

Normal mode analysis of molecular motions

No, it is not flogging a dead horse...

J. Pesonen¹

¹Department of Chemistry



UNIVERSITY OF HELSINKI

2012

Outline

- 1 Origins and originators of NMA
 - Origins
 - Originators
- 2 Curvilinear NMA
 - Coordinates
 - Kinetic energy
 - Potential
 - Lagrangian
 - Normal coordinates
 - On invariants
- 3 Cartesian NMA
- 4 Linearized NMA
- 5 Conclusions

Origins

- Based on the work done in classical mechanics involving systems of point masses connected by strings.

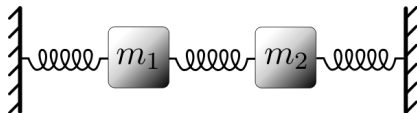


Figure: Coupled harmonic oscillators.

Origins (cntnd.)

- Adopted in 1920's to understand the structure of the observed vibration-rotation spectrum of several small molecules.

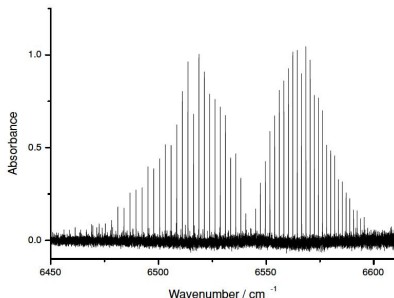


Figure: A part of absorption spectrum of $^{12}\text{C}^{13}\text{C}$, recorded in the Laboratory of physical chemistry, University of Helsinki.

Origins (cntnd.)

- NMA has recently gained popularity in modeling large scale collective motions of huge proteins.
 - Example: The lowest normal mode of a small protein, in backbone torsion angle space

Originators



Figure: Edgar Bright Wilson, Jr (December 18, 1908 – June 12, 1992)

- “s-vectors”.
- The “GF matrix method”.
- The famous 1955 text book *Molecular vibrations* by Wilson, Decius and Cross.

Originators (cntnd.)



Figure: Carl Henry Eckart (May 4, 1902 – October 23, 1973)

- Seminal paper: *Studies Concerning Rotating Axes and Polyatomic Molecules*, *Physical Review* **47**, 552-558 (1935).

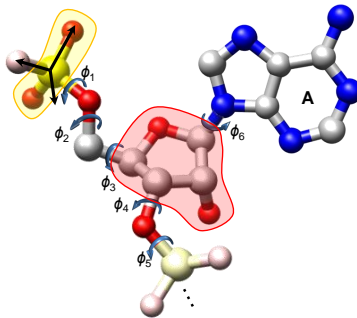
Originators (cntnd.)

- 1968, [James K. G. Watson](#)
 - Seminal paper *Simplification of the molecular vibration-rotation Hamiltonian*, Mol. Phys. **15**, 479-490 (1968).
 - Eckart's classical mechanical Hamiltonian into a proper quantum mechanical one.
 - Eckart-Watson Hamiltonian.

Coordinates

- The degrees of freedom that a polyatomic molecule possess are classified into three different types:
 - **Position** (of the center-of mass) – 3 Cartesian coordinates.
 - Translation.
 - **Orientation** (of the body-frame w.r.t. constant lab-frame) – 3 Euler angles.
 - Rotation.
 - **Shape** – N_s ($\leq 3N - 6$) internal coordinates.
 - Deformation, vibration.
 - Not all shape coordinates need to be active (rigid constraints in shape)!

Coordinates (cntnd.)



Kinetic energy

- The internal kinetic energy reads as

$$T_{\text{int}} = \sum_{ij} \dot{q}_i g_{ij} \dot{q}_j \quad (1)$$

- q_i is either a shape coordinate s_i or an Euler angle Θ_i .
- The

$$g_{ij} = \sum_{\alpha} m_{\alpha} \frac{\partial \mathbf{x}_{\alpha}}{\partial q_i} \cdot \frac{\partial \mathbf{x}_{\alpha}}{\partial q_j} \quad (2)$$

is the element of the **covariant metric tensor**.

Potential

- The potential V **harmonic** in shape coordinates $\Delta s_i = s_i - s_i^{(e)}$,

$$V_H = \frac{1}{2} \sum_{ij} f_{ij} \Delta s_i \Delta s_j \quad (3)$$

- Invariant in all rigid motions of the molecule.
- Any potential V can be used in normal mode calculations:

$$f_{ij} = \left. \frac{\partial^2 V}{\partial s_i \partial s_j} \right|_e \quad (4)$$

Lagrangian

- The Lagrangian

$$L = T - V \quad (5)$$

- Euler-Lagrange equations of motion

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0 \quad (6)$$

for all active coordinates q_i .

