UNIVERSITY OF CAMBRIDGE

Normal Mode Frequencies in Angle-Axis Framework

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Outline:

- *The maths & implementation*
- *An example - TIP4 water molecules*

Normal Mode Analysis

In normal mode analysis, we generally want to write the equation of motion in a set of coordinates **X** so that:

$$\frac{1}{2}\dot{X}^2 + \frac{1}{2}\lambda^2 X^2 = \text{constant} \quad \longleftrightarrow \quad \ddot{X} + \lambda^2 X = 0$$

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Unfortunately, this can be cumbersome, confusing, and it has to be done through several steps:

1. Diagonalization of the kinetic energy

$$E_K = E_{T/RB} + E_{ROT}$$

$$E_{T/RB} = \sum_{RB}\frac{1}{2}M_{RB}^{\alpha}\dot{x}_{\alpha,RB}^2$$

$$v_i = v_{RB} + \dot{R}_{RB} \times r_i^0$$

$$E_{ROT} = \sum_{RB}\sum_{i\in RB}\frac{1}{2}m_i\begin{pmatrix}x_i^0 & y_i^0 & z_i^0\end{pmatrix}\dot{R}_{T,RB}\dot{R}_{RB}\begin{pmatrix}x_i^0\\ y_i^0\\ z_i^0\end{pmatrix}$$

somehow

$$E_{ROT} = \sum_{RB}\frac{1}{2}\mathrm{M}_{RB}^{\alpha}\dot{\vartheta}_{\alpha,RB}^2$$

2. Normalization (rescaling) of the coordinates $x \to \frac{x}{\sqrt{M}};\vartheta = \frac{\vartheta}{\sqrt{\mathrm{M}}}$

3. Diagonalization of the Hessian to get λ's: $\mathrm{X} = B(x,\vartheta)$

Angle-Axis

$$E_{ROT} = \sum_{RB} \sum_{i \in RB} \frac{1}{2} m_i \begin{pmatrix} x_i^0 & y_i^0 & z_i^0 \end{pmatrix} \dot{R}_{T,RB} \dot{R}_{RB} \begin{pmatrix} x_i^0 \\ y_i^0 \\ z_i^0 \end{pmatrix} \longrightarrow E_{ROT} = \sum_{RB} \frac{1}{2} \mathrm{M}_{RB}^{\alpha} \dot{\vartheta}_{\alpha,RB}^{2}$$

In angle-axis:

$$\boldsymbol{R} = \boldsymbol{I} + (1 - \cos\theta)\tilde{\boldsymbol{p}}\tilde{\boldsymbol{p}} + \sin\theta\tilde{\boldsymbol{p}} \qquad (1)$$

where $\boldsymbol{I}$ is a 3×3 identity matrix, and $\tilde{\boldsymbol{p}}$ is the skew-symmetric matrix obtained from $\hat{\boldsymbol{p}}$:

$$\tilde{\boldsymbol{p}} = \frac{1}{\theta} \begin{pmatrix} 0 & -p_3 & p_2 \\ p_3 & 0 & -p_1 \\ -p_2 & p_1 & 0 \end{pmatrix}. \qquad (2)$$

Generally rather messy!

Angle-Axis

$$E_{ROT} = \sum_{RB} \sum_{i \in RB} \frac{1}{2} m_i \begin{pmatrix} x_i^0 & y_i^0 & z_i^0 \end{pmatrix} \dot{R}_{T,RB} \dot{R}_{RB} \begin{pmatrix} x_i^0 \\ y_i^0 \\ z_i^0 \end{pmatrix} \longrightarrow E_{ROT} = \sum_{RB} \frac{1}{2} \mathrm{M}_{RB}^{\alpha} \dot{\vartheta}_{\alpha,RB}^{2}$$

In angle-axis:

