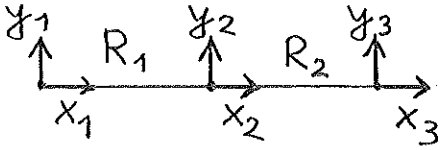
Computation of B-matrix for linear XYZ-molecules



$$\phi_0 = \angle(\vec{R}_1^{\,0}, \vec{R}_2^{\,0}) = 180°$$

Displacement coordinates:

Cartesian: see above $\quad \left[R_0 = R_1^{(0)} = R_2^{(0)} \right]$

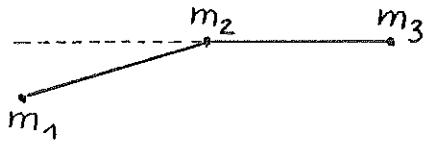
Internal: $r_1 = \delta R_1 = R_1 - R_0, r_2 = \delta R_2$

$r_3 = R_0 \delta\phi$

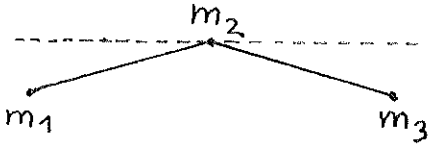
Geometrically one finds

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & -2 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ x_2 \\ y_2 \\ x_3 \\ y_3 \end{pmatrix}$$

$y_1 < 0$



$y_2 > 0$



Computation of the G-matrix for linear XYZ-molecules

$$\boldsymbol{G} = \boldsymbol{B}\boldsymbol{M}^{-1}\boldsymbol{B}^{\dagger} \quad ; \quad \boldsymbol{M}^{-1} = \operatorname{diag}\left(m_{ii}^{-1}\right)$$

$$m_{11} = m_{22} = m_1$$

$$m_{33} = m_{44} = m_2$$

$$m_{55} = m_{66} = m_3$$

$$\Rightarrow \quad G_{11} = \sum_i B_{1i}\frac{1}{m_{ii}}B_{1i} = \frac{1}{m_1} + \frac{1}{m_2};$$

$$G_{22} = \frac{1}{m_2} + \frac{1}{m_3};$$

$$G_{33} = \frac{1}{m_1} + \frac{4}{m_2} + \frac{1}{m_3};$$

$$G_{12} = -\frac{1}{m_2};$$

$$G_{13} = 0 = G_{23};$$

$$\mathbf{G} = \begin{pmatrix} \frac{1}{m_1} + \frac{1}{m_2} & -\frac{1}{m_2} & 0 \\ -\frac{1}{m_2} & \frac{1}{m_3} + \frac{1}{m_2} & 0 \\ 0 & 0 & \frac{1}{m_1} + \frac{1}{m_3} + \frac{4}{m_2} \end{pmatrix}$$

Comments

- Off-diagonal G-matrix elements explicitly revealed
- Reduced mass for diatomic molecules confirmed
- Some elements vanish: effect of symmetry!
- New: "effective mass" for bending mode