Lecture 17

Normal frequencies & coordinates

$\omega_1, \dots, \omega_n \Leftarrow$ resonant freqs of the system

$\vec{a}_1, \dots, \vec{a}_n \Leftarrow$ corresponding eigenvectors

The general solution is given by

$$\eta_i = \sum_k \underbrace{C_k}_{\text{complex}} \underbrace{a_{ik}}_{Re} e^{-i \underbrace{\omega_k}_{Re} t} \qquad (*) \qquad i=1,\dots,n$$

Why make C_k complex?

$$C_k = \alpha_k + i\beta_k$$

The physical solution is $Re\{\eta_i\}$, so that

$$Re\{\eta_i\} = \sum_k \left[\alpha_k a_{ik} \cos(\omega_k t) + \beta_k a_{ik} \sin(\omega_k t) \right] \equiv$$

$$\equiv \sum_k f_k a_{ik} \cos(\omega_k t + \delta_k), \quad \text{s.t.}$$

$$f_k a_{ik} \left[\cos(\omega_k t) \cos\delta_k - \sin(\omega_k t) \sin\delta_k \right] =$$

$\forall k$ $$= \alpha_k a_{ik} \cos(\omega_k t) + \beta_k a_{ik} \sin(\omega_k t), \text{ or}$$

$$\begin{cases} \alpha_k = f_k \cos\delta_k, \\ \beta_k = -f_k \sin\delta_k \end{cases} \Rightarrow \begin{cases} f_k = \sqrt{\alpha_k^2 + \beta_k^2}, \\ \tan\delta_k = -\dfrac{\beta_k}{\alpha_k} \end{cases}$$

So C_k basically encodes the amplitude f_k & the initial phase δ_k, which can be determined from the initial conditions.

What about the fact that we have $\pm\omega_k$ for each k?

Consider

$$\eta_i = \sum_k a_{ik}\left(C_k^+ e^{i\omega_k t} + C_k^- e^{-i\omega_k t}\right).$$

$$\begin{cases} C_k^+ = \alpha_k^+ + i\beta_k^+, \\ C_k^- = \alpha_k^- + i\beta_k^-. \end{cases}$$

Then

$$\mathrm{Re}\{\eta_i\} = \sum_k a_{ik}\Big(\alpha_k^+ \cos(\omega_k t) - \beta_k^+ \sin(\omega_k t) + $$

$$+ \alpha_k^- \cos(\omega_k t) + \beta_k^- \sin(\omega_k t)\Big) =$$

$$= \sum_k a_{ik}\Big(\underbrace{[\alpha_k^+ + \alpha_k^-]}_{\equiv\, \alpha_k} \cos(\omega_k t) + \underbrace{[\beta_k^- - \beta_k^+]}_{\equiv\, \beta_k} \sin(\omega_k t)\Big).$$

It is sufficient to use Eq. (*).

Initial conditions:

$$\begin{cases} \eta_i(0) = \sum_k a_{ik} \underbrace{\mathrm{Re}\{C_k\}}_{\alpha_k}, \\ \dot{\eta}_i(0) = \sum_k a_{ik}\, \omega_k \underbrace{\mathrm{Im}\{C_k\}}_{\beta_k} \end{cases} \Leftarrow \text{2n eq's, can be used to find } (\alpha_k, \beta_k) \quad k = 1, \dots, n$$

Indeed, $\tilde{A}T * | \ \vec{\eta}(0) = A\vec{\alpha}$, $\vec{\alpha} = \begin{pmatrix}\alpha_1 \\ \vdots \\ \alpha_n\end{pmatrix}$, or

$$\vec{\alpha} = \tilde{A} T \vec{\eta}(0). \qquad \Rightarrow \alpha_\ell = \sum_{j,k} \underbrace{\tilde{a}_{\ell j}}_{a_{j\ell}} T_{jk}\, \eta_k(0).$$

$\Rightarrow$

$$\tilde{A} T A = \mathbb{I}$$

Similarly,

$$\tilde{A}T^* \,\Big|\, \dot{\vec{\eta}}(0) = A\vec{\beta}', \text{ or}$$

$$\vec{\beta}' = \begin{pmatrix} \omega_1\beta_1 \\ \vdots \\ \omega_n\beta_n \end{pmatrix}$$

$$\vec{\beta}' = \tilde{A}T\dot{\vec{\eta}}(0) \Rightarrow \beta_\ell = \frac{1}{\omega_\ell}\sum_{j,k} a_{j\ell}T_{jk}\dot{\eta}_k(0).$$

