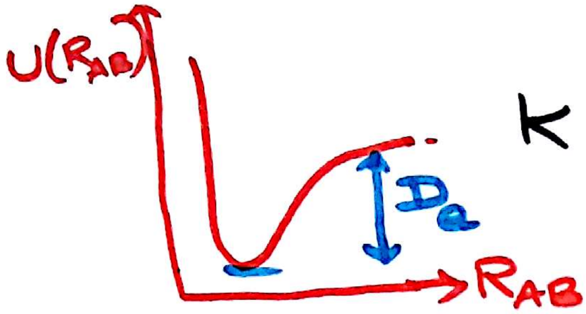
ANHARMONICITY

- HARMONIC POTENTIAL $U(R_{AB}) = \frac{1}{2} k (R_{AB} - R_0)^2$



$$k \equiv \left. \frac{d^2 U(R_{AB})}{dR_{AB}^2} \right|_{R_{AB} = R_0}$$

$\frac{1}{2} k x^2$

$x = R_{AB} - R_0$

- ANHARMONIC POTENTIAL (OR) MORSE POTENTIAL

$$U(R_{AB}) = D_e \left[1 - e^{-a(R_{AB} - R_0)} \right]^2$$

$x = R_{AB} - R_0$

$$= D_e \left[1 - \left(1 - ax + \frac{a^2 x^2}{2} - \frac{1}{6} a^3 x^3 + \cdots \right) \right]^2$$

$x \to 0$; IGNORE HIGHER ORDER TERMS

$$U(R_{AB}) \simeq D_e a^2 x^2$$
$$\simeq \frac{1}{2} (2 D_e a^2) x^2$$

$k = 2 D_e a^2$

$\Downarrow$

HARMONIC FORM

WHAT IF x IS LARGE !

$$U(R_{AB}) \simeq D_e \left[\left(ax - \frac{a^2 x^2}{2} \right)^2 \right]$$

$$\simeq D_e \left(a^2 x^2 + \frac{a^4 x^4}{4} - 2(ax)\left(\frac{a^2 x^2}{2} \right) \right)$$

$$\simeq \underbrace{\boxed{\frac{1}{2} (2 D_e a^2) x^2}}_{\text{HARMONIC}} \underbrace{- a^3 x^3 + \frac{a^4 x^4}{4} - \cdots}_{\text{ANHARMONIC}}$$

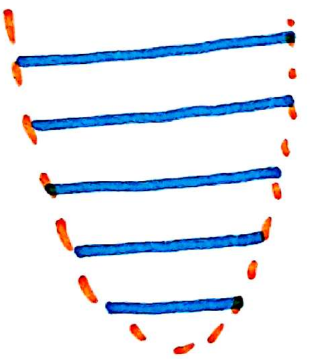
PERTURBATION TO HARMONIC POTENTIAL

$$E_v^{\text{HARMONIC}} = \left(v+\tfrac{1}{2}\right)\hbar\omega$$

$$E_v^{\text{ANHARMONIC}} = \left(v+\tfrac{1}{2}\right)\hbar\omega - \left(v+\tfrac{1}{2}\right)^2\hbar\omega\, x_e$$

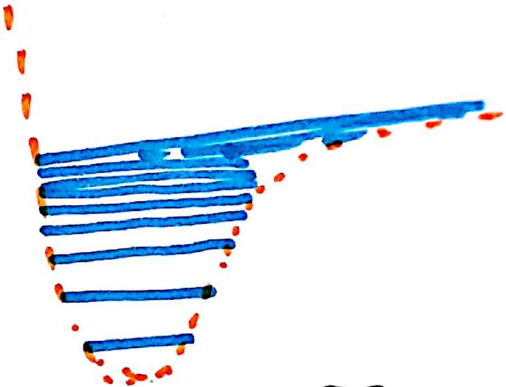
ANHARMONICITY CONSTANT (POSITIVE)

$$E_v^{\text{GENERAL}} = \left(v+\tfrac{1}{2}\right)\hbar\omega - \left(v+\tfrac{1}{2}\right)^2\hbar\omega\, x_e + \left(v+\tfrac{1}{2}\right)^3\hbar\omega\, t_e + \cdots$$



