Vibration Polyatomic

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Vibration in Polyatomic

Equations of Motion

$T = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{r}_i^2$

$V(r) = D_e\left(1 - e^{-\alpha(r-r_e)}\right)^2; morse\ potential$

1/2

$Each\ i^{th}\ \ atom\ has\ position\ x_i, y_i, z_i and\ veloctiy\ , v_{xi}, v_{yi}, v_{zi}$

Define mass-weighted generalized $(\sigma - ordinates)$

$\Delta x_i = x_i - x_i^e$

$q_i = \sqrt{m_i}\,\Delta x_i$

$This\ makes\ T = \frac{1}{2}\sum_{j=1}^{3N} \dot{q}_j{}^2$

$\dot{q}_j = \frac{d}{dt} q_j$

$V = PE = V(q_i, i = 1, \ldots 3N)$

Taylor expand V about equilibrium

$q_j = 0\ \forall j$

$V = V_o + \sum_{j=1}^{3N}\left(\frac{\partial V}{\partial q_j}\right)_0 q_j + \frac{1}{2}\sum_{j,k=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_k}\right)_0$

At equilibrium, the first order terms are all 0 since we are near the minimum

$V = V_o + \frac{1}{2}\sum_{j,k=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_k}\right)_0$

$V(\vec{q}) = \sum_{j,k=1}^{3N} b_{jk} q_j q_k$

$b_{jk} = \frac{1}{2}\left(\frac{\partial^2 V}{\partial q_j \partial q_k}\right)_0\ \ a\ 3N \times 3N\ matrix$

So far its just a generalization of diatomic

The Langragian Equation of Motion, a reformulation of Newtons equation of Motion

$L = T - V$

$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0, \qquad 3N\ \ 2nd\ order\ ODE\ equations$

$\ddot{q}_j + \sum_{k=1}^{3N} b_{jk} q_k = 0$

$Imagine\ b_{jk}\ is\ diagonal\ b_{jk} = b_{jk}\delta_{jk}$

Then the equation simplifies to

$\ddot{q_j} + b_{jj} q_j = 0$

This is simple harmonic oscillator

$q_j = A_j e^{\omega_j t + \phi_j}$

In general, if b_jk is nondiagonal we have a 3N coupled differential equations

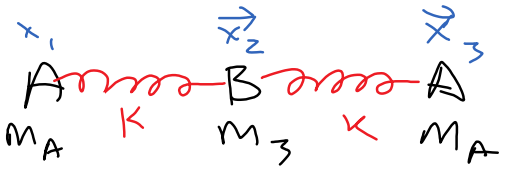
The solutions are called normal modes
Choose a coordinate system that makes b_{jk} diagonal
$\ddot{\vec{q}} + B\vec{q} = 0$
Q_n is some linear combination of the q_i that reults in transforming b_{jk} into a diagonal matrix B

$B\vec{q} = \lambda I\vec{q}$
$\det(B - \lambda I) = 0$
$\lambda_j \; are \; the \; 3N \; eigenvalues \; of \; B$
$in \; terms \; of \; the \; Q_n \rightarrow \ddot{Q_n} + \omega_n^2 Q_n = 0$
$Q_n = A_n \sin(\omega_n t + \psi_n) \; , \qquad \omega_n = \sqrt{\lambda_n}$

$$T = \frac{1}{2}\sum_{n=1}^{3N} \dot{Q}_n^2$$
$$V = \frac{1}{2}\sum_{n=1}^{3N} \lambda_n Q_n^2$$
$\Rightarrow 3N \; harmonic \; oscillators$
This formulation includes overall translation motion of the CM and Rigid Body Rotation KE
$6(5) \; of \; the \; \lambda_n are \; zero$
Linear molecules

The corresponding Q_n to these zeros describes overall translation and rotation of molecules
$The \; 3N - 6(5) \; coordinates \; are \; vibrations$

