Lect 9 Molecular vibration

§ General framework

Each atom has its equilibrium position $\vec{r}_i^{\,0}$, and its derivation from its equilibrium position is denoted as $\vec{u}_i = \vec{r}_i - \vec{r}_i^{\,0}$, where i is the index of atom. The potential

$$V = V_0 + \frac{1}{2} \sum_{i,i'} \sum_{\alpha\beta} \frac{\partial^2 V}{\partial u_\alpha(i)\, \partial_\beta u(j)} u_\alpha(i) u_\beta(j) + \cdots$$

Define the reduced displacement

$$W_\alpha(i) = (m_i)^{1/2} u_\alpha(i), \quad \text{and } D(ii')_{\alpha\beta} = (m_i m_j)^{1/2} \phi_{\alpha\beta}(ij)$$

where $\phi_{\alpha\beta}(ij) = \dfrac{\partial^2 V}{\partial u_\alpha(i)\, \partial u_\beta(j)}$

Then $$\boxed{H = \frac{1}{2} \sum_i \sum_\alpha P_\alpha^2(i) + \frac{1}{2} \sum_{ii'} \sum_{\alpha\beta} D_{\alpha\beta}(i,i')\, W_\alpha(i)\, W_\beta(i')}$$

where $P_\alpha(i) = \sqrt{m_i}\, \dot{u}_\alpha(i)$, which conjugates to $W_\alpha(i)$.

Then $$\mathcal{L} = T - V = \frac{1}{2} \sum_{i\alpha} \dot{W}_\alpha^2(i) - \frac{1}{2} \sum_{ii'} \sum_{\alpha\beta} D_{\alpha\beta}(i,i')\, W_\alpha(i)\, W_\beta(i')$$

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{W}_\alpha(i)}\right) = \frac{\partial \mathcal{L}}{\partial W_\alpha(i)} \Rightarrow \boxed{\ddot{W}_\alpha(i) = -\sum_{i'\beta} D_{\alpha\beta}(i,i')\, W_\beta(i')}$$

try Solution $W_\alpha(i) = e_\alpha(i)\, e^{-i\omega t}$, plug in

$$\Rightarrow \boxed{\omega^2 e_\alpha(i) = \sum_{i'\beta} D_{\alpha\beta}(i,i')\, e_\beta(i')}$$

dynamic equation
ω^2 is a positive eigenvalue of $D_{\alpha\beta}(i,i')$ and $e_\alpha(i)$ is eigenvector

§ Normal modes

There exist 3N solutions denoted as $e_\alpha(i|j)$, where $j=1,\cdots 3N$.

$e_\alpha(i|j)$ satisfies ortho-normal condition and the completeness . .

$$\boxed{\begin{aligned} \sum_{i,\alpha} e^*_\alpha(i|j)\, e_\alpha(i|j') &= \delta_{jj'} \\ \sum_{j} e^*_\alpha(i|j)\, e_\beta(i'|j) &= \delta_{\alpha\beta}\,\delta_{ii'} \end{aligned}} \leftarrow$$

basis for canonical modes

Canonical coordinates

$$w_\alpha(i) = \sum_{j=1}^{3N} e_\alpha(i|j)\, q_j \qquad \leftarrow \text{ define } P_j = \dot{q}_j$$

$$P_\alpha(i) = \dot{w}_\alpha(i) = \sum_{j=1}^{3N} e_\alpha(i|j)\, \dot{q}_j = \sum_{j=1}^{3N} e_\alpha(i|j)\, P_j$$

Then

$$\sum_{i,\alpha} P^2_\alpha(i) = \sum_{i,\alpha} \sum_{jj'} e^*_\alpha(i|j)\, P^*_j\, e_\alpha(i|j')\, P_{j'}$$

$$= \sum_{jj'} P^*_j P_{j'}\, \delta_{jj'} = \sum_j P^*_j P_j$$

$$\frac{1}{2} \sum_{ii'} \sum_{\alpha\beta} D_{\alpha\beta}(ii') \underbrace{\sum_{jj'} e^*_\alpha(i|j)\, q^*_j}_{w^*_\alpha(i)}\ \underset{w_\beta(j)}{e_\beta(i'|j')\, q_{j'}}$$