HARMONIC

ENERGY LEVELS ARE EQUALLY SPACED



ANHARMONIC

SPACING BETWEEN SUCCESSIVE LEVELS DECREASES WITH INCREASING V

(EFFECT OF ANHARMONICITY INCREASES WITH V)

SELECTION RULES CHANGE:

$|\Delta v| > 1 \Rightarrow$ ARE ALSO ALLOWED (WEAK)

$v=0 \rightarrow v=1$ FUNDAMENTAL

$v=0 \rightarrow v=2$ FIRST OVERTONE

$v=0 \rightarrow v=3$ SECOND OVERTONE

NORMAL MODES

- CONSIDER A POLYATOMIC SYSTEM
- $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \Rightarrow$ COORDINATES

  $(\vec{r}_{0,1}, \vec{r}_{0,2}, \ldots, \vec{r}_{0,N}) \Rightarrow$ EQUILIBRIUM CONFIGURATION
- $U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \Rightarrow$ POTENTIAL ENERGY OF THE SYSTEM

$$
\begin{aligned}
U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = {} & U(\vec{r}_{0,1}, \vec{r}_{0,2}, \ldots, \vec{r}_{0,N}) \\
& + \underbrace{\vec{\nabla}_{3N} U \Big|_0 \cdot \vec{\Delta r}_{3N}}_{0} \\
& + \frac{1}{2} \nabla^2_{3N \times 3N} U \Big|_0 \cdot \left(\vec{\Delta r}_{3N} \cdot \vec{\Delta r}_{3N}\right) + \cdots
\end{aligned}
$$

HERE

$$\vec{\nabla}_{3N} U \equiv \left(\frac{\partial U}{\partial \vec{r}_1}, \frac{\partial U}{\partial \vec{r}_2}, \ldots, \frac{\partial U}{\partial \vec{r}_N}\right)$$

$$\vec{\Delta r}_{3N} \equiv \left(\vec{r}_1 - \vec{r}_{0,1}, \vec{r}_2 - \vec{r}_{0,2}, \ldots, \vec{r}_N - \vec{r}_{0,N}\right)$$

RECALL PERTURBATION THEORY

$$\hat{H} = \hat{H}_0 + \hat{H}^{(1)}$$

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + D_e\left[1 - e^{-ax}\right]^2\psi(x) = E\,\psi(x)$$

HARMONIC OSCILLATOR

$$\simeq \boxed{-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}(2D_e a^2)x^2}$$

$$\left[\frac{1}{2}(2D_e a^2)x^2 - a^3x^3 + \frac{a^4}{4}x^4\right]\psi(x) = E\,\psi(x)$$

$$\simeq \left[\hat{H}_0 - a^3x^3 + \frac{a^4}{4}x^4\right]\psi(x) = E\,\psi(x)$$

$$\Rightarrow \hat{H}^{(1)} = -a^3x^3 + \frac{a^4}{4}x^4$$

$$E_v^{HAR} = \int_x \psi^*_{v,0}(x)\,\hat{H}_0\,\psi_{v,0}(x)\,dx = \langle\psi_{v,0}|\hat{H}_0|\psi_{v,0}\rangle$$

HARMONIC WAVE FUNCTION

$$E_v^{ANH} = \int_x \psi^*_v(x)\,\hat{H}\,\psi_v(x)\,dx = E_v^{HAR} + \Delta E$$

$$\psi_v(x) = \sum_i c_i\,\psi_{i,0}(x)$$

$$c_v \sim 1$$

SMALL PERTURBATION;

$$\Delta E \simeq \int_x \psi^*_{v,0}(x)\,\hat{H}^{(1)}\,\psi_{v,0}(x)\,dx$$

$$\Delta E = D\int_{-\infty}^{\infty} H_v(x)\, x^3 H_v(x)\, e^{-\alpha x^2}\, dx \rightarrow 0$$

$$+\, G\int_{-\infty}^{\infty} H_v(x)\, x^4 H_v(x)\, e^{-\alpha x^2}\, dx \rightarrow \neq 0$$