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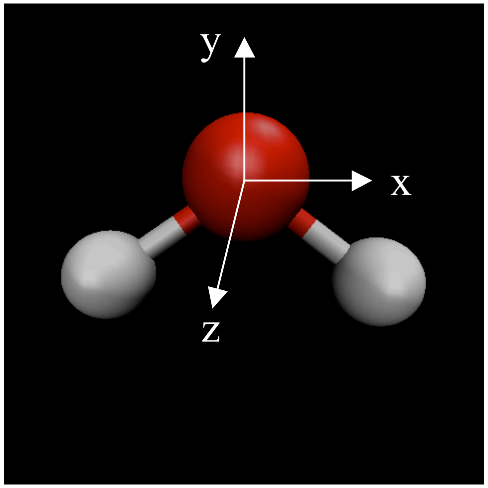
Generally rather messy! But very easy in the rotating frame (correponding to $\theta = 0$ or $\mathbf{p} = (0,0,0)$).

$$\dot{R}_{RB}^{0} = \begin{pmatrix} 0 & -\dot{p}_{RB}^{z} & \dot{p}_{RB}^{y} \\ \dot{p}_{RB}^{z} & 0 & -\dot{p}_{RB}^{x} \\ -\dot{p}_{RB}^{y} & \dot{p}_{RB}^{x} & 0 \end{pmatrix}$$

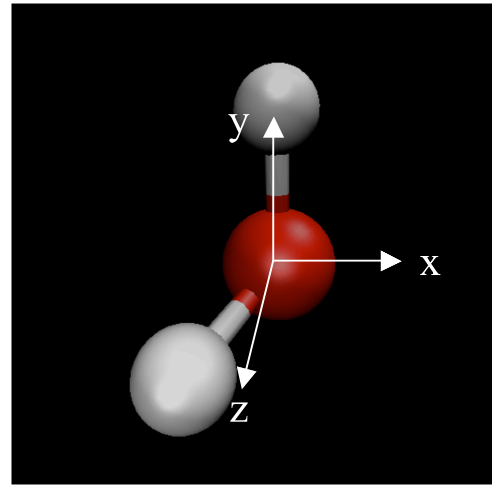
$$I_{RB} = \sum_{i \in RB} \begin{pmatrix} m_i\left(y_i^2 + z_i^2\right) & -m_i x_i y_i & -m_i x_i z_i \\ -m_i x_i y_i & m_i\left(x_i^2 + z_i^2\right) & -m_i y_i z_i \\ -m_i x_i z_i & -m_i y_i z_i & m_i\left(x_i^2 + y_i^2\right) \end{pmatrix}$$

$$E_{ROT} = \sum_{RB} \frac{1}{2} I_{RB}^{\alpha\beta} \dot{p}_{RB}^{\alpha} \dot{p}_{RB}^{\beta} \xrightarrow{\vartheta = Ap} E_{ROT} = \sum_{RB} \frac{1}{2} \mathrm{M}_{RB}^{\alpha} \dot{\vartheta}_{\alpha,RB}^{2}$$

In Pictures



R(**p**)



Stationary frame

Original reference geometry

Non-zero **p**

Rotating frame

Use new reference geometry

p = (0,0,0)

$$E_{ROT} = \sum_{RB} \frac{1}{2} I_{RB}^{\alpha\beta} \dot{p}_{RB}^{\alpha} \dot{p}_{RB}^{\beta}$$

Note on the Hessian

In the usual implementation, the Hessian is evaluated in the stationary frame! NOT the rotating frame.

This is incompatible with our analysis in the previous slide. Either is fine, but should be consistent!

