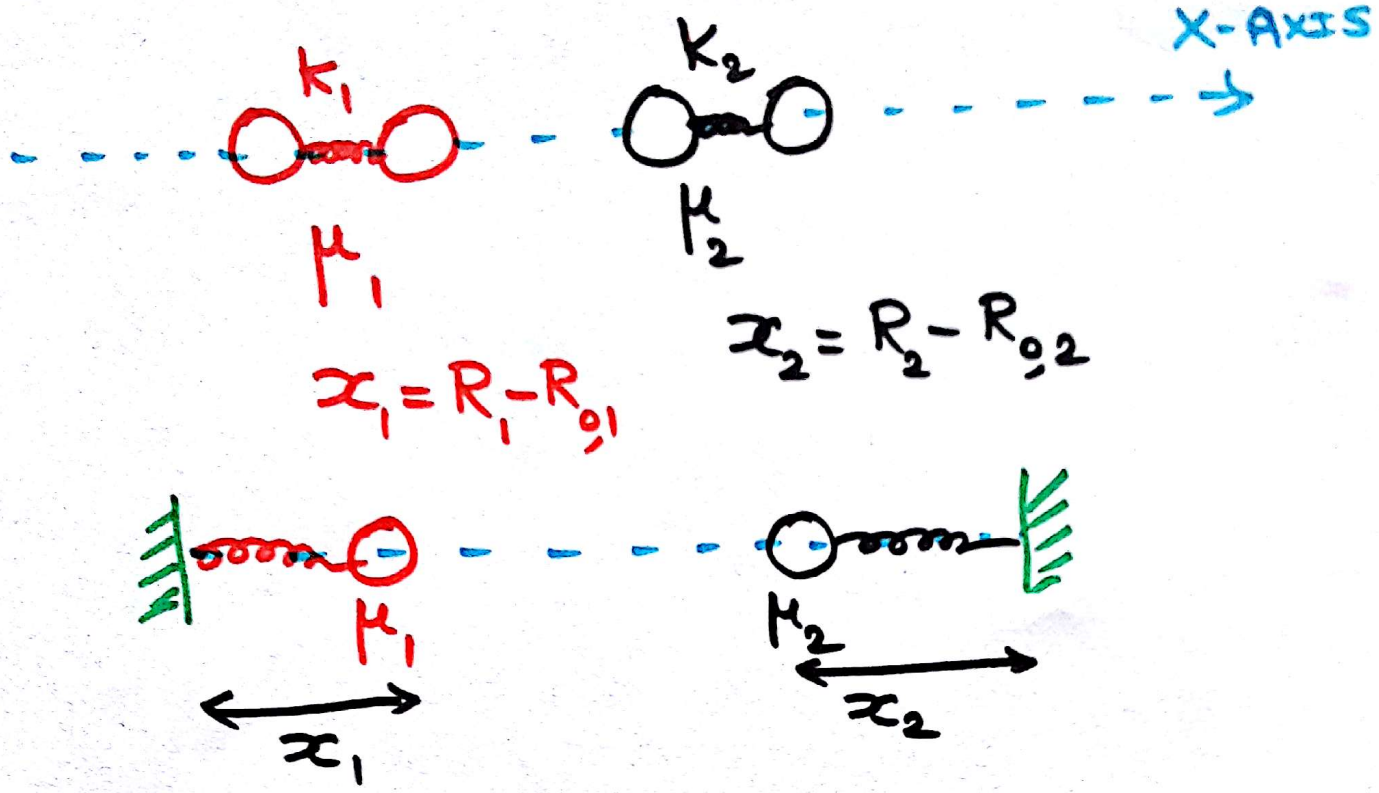
NORMAL MODES

- CONSIDER TWO DIATOMIC MOLECULES



- UNCOUPLED ⇒ TWO INDEPENDENT HARMONIC OSCILLATORS

$$\omega_1 = \sqrt{\frac{k_1}{\mu_1}} \quad ; \quad \omega_2 = \sqrt{\frac{k_2}{\mu_2}}$$