HERE

$[H_v(x)]^2 \Rightarrow$ EVEN | SYMMETRIC

$e^{-\alpha x^2} \Rightarrow$ EVEN | SYMMETRIC

$x^3 \Rightarrow$ ODD | ANTI SYMMETRIC

$x^4 \Rightarrow$ EVEN | SYMMETRIC

$$\boxed{\Delta E \neq 0}$$

$$\hat{H}^{(1)} = -\underset{\substack{\downarrow \\ \text{CUBIC ANHARMONICITY}}}{a^3 x^3} + \underset{\substack{\downarrow \\ \text{QUADRIC ANHARMONICITY}}}{\frac{a^4}{4} x^4}$$

IN GENERAL,

$$\hat{H}^{(1)} = \sum_{i=3}^{\infty} a_i x^i$$

$$E_0^{ANH} = \frac{1}{2}\hbar\omega - \frac{1}{4}\hbar\omega x_e$$

$$E_0^{ANH} = E_0^{HAR} - \frac{1}{4}\hbar\omega x_e$$

$$E_1^{ANH} = \frac{3}{2}\hbar\omega - \frac{9}{4}\hbar\omega x_e$$

$$E_1^{ANH} = E_1^{HAR} - \frac{9}{4}\hbar\omega x_e$$

$$\Delta E_{01}^{ANH} = E_1^{ANH} - E_0^{ANH}$$

$$= \left(E_1^{HAR} - E_0^{\cancel{ANH}\,HAR}\right) - \hbar\omega x_e{}^{2}$$

$$\boxed{\Delta E_{01}^{ANH} = \Delta E_{01}^{HAR} - 2\hbar\omega x_e}$$

|||ly

$$\boxed{\Delta E_{12}^{ANH} = \Delta E_{12}^{HAR} - 4\hbar\omega x_e}$$

$$\boxed{\Delta E_{23}^{ANH} = \Delta E_{23}^{HAR} - 6\hbar\omega x_e}$$

$$\Delta E_{01}^{ANH} > \Delta E_{12}^{ANH} > \Delta E_{23}^{ANH} > \cdots$$

BUT $\Delta E_{01}^{HAR} = \Delta E_{12}^{HAR} = \Delta_{23}^{HAR} = \cdots$

- INTENSITY OF EMISSION SPECTRUM DEPENDS ON THE POPULATIONS OF THE EXCITED STATES
- EXCITED STATES ARE LESS POPULATED

$0 \rightleftarrows 1$: INTENSE (FUNDAMENTAL)

$|\Delta V| > 1$: OVERTONES (WEAK)

- FOR A SINGLE DIATOMIC MOLECULE:

⇒ USING HARMONIC OSCILLATOR MODEL:

(NO ROTATION)

- SINGLE EMISSION FREQUENCY
- NO OVERTONES

⇒ USING ANHARMONIC OSCILLATOR MODEL:

- MULTIPLE EMISSION FREQUENCIES
- OVERTONES

ROUGH ESTIMATION OF POPULATION:

