

• HESSIAN FOR AN N-ATOM SYSTEM

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

$3N \times 3N$ 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 $U(\{q_i\}) = \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 U}{\partial q_i \partial q_j} \right)_0 q_i q_j$

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

$$\ddot{q}_j + \sum_{i=1}^{3N} H_{ji} q_i = 0$$

• DIAGONALIZATION OF THE HESSIAN

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

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

BLOCK MATRIX

$$X = \begin{pmatrix} X_1 & X_2 & \dots & X_N \end{pmatrix}$$

3N-
COLUMN
VECTOR

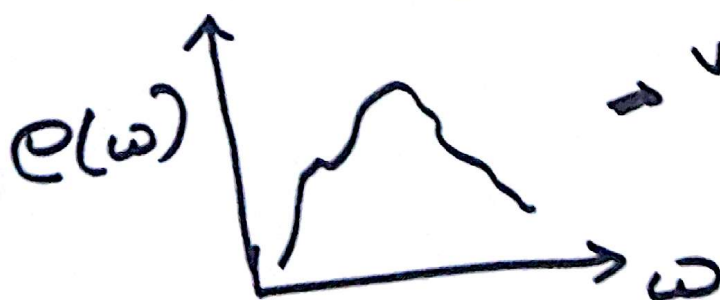
$$H X_i = \lambda_i X_i \quad (i=1,2,\dots,3N)$$

EIGEN
VECTORS

EIGEN (ω)
VALUES

• 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

$$Q_k = \sum_{i=1}^{3N} a_{ik} q_i$$

$$k = 1, 2, \dots, 3N$$

SUCH THAT

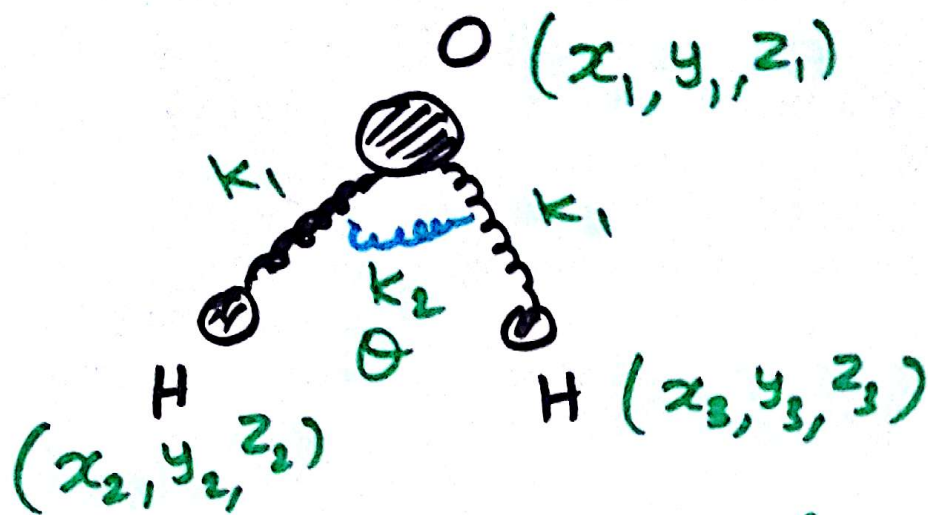
$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$

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

\Rightarrow HAMILTONIAN IS SEPARABLE

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

WATER MOLECULE



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

DIATOMIC MOLECULE

• NON-ROTATING HARMONIC VIBRATOR :

$$\text{ENERGY} \Rightarrow E_v^{\text{HAR}} = \left(v + \frac{1}{2}\right) \hbar \omega$$

VIBRATIONAL LEVELS ARE EQUALLY SPACED

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{SELECTION RULE} \Rightarrow \Delta v = \pm 1 \quad v = 0, 1, 2, \dots$$

• NON-ROTATING ANHARMONIC VIBRATOR :

$$\text{ENERGY} \Rightarrow E_v^{\text{ANH}} = \left(v + \frac{1}{2}\right) \hbar \omega - \left(v + \frac{1}{2}\right)^2 \hbar \omega x_e$$

$$\text{SELECTION RULE} \Rightarrow \Delta v = \pm 1, \pm 2, \pm 3, \dots$$

VIBRATIONAL LEVELS CROWD MORE CLOSELY TOGETHER WITH INCREASING v .

