FREE VIBRATIONS OF LINEAR TRIATOMIC PARTICLE

Dr D S Christy
Asst. Professor
St. John's College
Palayamkottai

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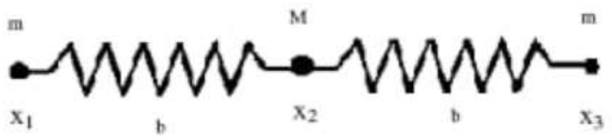
Consider a linear triatomic particle symmetric molecule of type YX_2 eg.Co_2 shown in figure.

Model of the Triatomic Molecule



Y is the central atom.

Further assume that there exist an elastic bond between the central atom and the end atoms of force constant K.

Let the mass of each end atom be m and that of central atom be M.

The displacements of atoms from equilibrium configuration by the generalized co-ordinates q_1, q_2, q_3.

KINETIC ENERGY $T = {}^{1}/_{2} m v^2$

$$T = {}^{1}/_{2} m \dot{q}_1{}^2 + {}^{1}/_{2} M \dot{q}_2{}^2 + {}^{1}/_{2} m \dot{q}_3{}^2$$

$$=\frac{1}{2}m(\dot{q}_1^{\,2}+\dot{q}_3^{\,2})+\frac{1}{2}M\dot{q}_2^{\,2}$$

$$2T=\begin{pmatrix}\dot{q}_1 & \dot{q}_2 & \dot{q}_3\end{pmatrix}\begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}\begin{pmatrix}\dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3\end{pmatrix}$$

$$T=T_{ij}=\begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}$$

POTENTIAL ENERGY $V = {}^{1}/_{2} k(q_2 - q_1)^2 + {}^{1}/_{2} k(q_3 - q_2)^2$

$$= {}^{1}/_{2}\underline{k}(q_2{}^2 + q_1{}^2 - 2q_1q_2 + q_3{}^2 + q_2{}^2 - 2q_3q_2)$$

$$= {}^{1}/_{2}\underline{k}(q_1{}^2 + 2q_2{}^2 + q_3{}^2 - 2q_1q_2 - 2q_3q_2)$$

$$2V = k(q_1{}^2 + 2q_2{}^2 + q_3{}^2 - 2q_1q_2 - 2q_3q_2)$$

$$= \begin{bmatrix} q_1 q_2 q_3 \end{bmatrix} \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix}$$

$$V = V_{ij} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

SECULAR EQUATION $|V - \omega^2 T| = 0$

$$V=\begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

$$T=\begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}$$

$$|V\text{-}\omega^2 T| = \left| \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix} - \omega^2 \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix} \right| = 0$$

$$\begin{vmatrix} k-\omega^2 m & -k & 0 \\ -k & 2k-\omega^2 M & -k \\ 0 & -k & k-\omega^2 m \end{vmatrix} = 0 \longrightarrow (1)$$

$$k-\omega^2 m[(2k-\omega^2 M)(k-\omega^2 m)]-k^2]+k(-k(k-\omega^2 m)=0$$

$$k-\omega^2 m[(2k^2-2k\omega^2 m)-k\omega^2 M+\omega^4 mM)-k^2]+k(-k^2-k\omega^2 m)=0$$

$$k-\omega^2 m[2k^2-2k\omega^2 m-k\omega^2 M+\omega^4 mM-2k^2]=0$$

$$-2k^2\omega^2 m - k^2\omega^2 M + k\omega^4 mM + 2k\omega^4 m^2 + k\omega^4 mM - \omega^6 m^2 M = 0$$

$$\omega^2[[-2k^2 m - k^2 M + k\omega^2 mM + 2km^2\omega^2 + k\omega^2 mM - \omega^4 m^2 M] = 0$$

$$\omega^2[[-k(mk-2mk) - \omega^2 mM] + [k(2m^2\omega^2 + Mm\omega^2] - \omega^4 m^2 M]] = 0$$

$$\omega^2 \, [[-k(mk-2mk) - \omega^2 mM] + \omega^2 m[k(2m+M) - \omega^2 Mm]]=0$$

$$\omega^2[(\omega^2 m - k)[k - M + 2m) - \omega^2 mM] = 0$$

$\omega^2 = 0$ therefore, $\omega_1=0$

$$\omega^2 m - k = 0$$

$$\omega^2 m = k$$

$$\omega^2 = \frac{k}{m}$$

$$\omega_2 = \sqrt{\frac{k}{m}}$$

$$k - M + 2m - \omega^2 mM = 0$$

$$-\omega^2 \text{mM} = k(M + 2m)$$

$$-\omega^2 = \frac{k(M+2m)}{mM}$$

$$\omega^2 = -\frac{k(M+2m)}{mM}$$

$$\boldsymbol{\omega} = \sqrt{-\frac{k(M+2m)}{mM}}$$

$$\omega_3 = \sqrt{\frac{k}{m}\left(1 + \frac{2m}{M}\right)}$$

The first case refers to Translatory motion ω_1 of the atoms and the rest two ω_2, ω_3 are the Oscillatory motion.