$$N_{V=1} \propto e^{-\beta E_{V=1}} \quad ; \quad \beta = \frac{1}{k_B T}$$

$$N_{V=0} \propto e^{-\beta E_{V=0}}$$

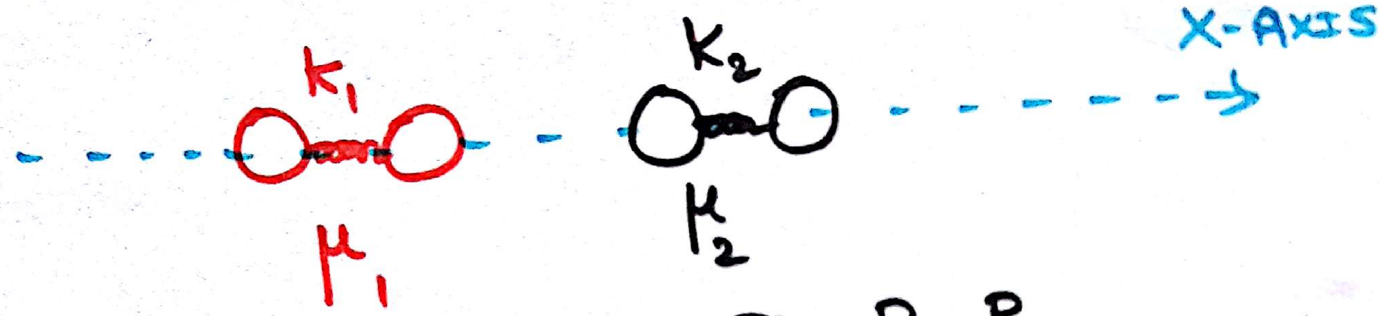
$$\frac{N_{V=1}}{N_{V=0}} = e^{-\beta\left[E_{V=1} - E_{V=0}\right]} = e^{-\beta h \nu}$$

TAKE $T = 300k$; $\nu_{IR} \sim 10^4 - 10^1 \ cm^{-1}$

$\boxed{\nu_{IR} = 1000 \ cm^{-1}}$

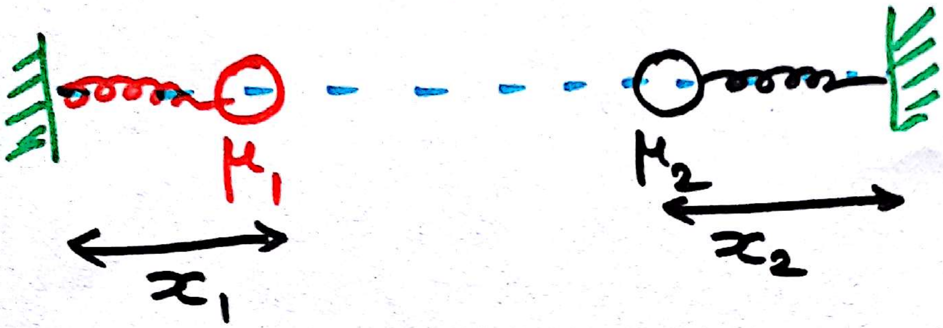
NORMAL MODES

- CONSIDER TWO DIATOMIC MOLECULES



$$x_2 = R_2 - R_{0,2}$$

$$x_1 = R_1 - R_{0,1}$$



- UNCOUPLED $\Rightarrow$ TWO INDEPENDENT HARMONIC OSCILLATORS

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

POTENTIAL ENERGY

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

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

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

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

$$U(x_1,x_2) = (x_1 \; x_2)\begin{pmatrix} \frac{1}{2}\mu_1\omega_1^2 & 0 \\ 0 & \frac{1}{2}\mu_2\omega_2^2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

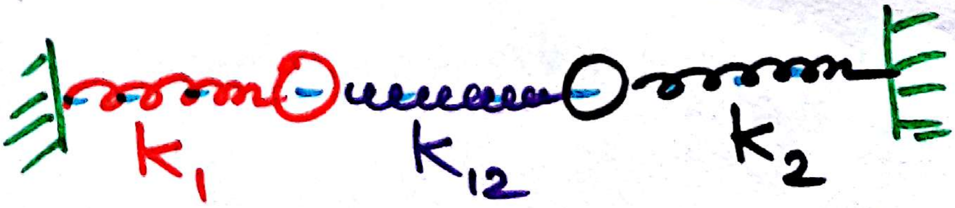
SINCE $k_1 = \dfrac{\partial^2 U}{\partial x_1^2}$; $\dfrac{\partial^2 U}{\partial x_1 \partial x_2} = 0$

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

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

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

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

$\Rightarrow$ NON-DIAGONAL HESSIAN ; EIGENVALUES $\Rightarrow \omega$

DIAGONALIZE $\Rightarrow$ EIGEN VECTORS $\Rightarrow$ MODES