POTENTIAL ENERGY

$$U(x_1, x_2) = U(x_1) + U(x_2)$$

$$= \frac{1}{2} k_1 x_1^2 + \frac{1}{2} k_2 x_2^2$$

$$= \frac{1}{2} \mu_1 \omega_1^2 x_1^2 + \frac{1}{2} \mu_2 \omega_2^2 x_2^2$$

$$U(x_1, x_2) = (x_1 \; x_2) \begin{pmatrix} \frac{k_1}{2} & 0 \\ 0 & \frac{k_2}{2} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$U(x_1,x_2) = (x_1\ x_2)\begin{pmatrix} \frac{1}{2}M_1\omega_1^2 & 0 \\ 0 & \frac{1}{2}M_2\omega_2^2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

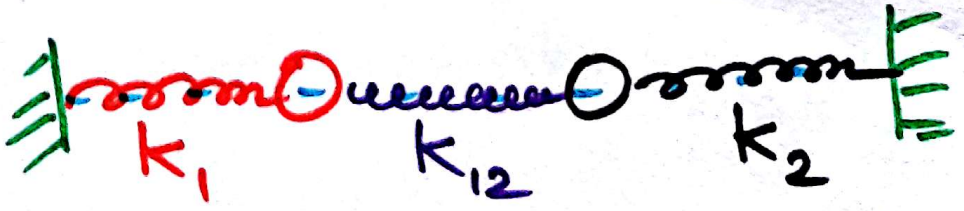
SINCE $\quad k_1 = \dfrac{\partial^2 U}{\partial x_1^2}\ ;\ \dfrac{\partial^2 U}{\partial x_1 \partial x_2} = 0$

$$k_2 = \frac{\partial^2 U}{\partial x_2^2}\ ;\ \frac{\partial^2 U}{\partial x_2 \partial x_1} = 0$$

$$U(x_1,x_2) = \frac{1}{2}(x_1\ x_2)\begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_2 \partial x_1} \\ \frac{\partial^2 U}{\partial x_1 \partial x_2} & \frac{\partial^2 U}{\partial x_2^2} \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

CURVATURE MATRIX OR HESSIAN MATRIX

- COUPLED OSCILLATORS



$$U(x_1,x_2) = \frac{1}{2}k_1 x_1^2 + \frac{1}{2}k_2 x_2^2 + \frac{1}{2}k_{12}(x_1-x_2)^2$$

SIMPLE FORM

$$= \frac{1}{2}k_1 x_1^2 + \frac{1}{2}k_2 x_2^2 + \frac{1}{2}k_{12}x_1^2 + \frac{1}{2}k_{12}x_2^2 - \frac{1}{2}k_{12}(2x_1x_2)$$

⇒ NON-DIAGONAL HESSIAN ; DIAGONALIZE ⇒ EIGEN VALUES ⇒ ω ; EIGEN VECTORS ⇒ MODES

- HESSIAN FOR AN N-ATOM SYSTEM

$$\mathcal{H} = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial x_1} & \cdots \\ \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \cdots \\ \frac{\partial^2 U}{\partial x_1 \partial z_1} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \frac{\partial^2 U}{\partial z_1^2} & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix}$$

$3N \times 3N$ MATRIX

- USE MASS-WEIGHTED COORDINATES

$$(q_{i,x}, q_{i,y}, q_{i,z}) = (\sqrt{m_i}\, x_i, \sqrt{m_i}\, y_i, \sqrt{m_i}\, z_i)$$

- HAMILTON'S EQUATIONS OF MOTION

KINETIC ENERGY $T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$

POTENTIAL ENERGY $U(\{q\}) = \frac{1}{2} \sum_{i=1}^{3N} \left(\frac{\partial^2 U}{\partial q_i \partial q_j} \right)_0 q_i q_j$

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} + \frac{\partial U}{\partial q_j} = 0$$

$$\ddot{q}_j + \sum_{i=1}^{3N} \mathcal{H}_{ij} q_i = 0$$

- DIAGONALIZATION of THE HESSIAN

$$X^{-1} \mathcal{H} X = \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \lambda_{3N} \end{pmatrix}$$

$$\Rightarrow \mathcal{H} X = X \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \lambda_{3N} \end{pmatrix}$$