Lagrangian (ctnd.)

- With the harmonic potential, the Lagrangian equations assume the form

$$\sum_j g_{ij} \ddot{q}_j + \sum_{j,k} \Gamma_{ijk} \dot{q}_j \dot{q}_k + \sum_j f_{ij} \Delta s_j = 0 \quad (7)$$

$$\sum_j g_{ij} \ddot{q}_j + \sum_{j,k} \Gamma_{ijk} \dot{q}_j \dot{q}_k = 0 \quad (8)$$

depending on whether q_j is Δs_j or an Euler angle Θ_j .

Lagrangian (cntnd.)

- Christoffel symbol of the first kind is given by

$$\Gamma_{ijk} = \sum_{\alpha}^N m_{\alpha} \frac{\partial \mathbf{x}_{\alpha}}{\partial q_i} \cdot \frac{\partial^2 \mathbf{x}_{\alpha}}{\partial q_j \partial q_k} \quad (9)$$

Normal coordinates

- Normal coordinates $\{Q_j\}$ through a linear coordinate relation

$$q_i = \sum_j A_{ij} Q_j \quad (10)$$

- Without the Christoffel symbol, Eqs. (7) and (8) can be expressed in the matrix form as

$$\ddot{Q} + A^{-1}g^{-1}fAQ = 0 \quad (11)$$

- In actual calculation, g is replaced by its reference value g_0 .

Normal coordinates (cntnd.)

- By using the trial solution

$$Q_j(t) = a_j \sin(\omega_j t) + b_j \cos(\omega_j t) \quad (12)$$

Eq. (11) can be written in a **normal form** as

$$(\mathbf{g}_0^{-1} \mathbf{f}) \mathbf{A} = \mathbf{A} \mathbf{\Omega}^2 \quad (13)$$

- The diagonal matrix $\mathbf{\Omega}^2$ contains the **mode frequencies** squared, ω_i^2 .
- $\omega_{N_s+1} = \omega_{N_s+2} = \omega_{N_s+3} = 0$.

Normal coordinates (cntnd.)

- Columns of the matrix A are the **eigenvectors** of $(N_s + 3) \times (N_s + 3)$ matrix

$$g_0^{-1}f = \begin{bmatrix} \star & \star & \star & \cdots & \star & 0 & 0 & 0 \\ \star & \star & \star & \cdots & \vdots & 0 & 0 & 0 \\ \star & \star & \star & \cdots & \star & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & 0 & 0 & 0 \\ \star & \star & \star & \cdots & \star & 0 & 0 & 0 \end{bmatrix} \quad (14)$$

Normal coordinates (cntnd.)

- Matrix A has the form

$$A = \left[\begin{array}{cccc|ccc} \star & \star & \dots & \star & 0 & 0 & 0 \\ \star & \star & \dots & \star & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ \star & \star & \dots & \star & 0 & 0 & 0 \\ \hline \star & \star & \dots & \star & \star & \star & \star \\ \star & \star & \dots & \star & \star & \star & \star \\ \star & \star & \dots & \star & \star & \star & \star \end{array} \right] \quad (15)$$

Normal coordinates (cntnd.)

- Coordinates are mapped as

$$\Delta s_i = \sum_{j=1}^{N_s} A_{\Delta s_i Q_j} Q_j \quad (16)$$

$$\Theta_i = \sum_{j=1}^{N_s+3} A_{\Theta_i Q_j} Q_j \quad (17)$$

Normal coordinates (cntnd.)

- **Fact:** rotational degrees of freedom **must** be included to NMA.
 - To get the correct eigenvalues!
 - Because orientation of a molecule generally changes even in the $I = 0$ case.
 - Example: Falling cat
 - Coriolis term never completely vanishes (i.e., Eckart frame does **not** eliminate Coriolis coupling, except in the reference conformation).

Normal coordinates (cntnd.)

- The Christoffel symbol in Eq. (7) can be made to vanish in Q_i - space by a quadratic relation

$$q_i = \sum_{j=1} A_{ij} Q_j + \sum_{j=1} B_{ijk} Q_j Q_k \quad (18)$$

where $B_{ijk} = -\frac{1}{2} \sum_{st} \Gamma_{st}^{(i)} \Big|_0 A_{sj} A_{tk}$. Unfortunately,

- Mixes shape coordinates $\{\Delta s_j\}$ with the rotational coordinates $\{\Theta_1, \Theta_2, \Theta_3\}$.
- Maps harmonic potentials up to quartic ones.