• RIGID (NON-VIBRATING) ROTATOR :

$$\text{ENERGY} \Rightarrow E_J = \frac{\hbar^2}{2I} J(J+1)$$

$$I = \mu r^2$$

$$J = 0, 1, 2, \dots$$

THE ENERGY DIFFERENCE BETWEEN TWO SUCCESSIVE/ADJACENT LEVELS INCREASES WITH J .

I INCREASES WITH J

$$\text{SELECTION RULE} \Rightarrow \Delta J = \pm 1$$

QUICK ROTATION INCREASES CENTRIFUGAL FORCE

• NON-RIGID ROTATOR :

$$E_J = B J(J+1) - D [J(J+1)]^2 + H [J(J+1)]^3 + \dots$$

STRETCHING: NO VIBRATION

ALL BONDS ARE ELASTIC TO SOME EXTENT
BOND LENGTH INCREASES WITH J

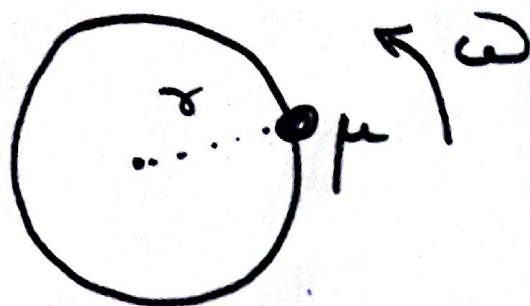
$$\text{SELECTION RULE} \Rightarrow \Delta J = \pm 1$$

ATOMS MOVE APART

NON-RIGID ROTATOR

• CENTRIFUGAL FORCE

$$F_D = \mu \omega^2 r$$



• RESTORING FORCE DUE TO CHEMICAL BOND

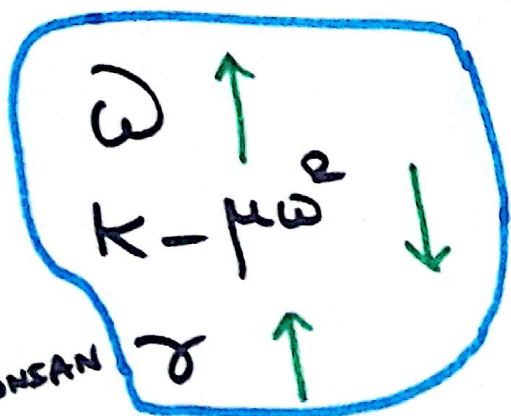
$$F_R = K(r - r_0)$$

$$F_D = F_R$$

$$K(r - r_0) = \mu \omega^2 r$$

$$r - r_0 = \frac{\mu \omega^2 r}{K}$$

$$r = \frac{K r_0}{K - \mu \omega^2}$$



$$L \Rightarrow \sqrt{J(J+1)} \hbar$$

HAMILTONIAN

$$\begin{aligned} H &= \frac{1}{2} I \omega^2 + \frac{1}{2} K (r - r_0)^2 \\ &= \frac{1}{2} I \omega^2 + \frac{1}{2} K \left(\frac{\mu \omega^2 r}{K} \right)^2 \\ &= \frac{L^2}{2I} + \frac{1}{2} \frac{(I \omega^2)^2}{K r^2} = \frac{L^2}{2I} + \frac{L^4}{2I^2 K r^2} \end{aligned}$$

DIATOMIC VIBRATING-ROTATOR

- ROTATIONAL ENERGY SEPARATIONS
 $1 - 10 \text{ cm}^{-1}$
- VIBRATIONAL ENERGY SEPARATIONS
 $\sim 3000 \text{ cm}^{-1}$

- APPROXIMATION:

BORN-OPPENHEIMER APPROXIMATION: MOLECULE EXECUTES ROTATIONS AND VIBRATIONS INDEPENDENTLY.

$$E_{\text{TOTAL}} = E_{\text{ROT}} + E_{\text{VIB}}$$
$$= B J(J+1) - D J^2(J+1)^2$$
$$+ (v + \frac{1}{2}) \hbar \omega - (v + \frac{1}{2})^2 \hbar \omega x_e$$

- SELECTION RULES:

$$\Delta v = \pm 1, \pm 2, \dots$$

$$\Delta J = \pm 1$$