Normal coordinates:

$$\eta_i = a_{ij}\xi_j, \text{ or } \vec{\eta} = A\vec{\xi}$$

Recall that $V = \frac{1}{2}\vec{\eta}^{+}V\vec{\eta}$.

$$\vec{\eta}^{+} = \vec{\xi}^{+}A^{+} = \vec{\xi}^{+}\tilde{A}, \text{ yielding}$$

$$V = \frac{1}{2}\vec{\xi}^{+}\underbrace{\tilde{A}VA}_{\lambda = \begin{pmatrix} \omega_1^2 & & \\ & \ddots & \\ 0 & & \omega_n^2 \end{pmatrix}}\vec{\xi} = \frac{1}{2}\sum_k \omega_k^2 |\xi_k|^2.$$

Further, $T = \frac{1}{2}\dot{\vec{\xi}}^{+}\underbrace{\tilde{A}TA}_{\mathbb{I}}\dot{\vec{\xi}} = \frac{1}{2}\dot{\vec{\xi}}^{+}\dot{\vec{\xi}} = \frac{1}{2}\sum_k \overbrace{|\dot{\xi}_k|^2}^{\dot{\xi}_k\dot{\xi}_k^*}.$

Thus T & V are diagonalized simultaneously.

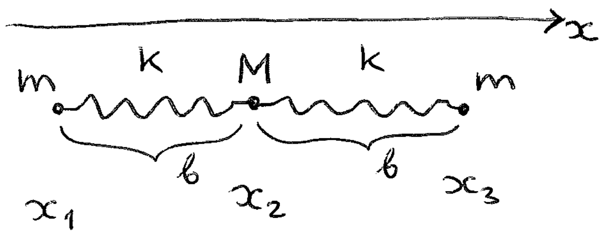
Finally, $\mathcal{L} = \frac{1}{2}\sum_k\left(\dot{\xi}_k\dot{\xi}_k^* - \omega_k^2\xi_k\xi_k^*\right)$

$$\Downarrow$$

EoM: $\ddot{\xi}_k + \omega_k^2\xi_k = 0$, solved by

normal coords of the system $\Rightarrow$ $\xi_k = \underbrace{C_k}_{\text{complex}} e^{-i\omega_k t} \Rightarrow \eta_i = \sum_k a_{ik}\xi_k$, as expected

Ex.: Linear triatomic molecule



$$V = \frac{k}{2}(x_2 - x_1 - b)^2 + \frac{k}{2}(x_3 - x_2 - b)^2$$

Introduce $\quad \eta_i = x_i - x_{0i}$, where

$$\begin{cases} x_{02} - x_{01} = b, \\ x_{03} - x_{02} = b. \end{cases}$$

Then $\quad V = \frac{k}{2}(\eta_2 - \eta_1)^2 + \frac{k}{2}(\eta_3 - \eta_2)^2 =$

$$= \frac{k}{2}\left[\eta_1^2 + 2\eta_2^2 + \eta_3^2 - 2\eta_1\eta_2 - 2\eta_2\eta_3\right], \text{ or}$$

$$V = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix} \quad \text{in matrix form.}$$

Next, $\quad T = \frac{m}{2}(\dot{\eta}_1^2 + \dot{\eta}_3^2) + \frac{M}{2}\dot{\eta}_2^2$, so that

$$T = \begin{pmatrix} m & & 0 \\ & M & \\ 0 & & m \end{pmatrix}$$

The secular eq'n:

$$|V-\underbrace{\omega^2}_{\lambda} T| = \begin{vmatrix} k-\omega^2 m & -k & 0 \\ -k & 2k-\omega^2 M & -k \\ 0 & -k & k-\omega^2 m \end{vmatrix} = 0, \text{ yielding}$$

$$(k-\omega^2 m)^2(2k-\omega^2 M) - k^2(k-\omega^2 m) - k^2(k-\omega^2 m) =$$

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

$$= \omega^2(k-\omega^2 m)\left[\omega^2 m M - 2mk - Mk\right] = 0, \text{ or}$$

$$\begin{cases} \omega_1 = 0, \quad \omega_2 = \sqrt{\dfrac{k}{m}}, \\ \omega_3 = \sqrt{\dfrac{k(2m+M)}{mM}} = \sqrt{\dfrac{k}{m}\left(1+\dfrac{2m}{M}\right)}. \end{cases}$$

$\omega_1 = 0 \Rightarrow \ddot{\xi}_1 = 0$ rigid translation along x-axis

"rigid body DoF"

Note that in this case,

$\eta_1 = \eta_2 = \eta_3 = \eta$, (the system is translated as a whole)

and $V = \frac{k}{2}(\eta_2-\eta_1)^2 + \frac{k}{2}(\eta_3-\eta_2)^2 = 0$

Starting from $\eta = 0$ (equil.), we can translate the system as a whole and V will remain 0 (even though $\eta \neq 0$) $\Rightarrow$
$\Rightarrow$ zero-freq. mode.