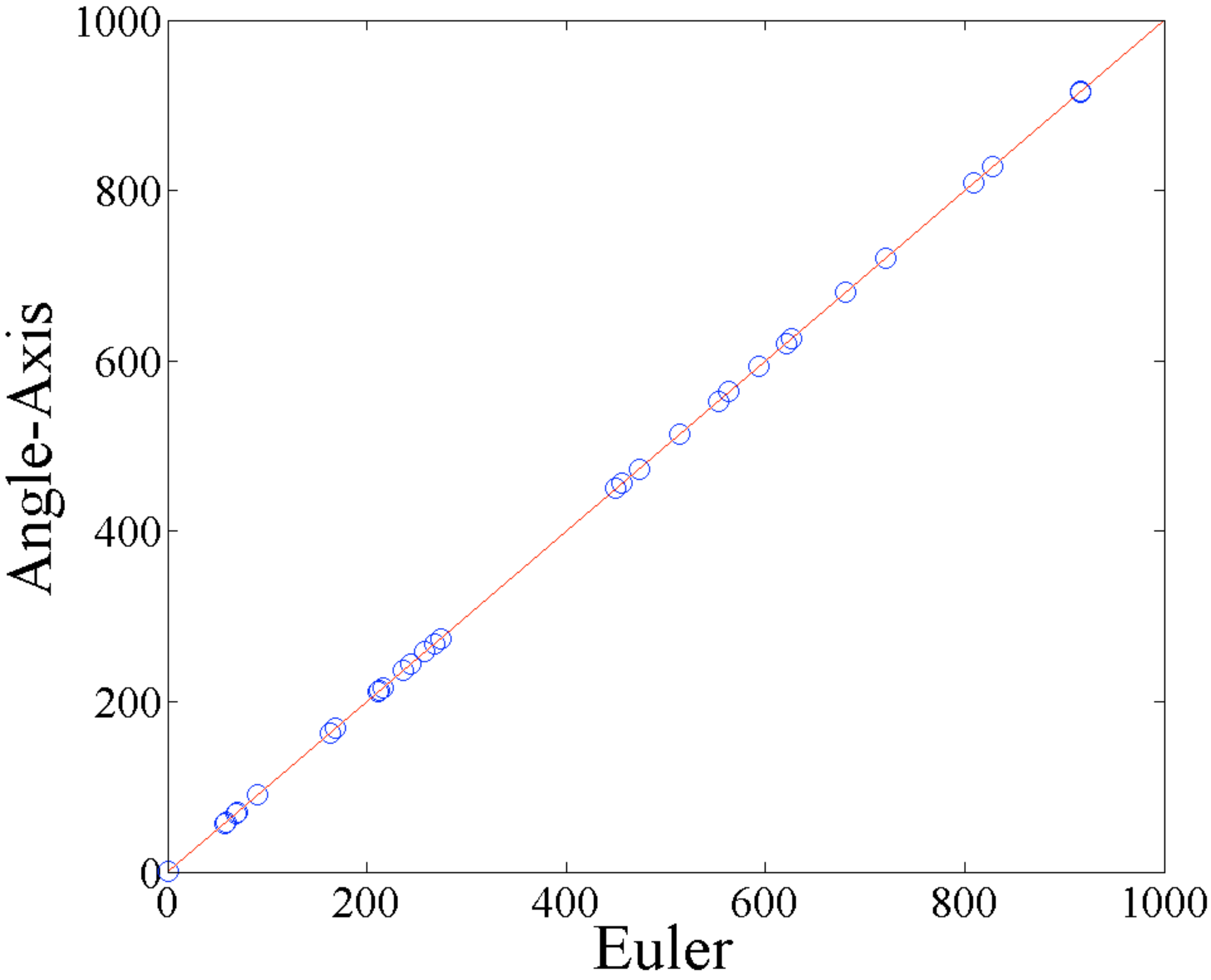
Rotating frame is much easier. Require only the following changes:

$r_i^0 \rightarrow R_{RB} r_i^0$	isotropic	Current Positions and Orientations
$\hat{e}_i^0 \rightarrow R_{RB} \hat{e}_i^0$	Single-site anisotropic	
$A_i^0 \rightarrow R_{RB} A_i^0 R_{T,RB}$	Site-site anisotropic	
$R_{RB} \rightarrow I = R_{RB}^0$	Rotation matrix in the rotating frame	Analytical expressions
$R_{RB}^k \rightarrow R_{RB}^{0,k}$	1st derivative of rotation matrix in the rotating frame	
$R_{RB}^{kl} \rightarrow R_{RB}^{0,kl}$	2nd derivative of rotation matrix in the rotating frame	

There was a mistake in the expression for $R_{RB}^{0,kl}$ in the PCCP paper.

TIP4 Water

As a test case, consider 8 molecules of TIP4 water.



Visualization

To visualise the normal modes, we need 4 steps of coordinate transformations!

4. Cartesian to angle-axis

3. Diagonalization of kinetic energy

$$\vartheta = Ap$$

2. Normalization of centre of mass coordinates

$$x \rightarrow \frac{x}{\sqrt{M}}; \vartheta = \frac{\vartheta}{\sqrt{\mathrm{M}}}$$

1. Diagonalization of the Hessian

$$\mathrm{X} = B(x, \vartheta)$$

MOVIE TIME!!!