$\uparrow$
real

$$= \frac{1}{2} \sum_{jj'} q^*_j q_{j'} \sum_{ii',\alpha\beta} e^*_\alpha(i|j)\, D_{\alpha\beta}(i,i')\, e_\beta(i'|j')$$

$$= \frac{1}{2} \sum_{jj'} q^*_j q_{j'} \sum_{i,\alpha} e^*_\alpha(i|j) \underbrace{\sum_{i'\beta} D_{\alpha\beta}(i,i')\, e_\beta(i'|j')}_{\omega^2_{j'} e_\alpha(i|j')}$$

$$= \frac{1}{2} \sum_{jj'} q^*_j q_{j'} \overbrace{\delta_{jj'}}^{\omega^2_{j'}} = \frac{1}{2} \sum_j q^*_j q_j\, \omega_j$$

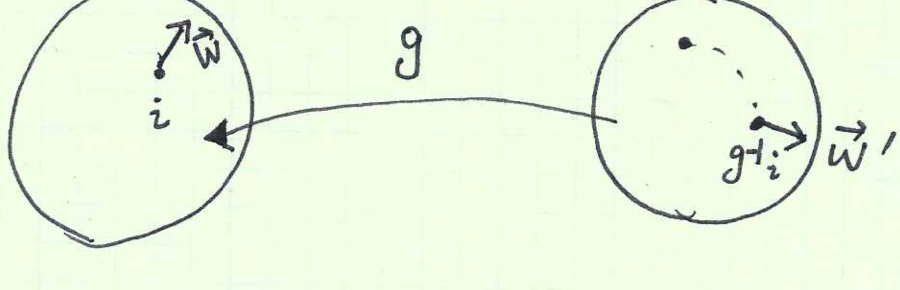
$$H = \frac{1}{2}\sum_{j=1}^{3N} P_j^* P_j + \frac{1}{2}\sum_{j=1}^{3N} \omega_j^2 q_j^* q_j$$

Since $D_{\alpha\beta}(i,i')$ is a real symmetric matrix, it can be diagnalized by real eigenvectors. Or if q_j is complex, then q_j^* is also an eigen-model with the same energy. We can either use their real and imaginary parts as two independent but degenerate mode — linear polarized. Or we combine them as a pair of complex mode, as left/right circularly polarized modes.

⊛ Displacement representation

The displacement vector $W_\alpha(i)$ forms a 3N dimensional $\underbrace{\text{representation}}_{}$ space for a of the symmetry group of the molecule. The symmetry operation, say a rotation g. When it acts on a vector we have $(g\hat{e})_\alpha = R_{\alpha\beta}\hat{e}_\beta$. Then its action on the displacement vector is.

$$(gW)_\alpha(i) = R_{\alpha\beta}^{(g)} W_\beta(g^{-1}i)$$



The potential transformation

$$V' = \sum_{ii',\alpha\beta} D_{\alpha\beta}(i,i')\,(gW)_\alpha(i)\,(gW)_\beta(i')$$

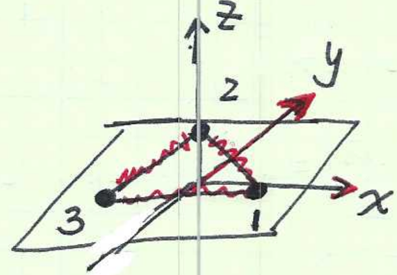
$$= \sum_{ii',\alpha\beta} D_{\alpha\beta}(i i') \, R_{\alpha\alpha'}(g) \, w_{\alpha'}(g^{-1} i) \, R_{\beta\beta'}(g) \, w_{\beta'}(g^{-1} i')$$