BLOCK MATRIX

$$X = (X_1 \; X_2 \ldots, X_N)$$

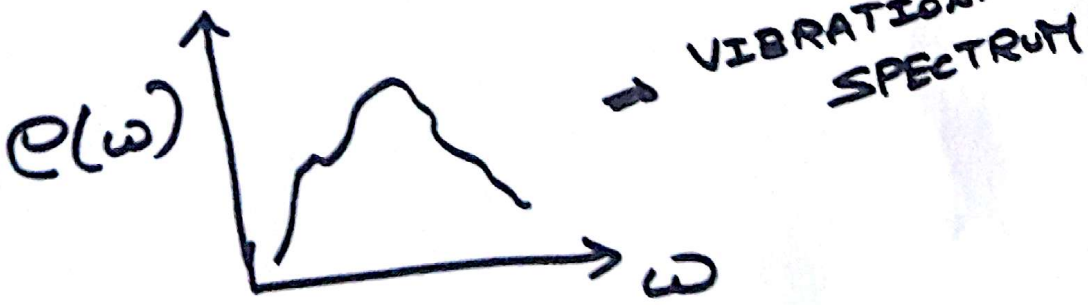
X_1 → 3N-COLUMN VECTOR

$$\mathcal{H} X_i = \lambda_i X_i \quad (i = 1, 2, \ldots 3N)$$

X_i → EIGEN VECTORS; λ_i → EIGEN VALUES (ω_i)

- VIBRATIONAL DENSITY of STATES:

$$\rho(\omega) = \sum_{i=1}^{3N-6} \delta(\omega - \omega_i)$$



⇒ VIBRATIONAL SPECTRUM

3N-6 ⇒ NON-LINEAR MOLECULES
3N-5 ⇒ LINEAR MOLECULES

- DEFINE NORMAL COORDINATES

$$Q_k = \sum_{i=1}^{3N} a_{ik} q_i \qquad k = 1, 2, \ldots, 3N$$

SUCH THAT

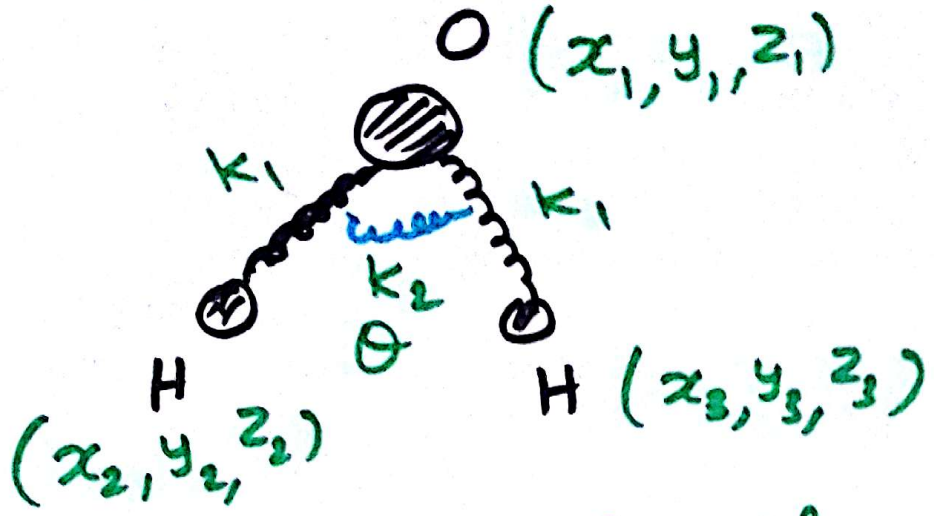
$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$

$$U = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

$\Rightarrow$ HAMILTONIAN IS SEPARABLE

$$H = \left(\frac{1}{2}\dot{Q}_1^2 + \lambda_1 Q_1^2\right) + \left(\frac{1}{2}\dot{Q}_2^2 + \lambda_2 Q_2^2\right) + \ldots + \left(\frac{1}{2}\dot{Q}_{3N}^2 + \lambda_{3N} Q_{3N}^2\right)$$

WATER MOLECULE



$$U(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{2} k_1 (\vec{r}_1 - \vec{r}_2)^2 + \frac{1}{2} k (\vec{r}_1 - \vec{r}_3)^2 + \frac{1}{2} k_2 (\theta - \theta_0)^2$$