An example – a linear triatomic



The potential here is
$$V(x_1, x_2, x_3) = \frac{1}{2}k(x_2 - x_1)^2 + \frac{1}{2}k(x_3 - x_2)^2$$
$B \; matrix$
$b_{11} = b_{33} = \frac{k}{m_A}, \; both \; particles \; 1 \; and \; 3 \; are \; attached \; to \; particle \; B$
$$b_{12} = b_{23} = -\frac{k}{\sqrt{m_A m_b}}, something \; standard \; deviation$$
$$b_{22} = \frac{2k}{M_B} \; there \; are \; 2 \; masses \; connected \; to \; particle \; B$$
$b_{13} = 0$, $1 \; and \; 3 \; are \; not \; connected$
$$B - \lambda I = \begin{bmatrix} b_{11} - \lambda & b_{12} & 0 \\ b_{12} & b_{22} - \lambda & b_{12} \\ 0 & b_{12} & b_{11} - \lambda \end{bmatrix}$$
$$\det[B - \lambda I] = (b_{11} - \lambda)^2(b_{22} - \lambda) - 2(b_{11} - \lambda)b_{12}^2 = 0$$
$$\lambda_1 = \frac{k}{m_A} \rightarrow v_1 = \frac{1}{2\pi}\sqrt{\frac{k}{m_A}}$$
$$\lambda_2 = k_{m_A} + \frac{2k}{m_B} \rightarrow v_2 = \frac{1}{2\pi}\sqrt{\frac{k}{m_A} + \frac{2k}{m_b}}$$
$\lambda_3 = 0$
The normal modes
Orthogonal eigenvectors of B

$$\sum_k |l_{ik}|^2 = \sum l_{ik}^* l_{ik} = 1$$

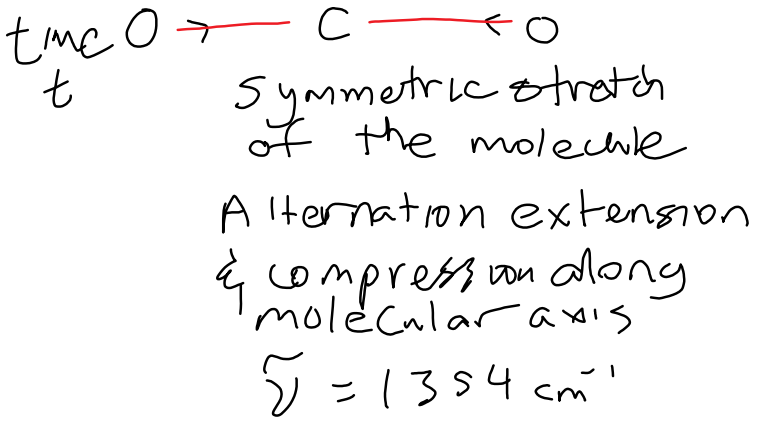
$$\vec{l}_1 = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\0\\-1\end{bmatrix}, \qquad \vec{l}_2 = \begin{bmatrix}b\\2a\\b\end{bmatrix}, \qquad \vec{l}_1 = \begin{bmatrix}a\\b\\a\end{bmatrix}$$

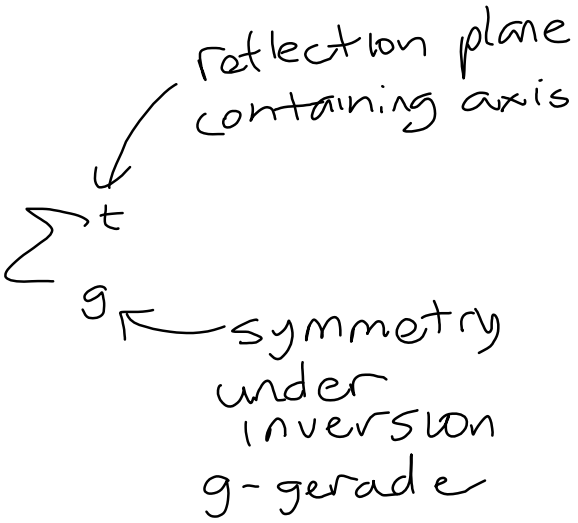
$$a = \sqrt{\frac{m_A}{2M}}, \qquad M = M_A + M_A + M_B$$