In order to calculate the normal co-ordinates η_1, η_2, η_3

In order to calculate the normal co-ordinates η_1, η_2, η_3

$$q_j = \sum_k a_{jk} \eta_k$$

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} a_{11} \\ a_{21} \\ a_{31} \end{pmatrix} \begin{pmatrix} a_{12} & a_{13} \\ a_{22} & a_{23} \\ a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{pmatrix}$$

calculation of the components a_{11}, a_{21}, a_{31} of eigen vector a_1 ,

$$\sum_j (V_{ij} - \omega^2 T_{ij})\, a_j = 0 \qquad (i=1,2,3\ldots)$$

CASE 1:

Substitute ω_1=0 in equation 1,

Equation 1 becomes, $$\begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix} \begin{bmatrix} a_{11} \\ a_{21} \\ a_{31} \end{bmatrix} = 0$$

ka_{11} - ka_{21}=0 ⟶ (a)

-ka_{11}+2$ka_{21} - ka_{31}$=0 ⟶ (b)

-ka_{21}+ka_{31}=0 ⟶ (c)

From a , ka_{11} = ka_{21}

From c , - ka_{21}=$-ka_{31}$

ka_{21}= ka_{31}

substitute the value of ka_{21} in equation b, substitute the value of ka_{21} in equation b,

-ka_{11} +ka_{31} $- ka_{31}$=0

-ka_{11}+ka_{31}=0

ka_{11}= ka_{31}

from the results,

$$a_{11}=a_{21}=a_{31}=\boldsymbol{\alpha}$$

Therefore $a_1 = \begin{pmatrix} \alpha_{a_{11}} \\ \alpha_{a_{21}} \\ \alpha_{a_{31}} \end{pmatrix}$

CASE 2:

Substitute $\omega_2=\sqrt{\frac{k}{m}}$ in equation 1 and calculate the components a_{11}, a_{21}, a_{31} of eigen vectors a_2

Equation 1 becomes, $\begin{pmatrix} k-\frac{k}{m}m & -k & 0 \\ -k & 2k-\frac{k}{m}M & -k \\ 0 & -k & k-\frac{k}{m}m \end{pmatrix}\begin{bmatrix} a_{12} \\ a_{22} \\ a_{32} \end{bmatrix}=0$

$$\begin{pmatrix} 0 & -k & 0 \\ -k & 2k-\frac{kM}{m} & -k \\ 0 & -k & 0 \end{pmatrix}\begin{bmatrix} a_{12} \\ a_{22} \\ a_{32} \end{bmatrix}=0$$

$$-ka_{22}=0$$

$$so,\ a_{22}=0$$

$$-ka_{12}+(2k-\frac{kM}{m})\,a_{22}-ka_{32}=0$$

Substituting the value of $a_{22}=0$ in the above equation,

$$-\,ka_{12}=ka_{32}$$

$$-a_{12}=a_{32}$$

From these,compounds of a_2 are,

$$a_2 = \begin{pmatrix} \beta_{a_{12}} \\ \beta_{a_{22}} \\ \beta_{a_{32}} \end{pmatrix}$$

CASE 3:

Substitute $\omega_{3=}\sqrt{\frac{k}{m}(1+\frac{2m}{M})}$

$\omega_3{}^2 = \frac{k}{m}(1+\frac{2m}{M})$ in equation 1 and the compounds of a_3 are a_{13}, a_{23}, a_{33}.

Equation 1 becomes,

$$\begin{pmatrix} k-[\frac{k}{m}\left(1+\frac{2m}{M}\right)] & -k & 0 \\ -k & 2k-\left[\frac{k}{m}\left(1+\frac{2m}{M}\right)\right]M & -k \\ 0 & -k & k-[\frac{k}{m}(1+\frac{2m}{M})m] \end{pmatrix}\begin{pmatrix} a_{13} \\ a_{23} \\ a_{33} \end{pmatrix}=0$$

$$\begin{pmatrix} -\frac{2mk}{M} & -k & 0 \\ -k & \frac{-KM}{m} & -k \\ 0 & -k & -\frac{2mk}{M} \end{pmatrix} \begin{bmatrix} a_{13} \\ a_{23} \\ a_{33} \end{bmatrix} = 0$$

$$-\frac{2mk}{M} a_{13} - \mathrm{k}\, a_{23} = 0 \longrightarrow \text{(e)}$$

$-k\, a_{23} - \frac{-KM}{m} a_{13} - k\, a_{33} = 0 \longrightarrow$ (f)

