Lecture 8 (Oct. 28)

- Small oscillations summary:

(0) linearize about equilibrium $\left.\frac{\partial U}{\partial q_\sigma}\right|_{\bar{q}} = 0$; $q_\sigma = \bar{q}_\sigma + \eta_\sigma$, $\sigma \in \{1, \ldots, n\}$ (may be multiple solutions)

(1) obtain T and V matrices:

$$T_{\sigma\sigma'} = \left.\frac{\partial^2 T}{\partial \dot{q}_\sigma \partial \dot{q}_{\sigma'}}\right|_{\bar{q}} , \quad V_{\sigma\sigma'} = \left.\frac{\partial^2 U}{\partial q_\sigma \partial q_{\sigma'}}\right|_{\bar{q}}$$

both real, symmetric

Lagrangian is then

$$L = \frac{1}{2}\dot{\eta}_\sigma T_{\sigma\sigma'} \dot{\eta}_{\sigma'} - \frac{1}{2}\eta_\sigma V_{\sigma\sigma'} \eta_{\sigma'} + \cancel{\mathcal{O}(\eta^3, \eta^2\dot{\eta}, \ldots)}$$

(2) Solve $P(\omega) \equiv \det(\omega^2 T - V) = 0$ for normal mode frequencies ω_i^2. $P(\omega) = a_n \omega^{2n} + a_{n-1}\omega^{2(n-1)} + \ldots + a_0$.

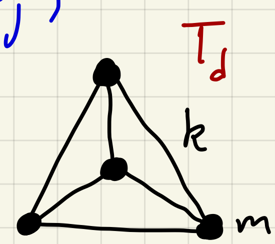
(3) For each ω_i^2, solve $(\omega_i^2 T - V)\vec{\psi}^{(i)} = 0$. The overall <u>length</u> of $\vec{\psi}^{(i)}$ is as yet undetermined.

(4) Necessarily, if $\omega_i^2 \neq \omega_j^2$, then

$$\langle \vec{\psi}^{(i)} | \vec{\psi}^{(j)} \rangle \equiv \psi_\sigma^{(i)} T_{\sigma\sigma'} \psi_{\sigma'}^{(j)} = 0 \quad (\omega_i^2 \neq \omega_j^2)$$

Degenerate eigenvalues: use Gram-Schmidt.

Now normalize: $\langle \vec{\psi}^{(i)} | \vec{\psi}^{(j)} \rangle = \delta_{ij}$



(5) Modal matrix is $A_{\sigma j} = \psi_\sigma^{(j)}$ $\quad \underbrace{A^{-1}}_{} = A^t T$

Normal modes: $\eta_\sigma = A_{\sigma j}\xi_j$; $\xi_j = A^{-1}_{j\sigma}\eta_\sigma$

Also:

$$A^t T A = \mathbb{1} , \quad A^t V A = \mathrm{diag}(\omega_1^2, \ldots, \omega_n^2)$$

$4 \times 3 = 12$

$6 = 3 + 3$ ZM

$1 + 2 + 3$

remaining

(6) L in terms of normal modes: $\quad \eta = A\xi$

$$L = \frac{1}{2}\dot{\eta}^t T \dot{\eta} - \frac{1}{2}\eta^t V \eta$$
$$= \frac{1}{2}\dot{\xi}^t (A^t T A)\dot{\xi} - \frac{1}{2}\xi^t (A^t V A)\xi$$
$$= \sum_{i=1}^{n} \frac{1}{2}\left(\dot{\xi}_i^2 - \omega_i^2 \xi_i^2\right) \Rightarrow \ddot{\xi}_j = -\omega_j^2 \xi_j$$

So the normal modes are decoupled!

(7) Solution:

$$\xi_j(t) = \xi_j(0)\cos\omega_j t + \omega_j^{-1}\dot{\xi}_j(0)\sin\omega_j t$$
$$\eta_\sigma(0) = A_{\sigma j}\xi_j(0), \quad \dot{\eta}_\sigma(0) = A_{\sigma j}\dot{\xi}_j(0)$$
$$\Rightarrow \quad \xi_j(0) = A^{-1}_{j\sigma}\eta_\sigma(0), \quad \dot{\xi}_j(0) = A^{-1}_{j\sigma}\dot{\eta}_\sigma(0)$$