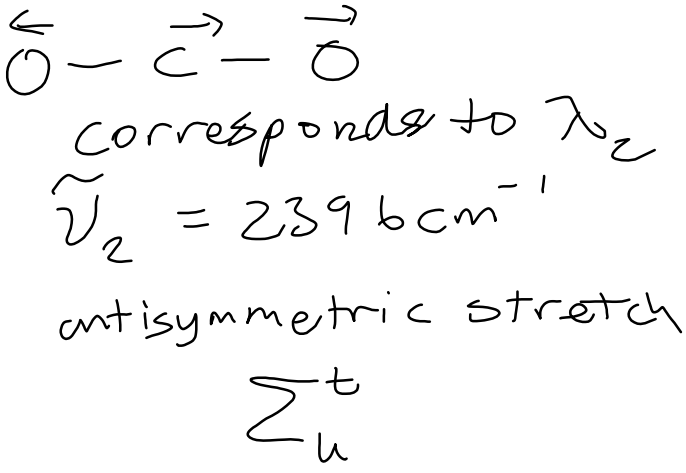
$$b = \sqrt{\frac{m_b}{2M}}$$

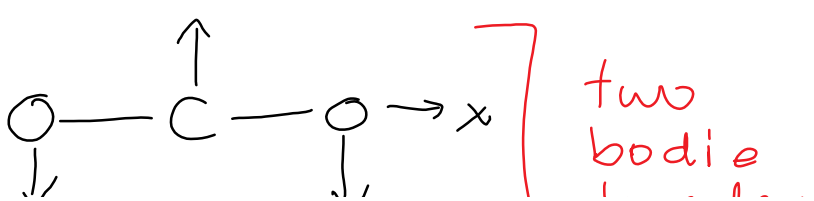
$S = unitary\ orthogonal\ matrix\ of\ these\ columns$
$\Rightarrow unitary\ transformation\ to\ diagonlize\ B$

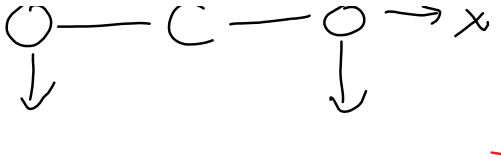
$Recall \quad q_i = \sqrt{m_i}(x_i)$
$\vec{Q} = S^t \vec{q}$
$Q_1 = \sqrt{\frac{m_A}{2}}(x_1 - x_3)$
$CO_2, \qquad 3N - 5 = 9 - 5 = 4$











bodie bending modes

$\tilde{\nu} = 673\,cm^{-1}$

(non linear triatomic H_2O $3N-6$ modes { one bending mode is missing

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Quantum treatment

Classically

$$E_{tot} = T + V = \frac{1}{2}\sum_{i=1}^{3N} \dot{Q}_i^{\,2} + \frac{1}{2}\sum_{j=1}^{3N} \lambda_j Q_j^2$$

$$E_{tot}^{vib} = \frac{1}{2}\sum_{i=1}^{3N-6(5)} \dot{Q}_i^{\,2} + \frac{1}{2}\sum_{j=1}^{3N-6(5)} \lambda_j Q_j^2 \text{, subtract the translation and rotational}$$

$$\hat{H} = \sum_{j=1}^{3N-6}\left(-\frac{\hbar^2}{2}\partial_{Q_i}^2 + \lambda_i Q_i^2\right)$$

Some $3N-6$ *independent Q.H.Osc. solutions of the Schrodinger Equation*

$$\psi_{vib}(Q_i, \dots, Q_{3N-6(5)}) = \chi_{v_1}(Q_1)\chi_{v_2(Q_2)} \cdots \chi_{v_{3N-6}(5)}(Q_{3N-6(5)})$$

each

$$\chi_{v_i}(Q_i) = N_{v_i} H(\sqrt{\alpha_i} Q_i) e^{-\frac{\alpha_i Q_i^2}{2}}$$

$$\alpha_i = \frac{2\pi v_i}{\hbar}$$

The vibratonal state of molecule is specificed by $3N-6$ vibrational quantum $\#'s$

v_i' *each* 0,1,2,3, … ∞

The corresponding energy

$$E_{vib} = \sum_{i=1}^{3N-6(5)}\left(N_1 + \frac{1}{2}\right)h\nu_i$$

The vibrational spectrum difference is the sum of $3N-6$ *individual vibrational spectra*