrm{V}}}}$$

cf.

$$\omega_0 = 0\ ,\quad \omega_1 = \sqrt{\frac{K}{m^*}}\quad \left(m^* = \frac{1}{\mu_1+\mu_2}\right)$$

Natural oscillation of a linear triatomic molecule



$$\mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2} = \begin{pmatrix} \mu_1 K_{12} & -\sqrt{\mu_1\mu_2}K_{12} & 0 \\ -\sqrt{\mu_1\mu_2}K_{12} & \mu_2(K_{12}+K_{23}) & -\sqrt{\mu_2\mu_3}K_{23} \\ 0 & -\sqrt{\mu_2\mu_3}K_{23} & \mu_3 K_{23} \end{pmatrix}$$

$$\omega^2 = 0,\ \frac{1}{2}\left\{(\mu_1+\mu_2)K_{12} + (\mu_2+\mu_3)K_{23} \pm \sqrt{\{(\mu_1+\mu_2)K_{12} - (\mu_2+\mu_3)K_{23}\}^2 + 4\mu_2^2 K_{12}K_{23}}\right\}$$

$m_1 = m_3$
$K_{12} = K_{23} = K$

$$\Rightarrow \quad \hat{\mathbf{X}} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & \frac{\mu_1}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \\ \frac{1}{\sqrt{3}} & 0 & -\frac{2\mu_2}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & \frac{\mu_1}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \end{pmatrix}$$

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{M}\hat{\mathbf{X}} = \begin{pmatrix} \frac{2m_1+m_2}{3} & 0 & 0 \\ 0 & m_1 & 0 \\ 0 & 0 & \frac{m_1 m_2(2m_1+m_2)}{2m_1^2+m_2^2} \end{pmatrix} \qquad \hat{\mathbf{X}}^{\mathrm{T}}\mathbf{K}\hat{\mathbf{X}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & K & 0 \\ 0 & 0 & \frac{(\mu_1+2\mu_2)}{\mu_1^2+2\mu_2^2}K \end{pmatrix}$$