Next, consider $\omega_2 = \sqrt{\frac{k}{m}}$ $\Leftarrow$ no dependence on M, central atom stationary (?)

Eigenvectors: $j = 1, 2, 3$

$$\begin{cases} (k - \omega_j^2 m)\, a_{1j} - k a_{2j} = 0, \\ -k a_{1j} + (2k - \omega_j^2) M a_{2j} - k a_{3j} = 0, \\ -k a_{2j} + (k - \omega_j^2 m) a_{3j} = 0 \end{cases}$$

Normalization: $\tilde{A} T A = \mathbb{I}$, yielding

$$\underbrace{\begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix}}_{\tilde{A}} \underbrace{\begin{pmatrix} m & & 0 \\ & M & \\ 0 & & m \end{pmatrix}}_{T} \underbrace{\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}}_{A} =$$

$$= \begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & 1 \end{pmatrix}, \text{ or}$$

$$m a_{1j}^2 + M a_{2j}^2 + m a_{3j}^2 = 1.$$

If $\omega_1 = 0$, we have $a_{11} = a_{21} = a_{31}$, as expected from a uniform translation.

Then with normal'n

$$\underline{\underline{a_{11} = a_{21} = a_{31} = \frac{1}{\sqrt{2m+M}}}}.$$

For ω_2, $k-\omega_2^2 m=0$ and we obtain:

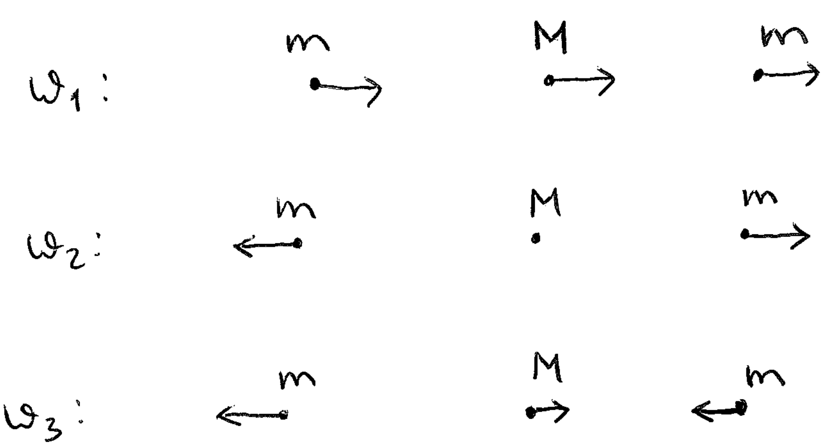
$a_{22}=0$ and $a_{12}=-a_{32}$.

With normal'n,
$$\begin{cases} a_{12} = \dfrac{1}{\sqrt{2m}}, \\ a_{22} = 0, \\ a_{32} = -\dfrac{1}{\sqrt{2m}}. \end{cases}$$
$\Leftarrow$ center atom stationary (!)

Atoms 1 & 3 vibrate exactly out of phase, with the same amplitude.

Finally, for ω_3

$$\begin{cases} a_{13} = a_{33} = \dfrac{1}{\sqrt{2m\left(1+\frac{2m}{M}\right)}}, \\[2ex] a_{23} = -\dfrac{2}{\sqrt{2M\left(2+\frac{M}{m}\right)}} \end{cases}$$
exactly in phase



Finally, we can find normal coords $\vec{\xi}$ by using $\vec{\eta} = A\vec{\xi}$:

$$\begin{cases} \xi_1 = \dfrac{1}{\sqrt{2m+M}}\left(\sqrt{m}\,\eta_1 + \sqrt{M}\,\eta_2 + \sqrt{m}\,\eta_3\right), \\[2ex] \xi_2 = \dfrac{1}{\sqrt{2}}\left(\eta_1 - \eta_3\right), \\[2ex] \xi_3 = \dfrac{1}{\sqrt{2m+M}}\left(\sqrt{\dfrac{M}{2}}(\eta_1+\eta_3) - \sqrt{2m}\,\eta_2\right). \end{cases}$$

A general vibration will be a linear ~~comb~~ combination of normal modes 2 & 3 with c_2 & c_3 providing amplitudes & initial phases.

In general, a molecule with n atoms will have $3n$ DoF. However, there will be 3 translational & 3 rigid rotation zero-freq. modes $\Rightarrow$ $3n-6$ <u>vibrational</u> modes.