$$= \sum_{ii',\alpha\beta} \boxed{R^{-1}_{\alpha'\alpha}(g) \, D_{\alpha\beta}(g r_i^0, g r_j^0) \, R_{\beta\beta'}(g)} \, w_{\alpha'}(r_i) \, w_{\beta'}(r_{i'})$$

hence symmetry condition requires

$$\boxed{D_{\alpha\beta}(r_i^0, r_j^0) = R^{-1}_{\alpha\alpha'}(g) \, D_{\alpha'\beta'}(g r_i^0, g r_j^0) \, R_{\beta'\beta}(g)}$$

we can decompose $D_{\alpha\beta}(r_i, r_j)$ into diagonal blocks under the help of group theory. (here r_i^0, r_j^0 just index of the equlibrium positions of atoms).



(*) D_3 molecule — D_{3h}

$w_\alpha(i) = (x_1 \, y_1 \, z_1, \; x_2 \, y_2 \, z_2, \; x_3 \, y_3 \, z_3)^T$

we have 9 degress of freedom

$\swarrow D_3$

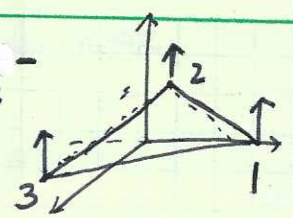
	E	$2C_3$	$3C_2$
χ	9	0	-1
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$\# A_1 = \frac{1}{6}(9-3) = 1$

$\# A_2 = \frac{1}{6}(9+3) = 2$

$\# E = \frac{1}{6}(2 \times 9) = 3$

A_2 –

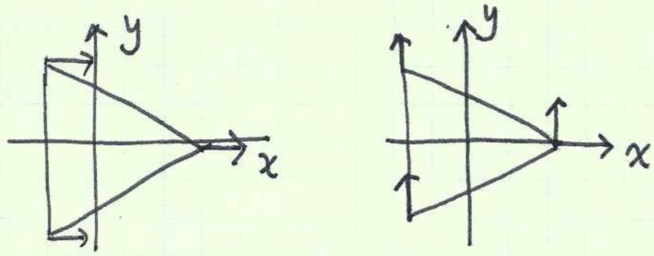


$e_{A_2}^- = \frac{1}{\sqrt{3}} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$ translation along $\hat{z}$-axis

0-mode

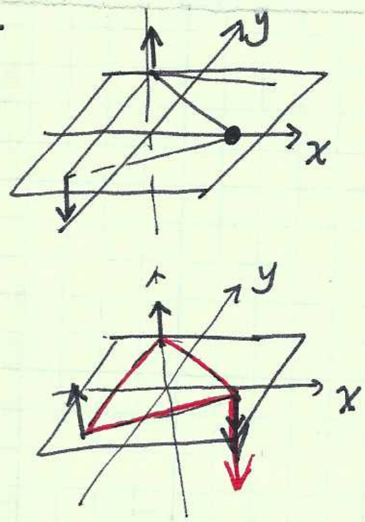
translations along $\hat{x}$ and $\hat{y}$

E^+



$$e^{(1)}_{E^+} = \frac{1}{\sqrt{3}}\begin{pmatrix}1\\0\\0\\1\\0\\0\\1\\0\\0\end{pmatrix} \qquad e^{(2)}_{E^+} = \frac{1}{\sqrt{3}}\begin{pmatrix}0\\1\\0\\0\\1\\0\\0\\1\\0\end{pmatrix}$$

E^-



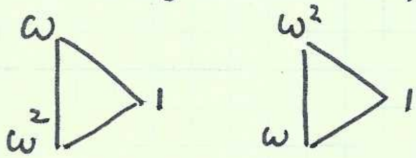
$$e^{(1)}_{E^-} = \frac{1}{\sqrt{3}}\begin{pmatrix}0\\0\\0\\0\\1\\0\\0\\-1\\0\end{pmatrix}$$ rotation around $\hat{x}$

$$e^{(2)}_{E^-} = \frac{1}{\sqrt{6}}\begin{pmatrix}0\\0\\2\\0\\0\\-1\\0\\0\\-1\end{pmatrix}$$ rotation around $\hat{y}$