On invariants

- **Fact:** Total energy $E = T + V$ and angular momentum are not preserved in NMA!

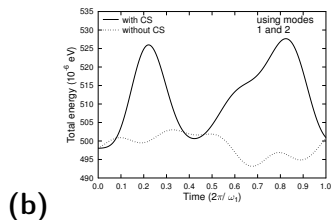
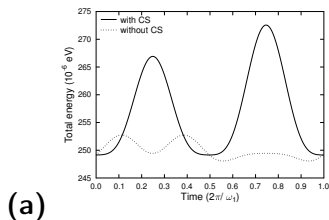
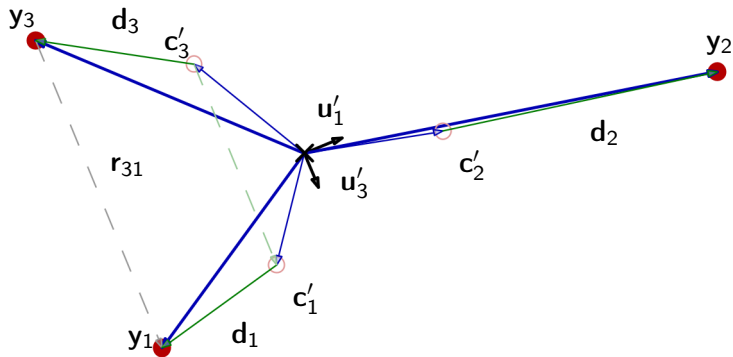


Figure: Total energy calculated directly from the trajectories of the atoms. (a) The lowest (b) two lowest vibrational normal modes are excited.

Cartesian NMA

- $\mathbf{x}_\alpha = \mathbf{y}_\alpha + \mathbf{X} = \mathbf{c}'_\alpha + \mathbf{d}_\alpha + \mathbf{X}.$



Cartesian NMA (cntd.)

- $2T = \sum_{\alpha} m_{\alpha} \dot{\mathbf{y}}_{\alpha}^2 + M \dot{\mathbf{X}}^2$, so

$$2T_{\text{int}} = \sum_{\alpha} m_{\alpha} \left(\dot{\mathbf{d}}_{\alpha} + \dot{\mathbf{c}}'_{\alpha} \right)^2 \quad (19)$$

$$2V = \sum_{\alpha\beta} \sum_{ij} F_{\alpha\beta} d'_{\alpha i} d'_{\beta j} \quad (20)$$

with $d'_{\alpha i} = \mathbf{d}_{\alpha} \cdot \mathbf{u}'_i$.

Cartesian NMA (cntd.)

- In order to make NMA, it is assumed that $\dot{\mathbf{c}}'_\alpha \approx 0$, i.e., \mathbf{c}'_α is undistinguishable from \mathbf{c}_α .
 - This implies that molecule **does not rotate!**
 - Under this assumption $2T \approx \sum_\alpha m_\alpha (\dot{d}'_{\alpha 1}{}^2 + \dot{d}'_{\alpha 2}{}^2 + \dot{d}'_{\alpha 3}{}^2)$ and consequently,

$$\mathbf{g} \approx \begin{bmatrix} m_1 & 0 & 0 & 0 & 0 \\ 0 & m_1 & 0 & 0 & 0 \\ 0 & 0 & m_1 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & & m_N \end{bmatrix} \quad (21)$$

Linearized NMA

- The version of Cartesian NMA formulated by [Wilson and coworkers](#) in 1930s.
- [Defines](#) linearized versions of the true curvilinear shape coordinates as

$$\Delta \bar{s}_i(\mathbf{d}_1, \mathbf{d}_2, \dots) = \sum_{\alpha=1}^N \mathbf{d}_\alpha \cdot \xi_\alpha^{(s_i)} \quad (22)$$

where $\xi_\alpha^{(s_i)} = \nabla_{\mathbf{x}_\alpha} s_i|_0$.

Linearized NMA (cntd.)

- Atomic displacements given by

$$\mathbf{d}_\alpha = \sum_{i=1}^{N_s} \xi_{s_i}^{(\alpha)} \Delta \bar{s}_i \quad (23)$$

where

$$\xi_{s_i}^{(\alpha)} = \left. \frac{\partial \mathbf{x}_\alpha}{\partial s_i} \right|_0 \quad (24)$$

- Notice: the vectors $\xi_{s_i}^{(\alpha)}$ rotate along with the body-frame!

Linearized NMA (cntd.)

- $\Delta \bar{s}_i$ can be a mix of different types of actual deformations .