$$\eta_\sigma(t) = A_{\sigma j}\,\xi_j(t)$$

$A^{-1} = A^t T$

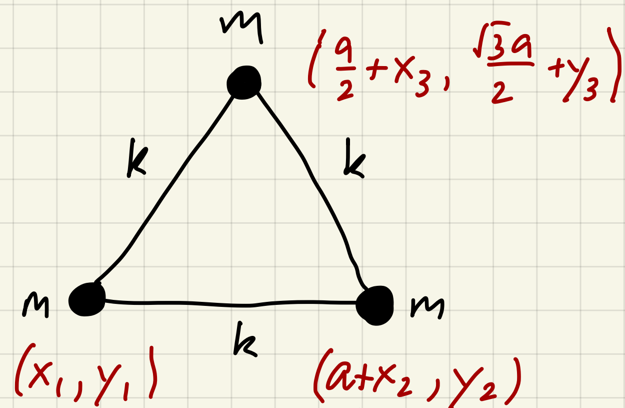
$$= \sum_{j,\sigma'} A_{\sigma j}\cos\omega_j t\, A^{-1}_{j\sigma'}\,\eta_{\sigma'}(0) + A_{\sigma j}\,\omega_j^{-1}\sin\omega_j t\, A^{-1}_{j\sigma'}\,\dot{\eta}_{\sigma'}(0)$$

$$W_{\sigma\sigma'}\ddddot{\eta}_{\sigma'} + T_{\sigma\sigma'}\ddot{\eta}_{\sigma'} = V_{\sigma\sigma'}\eta_\sigma$$

eigenvectors

$$\eta_\sigma = \psi_\sigma e^{-i\omega t} \Rightarrow \underbrace{(\omega^4 W - \omega^2 T + V)}_{\det \equiv 0 \Rightarrow \omega_i^2}\vec{\psi} = 0$$

Planar triatomic molecule



$$\# \text{ DOF}: \ 6 \ \overbrace{\{x_1, y_1, x_2, y_2, x_3, y_3\}}^{\vec{\eta}}$$

$$\text{Equilibrium}: \{0,0,0,0,0,0\}$$

KE is easy:

$$T = \frac{1}{2} m \left(\dot{x}_1^2 + \dot{y}_1^2 + \dot{x}_2^2 + \dot{y}_2^2 + \dot{x}_3^2 + \dot{y}_3^2\right) = \frac{1}{2} m \sum_{\sigma=1}^{6} \dot{\eta}_\sigma^2$$

$$T_{\sigma\sigma'} = m\,\delta_{\sigma\sigma'}$$

PE is more challenging: $U = \frac{1}{2}k\left[(d_{12}-a)^2 + (d_{23}-a)^2 + (d_{13}-a)^2\right]$

$$d_{12}^2 = (a + x_2 - x_1)^2 + (y_2 - y_1)^2$$
$$d_{23}^2 = \left(-\frac{a}{2} + x_3 - x_2\right)^2 + \left(\frac{\sqrt{3}}{2}a + y_3 - y_2\right)^2$$
$$d_{12}^2 = \left(\frac{a}{2} + x_3 - x_1\right)^2 + \left(\frac{\sqrt{3}}{2}a + y_3 - y_1\right)^2$$

Note: when $x_{1,2,3} = y_{1,2,3} = 0$, $d_{ij}^2 = a^2 \ \forall\, i \neq j$

Expand to linear order in gd's:

$$d_{12} = a + x_2 - x_1 + \ldots$$
$$d_{23} = a - \frac{1}{2}(x_3 - x_2) + \frac{\sqrt{3}}{2}(y_3 - y_2) + \ldots$$
$$d_{13} = a + \frac{1}{2}(x_3 - x_1) + \frac{\sqrt{3}}{2}(y_3 - y_1) + \ldots$$

$$U = \frac{1}{2}k(x_2 - x_1)^2 + \frac{1}{8}k\left(x_2 - x_3 + \sqrt{3}\,y_3 - \sqrt{3}\,y_2\right)^2 + \frac{1}{8}k\left(x_3 - x_1 + \sqrt{3}\,y_3 - \sqrt{3}\,y_1\right)^2 + \mathcal{O}(\eta^3)$$

$$U = \frac{1}{2}k(\eta_3 - \eta_1)^2 + \frac{1}{8}k(\eta_3 - \eta_5 + \sqrt{3}\eta_6 - \sqrt{3}\eta_4)^2$$
$$+ \frac{1}{8}k(\eta_5 - \eta_1 + \sqrt{3}\eta_6 - \sqrt{3}\eta_2)^2 + \mathcal{O}(\eta^3)$$

$$V_{\sigma\sigma'} = \left.\frac{\partial^2 U}{\partial\eta_\sigma \partial\eta_{\sigma'}}\right|_{\bar{\eta}} = k \begin{pmatrix} 5/4 & & \\ & \ddots & \\ & & \end{pmatrix}_{6\times 6}$$

See §5.9.3 for complete solution.