Now we have 4-planar modes left.

let us view them through the angular momentum addition

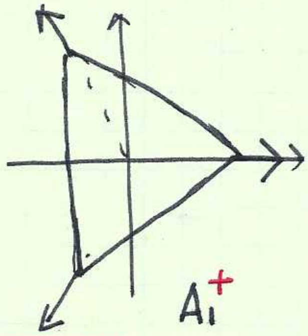
For $\hat{x} \pm i\hat{y}$ circular polarization $L_z = \pm 1$



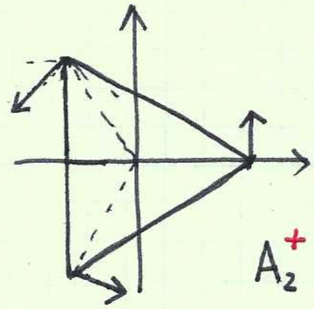
also have $L_z = \pm 1$.

Now let's combine them to arrive at $L_z = 0$, ie A_1 or A_2

$$\begin{pmatrix}1\\-i\\0\\ \hline \begin{pmatrix}1\\-i\end{pmatrix}\omega\\0\\ \hline \begin{pmatrix}1\\-i\end{pmatrix}\omega^2\\0\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}1\\i\\0\\ \hline \begin{pmatrix}1\\i\end{pmatrix}\omega^2\\0\\ \hline \begin{pmatrix}1\\i\end{pmatrix}\omega\\0\end{pmatrix} \Rightarrow \text{Re and Im} \begin{pmatrix}1\\0\\0\\-\frac{1}{2}\\\frac{\sqrt{3}}{2}\\0\\-\frac{1}{2}\\-\frac{\sqrt{3}}{2}\\0\end{pmatrix}, \begin{pmatrix}0\\1\\0\\-\frac{\sqrt{3}}{2}\\-\frac{1}{2}\\0\\\frac{\sqrt{3}}{2}\\-\frac{1}{2}\\0\end{pmatrix}$$



A_1^+



A_2^+

$\leftarrow$ rotation around $\hat{z}$ $\rightarrow$ zero mode

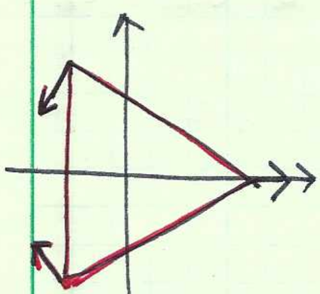
$\boxed{\text{breath mode}}$ $\leftrightarrow$ they are not degenerate.

Further combine $L_z = \pm 2 \equiv \mp 1 \mod (3)$

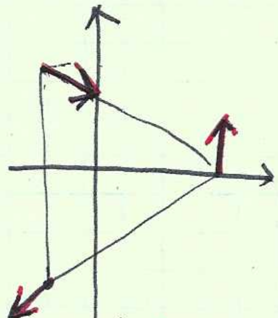
$$\begin{pmatrix} 1 \\ -i \\ 0 \\ \hline \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \omega^2 \\ \hline \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \omega \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 \\ i \\ 0 \\ \hline \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \omega \\ \hline \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \omega^2 \end{pmatrix}$$

or its Real and imaginary parts.

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ \hline -1/2 \\ -\sqrt{3}/2 \\ 0 \\ \hline -1/2 \\ \sqrt{3}/2 \\ 0 \end{pmatrix} \quad \begin{pmatrix} 0 \\ 1 \\ 0 \\ \hline \sqrt{3}/2 \\ -1/2 \\ 0 \\ \hline -\sqrt{3}/2 \\ -1/2 \\ 0 \end{pmatrix}$$



E^+



E^+