$-k\, a_{23} - \frac{2mk}{M} a_{33} = 0 \longrightarrow$ (g)

From equations (e) and (g),

$a_{13} = a_{33} = \boldsymbol{\gamma}$

From equation (f),

$$a_{23} = -\frac{-KM}{m} a_{13} - k\, a_{33} = 0$$

$$a_{23} = \frac{-2m}{M} a_{13}$$

$$a_{23} = \frac{-2m}{M} \boldsymbol{\gamma}$$

The compounds of a_3 are,

$$a_3 = \begin{pmatrix} \gamma \\ \frac{-2m}{M}\gamma \\ \gamma \end{pmatrix}$$

The Eigen value a_1, a_2, a_3 are found and if $\boldsymbol{\alpha, \beta \gamma}$ are known we can apply for the following orthogonality,

$$a^T \text{Ta=I} \longrightarrow (2)$$

$$a_{ij}=\begin{pmatrix} \alpha & \beta & \gamma \\ \alpha & 0 & \frac{-2m}{M}\gamma \\ \alpha & -\beta & \gamma \end{pmatrix}$$

$$(a_{ij})^T=\begin{pmatrix} \alpha & \alpha & \alpha \\ \beta & 0 & -\beta \\ \gamma & \frac{-2m}{M}\gamma & \gamma \end{pmatrix}$$

$$T_{ij}=\begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}$$

$$\mathrm{I}=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Substituting the values of a_{ij}, T_{ij}, $(a_{ij})^T$,I in equation (2),

$$\begin{pmatrix} \alpha & \alpha & \alpha \\ \beta & 0 & -\beta \\ \gamma & \frac{-2m}{M}\gamma & \gamma \end{pmatrix} * \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix} * \begin{pmatrix} \alpha & \beta & \gamma \\ \alpha & 0 & \frac{-2m}{M}\gamma \\ \alpha & -\beta & \gamma \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} \alpha & \alpha & \alpha \\ \beta & 0 & -\beta \\ \gamma & \frac{-2m}{M}\gamma & \gamma \end{pmatrix} * \begin{pmatrix} \alpha m & \beta m & \gamma m \\ \alpha M & 0 & -2\gamma m \\ \alpha m & -\beta m & \gamma m \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} \alpha^2(2m+M) & 0 & 0 \\ 0 & 2\beta^2 m & 0 \\ 0 & 0 & \gamma^2 2m(1+\frac{2m}{M}) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

From the above equation we can find $\boldsymbol{\alpha}$,,

a) $\alpha^2(2m + M)$=1

α^2=1/$(2m + M)$

$\boldsymbol{\alpha}$=1/$\sqrt{(2m + M)}$ ⟶ (3)

b) $2\beta^2 m$=1

β^2=1/2m

$\boldsymbol{\beta}$=1/$\sqrt{2m}$ ⟶ (4)

c) $\gamma^2 2m(1 + \frac{2m}{M})$=1

γ^2=1/$2m(1 + \frac{2m}{M})$

$$\boldsymbol{\gamma}=1/\sqrt{2m(1+\frac{2m}{M})} \longrightarrow (5)$$

Using the Eigen value a_1, a_2, a_3 and the equations (3),(4),(5) we can write the normal coordinates η_1,η_2,η_3 associated with normal frequencies ω_1, ω_2, ω_3

$$\begin{matrix} q_1 \\ q_2 \\ q_3 \end{matrix} = \begin{pmatrix} 1/\sqrt{(2m+M)} & 1/\sqrt{2m} & 1/\sqrt{2m(1+\frac{2m}{M})} \\ 1/\sqrt{(2m+M)} & 0 & -2\text{M/m}\sqrt{2m(1+\frac{2m}{M})} \\ 1/\sqrt{(2m+M)} & -1/\sqrt{2m} & 1/\sqrt{2m(1+\frac{2m}{M})} \end{pmatrix} \begin{bmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{bmatrix}$$

From the above equation we find $a_{22} = 0$ and $a_{12} = - a_{32}$ which indicates that the central atom doesnot take part in motion and the end atoms oscillate with equal amplitude but in opposite in phase.

In case 3, we find that $a_{13}=a_{33}=\boldsymbol{\gamma}$ and $a_{23}=\frac{-2m}{M}\ \gamma$ which indicates that end atoms vibrate in phase with equal amplitude whereas the central atom vibrates with a different amplitude.

Since in case 3 the molecules is asymmetrically stretched,oscillating dipole moment will be associated with the motion and corresponding band will appear in the Infrared region.

THANKYOU