Example

Consider a triatomic molecule, whose shape is parametrized by two bond lengths $r_{31} = |\mathbf{r}_{31}| = |\mathbf{x}_1 - \mathbf{x}_3|$, r_{32} , and the angle θ_{132} between \mathbf{r}_{31} and \mathbf{r}_{32} . In bond-z body-frame (where the axes $\mathbf{u}'_3 \parallel \mathbf{r}_{31}$ and \mathbf{u}'_1 are in the plane of the molecule and),

$$\Delta \bar{r}_{31} = \Delta r_{31} \quad (25)$$

$$\Delta \bar{r}_{32} = r_{32} \cos(\Delta \theta_{132}) - r_{32}^{(e)} \quad (26)$$

$$\Delta \bar{\theta}_{132} = \frac{r_{32}}{r_{32}^{(e)}} \sin(\Delta \theta_{132}) \quad (27)$$

Linearized NMA (cntd.)

- Relations $\bar{s}_i = f_i(s_1, s_2, \dots)$ depend on the choice of body-frame!

Example

New body-axes $\{\mathbf{u}''_3, \mathbf{u}''_1\}$ by turning $\{\mathbf{u}'_3, \mathbf{u}'_1\}$ in the molecular plane by the angle φ . Then,

$$\Delta \bar{r}_{31} = r_{31} \cos(\Delta\varphi) - r_{31}^{(e)} \quad (28)$$

$$\Delta \bar{r}_{32} = r_{32} \cos[\Delta(\theta_{132} - \varphi)] - r_{32}^{(e)} \quad (29)$$

Linearized NMA (cntd.)

- Kinetic energy reads as

$$T_{\text{int}} = \sum_{ij} \left(\dot{\bar{s}}_i g_{\bar{s}_i \bar{s}_j} \dot{\bar{s}}_j + \dot{\bar{s}}_i g_{\bar{s}_i \omega'_j} \omega'_j + \omega'_i g_{\omega'_i \omega'_j} \omega'_j \right) \quad (30)$$

where $\omega'_i = \omega_i \cdot \mathbf{u}'_i$ (and $\dot{\mathbf{c}}'_\alpha = \omega_i \times \mathbf{c}'_\alpha$).

- $g_{\bar{s}_i \bar{s}_j}$ are constant, but $g_{\bar{s}_i \omega'_j}$ and $g_{\omega'_i \omega'_j}$ are **not**.
 - They are functions of the linearized shape coordinates.

Linearized NMA (cntd.)

- In actual NMA calculation,
 - An Eckart body-frame is used, so

$$\mathfrak{g}_0 = \left[\begin{array}{cccc|ccc}
 \star & \star & \dots & \star & 0 & 0 & 0 \\
 \star & \star & \dots & \star & 0 & 0 & 0 \\
 \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
 \star & \star & \dots & \star & 0 & 0 & 0 \\
 \hline
 0 & 0 & \dots & 0 & \star & \star & \star \\
 0 & 0 & \dots & 0 & \star & \star & \star \\
 0 & 0 & \dots & 0 & \star & \star & \star
 \end{array} \right] \quad (31)$$


and $\dot{\hat{s}}_i g_{\hat{s}_i} \omega'_j \Big|_0 = 0$.

- “infinitesimal nuclear displacements” assumed.

Conclusions

- Two different NMAs – curvilinear NMA and “standard” linearized (or Cartesian) NMA.
 - Especially physics textbooks often confuse curvilinear and linearized NMA!
- Notice that Cartesian and linearized NMAs are actually based on **fundamentally different assumptions**:
 - Atoms move finitely, but the body-frame does not rotate (Cartesian NMA).
 - Atoms move infinitesimally, but the body-frame is allowed to rotate finitely (linearized NMA).
- **Rotation truly matters!**

Acknowledgements

- Motions in Macromolecular Function: New Approaches to Visualize and Simulate Protein Flexibility, awarded by 
 - Krister O. E. Henriksson¹
 - Jose Ramon Lopez-Blanco and Pablo Chacon²

¹Department of Physics, University of Helsinki.

²Department of Biological Physical Chemistry, CSIC, Madrid.

Further Reading



B. T. Sutcliffe.

Calculations of the Vibration-Rotation Spectra of Small Molecules.

In *Chemical Modelling: Applications and Theory, vol. 3* (RSC, 2004), edited by A. Hinchliffe.



J. Pesonen.

Kinetic energy operators in linearized internal coordinates.

Journal of Chemical Physics, **128**(4):044319, 2008.



J. Pesonen et. al.

Normal mode analysis of molecular motions in curvilinear coordinates on a non-Eckart body-frame.

Journal of Mathematical Chemistry, **50**, 1521-1549, 2012.