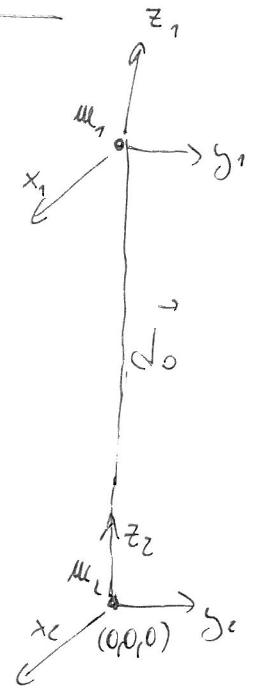
dimer

1, Hamiltonian

$\vec{d_0} = d_0 \vec{e_z}$



$$\vec{d} = (x_1 - x_2)\vec{e_x} + (y_1 - y_2)\vec{e_y} + (d_0 + z_1 - z_2)\vec{e_z}$$

$$V = \frac{1}{2} k \left(d_0 - |\vec{d}|\right)^2$$

$$|\vec{d}| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (d_0 + z_1 - z_2)^2}$$

$$\simeq / x_i \ll d_0 / = d_0 \sqrt{\frac{(x_1 - x_2)^2}{d_0^2} + \frac{(y_1 - y_2)^2}{d_0^2} + \left(1 + \frac{z_1 - z_2}{d_0}\right)^2}$$

$$= d_0 \sqrt{1 + 2\frac{z_1 - z_2}{d_0} + \frac{(x_1 - x_2)^2}{d_0^2} + \frac{(y_1 - y_2)^2}{d_0^2}}$$

$$= d_0 + (z_1 - z_2) + O\left(\frac{(x_1 - x_2)^2}{d_0}\right)$$

$$\Rightarrow \boxed{V \sim \frac{1}{2} k (z_1 - z_2)^2}$$

$$z_1 = \frac{q_3}{\sqrt{m_1}} \qquad z_2 = \frac{q_6}{\sqrt{m_2}} \qquad \Rightarrow V = \frac{1}{2} k \left(\frac{q_3}{\sqrt{m_1}} - \frac{q_6}{\sqrt{m_2}}\right)^2$$

$$\Rightarrow V = \frac{1}{2} k \left[q_3^2 \frac{1}{m_1} + q_6^2 \frac{1}{m_2} - 2 \frac{q_3 q_6}{\sqrt{m_1 m_2}} \right]$$

$$\Rightarrow B = \frac{1}{2} k \begin{pmatrix} \frac{1}{m_1} & -\frac{1}{\sqrt{m_1 m_2}} \\ -\frac{1}{\sqrt{m_1 m_2}} & \frac{1}{m_2} \end{pmatrix}$$

2, diagonalization: $\left(\frac{1}{m_1} - \lambda\right)\left(\frac{1}{m_2} - \lambda\right) - \frac{1}{m_1 m_2} = \frac{1}{m_1 m_2} - \lambda\left(\frac{1}{m_1} + \frac{1}{m_2}\right) + \lambda^2$

$$- \frac{1}{m_1 m_2} = 0 \Rightarrow \lambda\left(\lambda - \frac{m_1 + m_2}{m_1 m_2}\right) = 0$$

$\Rightarrow$ $\lambda_1 = 0$ ... translations

$\lambda_2 = \frac{m_1 + m_2}{m_1 m_2} \cdot \frac{1}{2} k$ ... vibrations

$$\Leftrightarrow \quad Q_{tr} = q_3 \sqrt{\frac{m_1}{m_1+m_2}} + q_6 \sqrt{\frac{m_2}{m_1+m_2}} \quad \text{... translation} \qquad (1)$$

$$Q_{vib} = q_3 \sqrt{\frac{m_2}{m_1+m_2}} - q_6 \sqrt{\frac{m_1}{m_1+m_2}} \quad \text{... vibration} \qquad (2)$$

Note: • $Q_{tr} \neq$ "(q_3, q_6)"!

• $q_i = x_i \sqrt{m_i} \Rightarrow Q_{tr} = z_1 \frac{m_1}{\sqrt{m_1+m_2}} + z_2 \frac{m_2}{\sqrt{m_1+m_2}}$

$\Rightarrow$ it is not even $\propto$ "(z_1, z_2)" which would be "natural" as it is translation $\Rightarrow$ both atoms move by the same distance

3, Inversion:

a, $\sqrt{m_1}(1) + \sqrt{m_2}(2) \Rightarrow Q_{tr}\sqrt{m_1} + Q_{vib}\sqrt{m_2} = q_3 \frac{m_1+m_2}{\sqrt{m_1+m_2}}$

$$\Rightarrow q_3 = \frac{1}{\sqrt{m_1+m_2}}\left(Q_{tr}\sqrt{m_1} + Q_{vib}\sqrt{m_2}\right) \qquad z_1 = \frac{q_3}{\sqrt{m_1}}$$

$$\Rightarrow \boxed{z_1 = \frac{1}{\sqrt{m_1+m_2}}\left(Q_{tr} + Q_{vib}\sqrt{\frac{m_2}{m_1}}\right)}$$

b, $\sqrt{m_2}(1) - \sqrt{m_1}(2) \Rightarrow Q_{tr}\sqrt{m_2} - Q_{vib}\sqrt{m_1} = q_6 \frac{m_1+m_2}{\sqrt{m_1+m_2}}$

$$\Rightarrow q_6 = \frac{1}{\sqrt{m_1+m_2}}\left(Q_{tr}\sqrt{m_2} - Q_{vib}\sqrt{m_1}\right)$$

$$\Rightarrow \boxed{z_2 = \frac{1}{\sqrt{m_1+m_2}}\left(Q_{tr} - Q_{vib}\sqrt{\frac{m_1}{m_2}}\right)}$$

$\Rightarrow$ only now we see the meaning of Q_{tr} & Q_{vib}:

$Q_{vib} = 0 \Rightarrow z_1 = z_2$ & Q_{tr} indeed corresponds to translation without deformation

$Q_{tr} = 0 \Rightarrow \frac{z_1}{z_2} = -\frac{m_2}{m_1}$ meaning center of mass does not move!

• note that it is not trivial to guess normal coordinates and, in particular, obtain the internal ones by "subtraction" of translations & rotations as these are nontrivial due to the "mass scaling"