Derivation of the Fundamental Equations of Vibrational Spectroscopy

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Overview

- Lagrangian
  - Overview
  - Cartesian and Internal Coordinates
  - Displacement Coordinates
  - Relationship Between Internal and Cartesian Coordinates
  - Kinetic Energy in Internal Coordinates
  - Potential Energy in Internal Coordinates
- Euler-Lagrange Equation
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  - Newtonian Mechanics Example
  - Vibrational Euler-Lagrange Equation
  - Possible Solutions
  - Normal Mode Vectors
  - Normal Coordinate
  - Basic Equation of Vibrational Spectroscopy

Lagrangian for Vibrational Spectroscopy

- Lagrangian
  - Difference between kinetic and potential energy descriptions.
- Kinetic Energy
  - 3K Cartesian displacement coordinate velocity $\dot{\mathbf{x}}$ elements.
  - **M** is a 3K symmetric square matrix of atomic masses.
- Potential Energy
  - 3K Cartesian displacement coordinate **x** elements.
  - **f** is a 3K symmetric square matrix of force constants.
- The dot indicates differentiation with respect to time.

$$L(\mathbf{x}, \dot{\mathbf{x}}) = T(\dot{\mathbf{x}}) - V(\mathbf{x})$$

$$= \frac{1}{2} \dot{\mathbf{x}}^{\dagger} \mathbf{M} \dot{\mathbf{x}} - \frac{1}{2} \mathbf{x}^{\dagger} \mathbf{f} \mathbf{x}$$

Cartesian and Internal Coordinates

- External References
  - The position of the atoms is with respect to external reference points such as the grid of Cartesian space.
- Internal References
  - The position of atoms are with respect to other atoms in the molecule.
  - Atomic positions are described using bond lengths and angles.

- Example of an External Reference

O	-1.9	1.5	0.0
H	-0.9	1.5	0.0
H	-2.2	2.4	0.0

- Example of an Internal Reference

O				
H	1	B1		
H	1	B1	2	A2

B1 0.96
A2 104.5

Displacement Coordinates

- Displacement Coordinates
  - Cartesian displacement coordinates are the difference between a certain position and the equilibrium position.
  - Internal displacement coordinates are the difference between a certain internal coordinate and its equilibrium value.

$$\Delta x = x - x_e \equiv x$$

$$\Delta r = r - r_e \equiv r$$

Potential Energy of Displacement

- Potential Energy
  - Describes the potential energy of a system connected with springs.
- Hooke's Law
  - Analogous to the integrated Hooke's Law equation with respect to **x.**
- Displacement
  - The potential energy is zero when the atoms are at their equilibrium distance from each other and greater than zero otherwise.

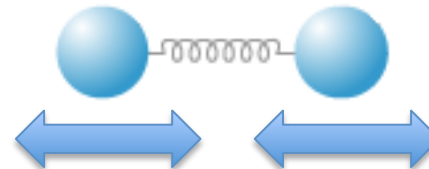$$V(\mathbf{x}) = \frac{1}{2}\mathbf{x}^{\dagger}\mathbf{f}\mathbf{x}$$

$$F = -kx \rightarrow V = \frac{1}{2}kx^2$$
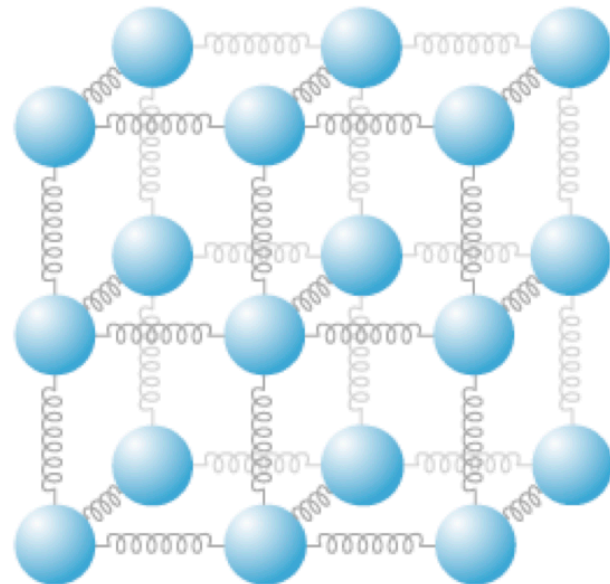
Kinetic Energy of Displacement

- Kinetic Energy
  - A function describing the kinetic energy of a vibrating molecule.

- Atomic Motion
  - The vibrating molecule's atoms have a kinetic energy proportional to the frequency of their oscillations.
  - Analogous to ½mv²

$$T(\dot{x}) = \frac{1}{2}\dot{x}^\dagger M\dot{x}$$

Relationship Between Internal and Cartesian Coordinates

- The **B** Matrix
  - Provides a relationship between internal and Cartesian coordinates.
  - $3K - L$ **r** internal displacement coordinates.
  - $3K$ **x** Cartesian coordinates.
  - **B** is a rectangular $3K$ by $3K - L$ matrix.
  - It has no inverse.

$$r = Bx$$

$$B_{ni} = \left(\frac{\delta r_n(x)}{\delta x_i} \right) x$$

Kinetic Energy in Internal Coordinates

- Kinetic Energy Description
  - Because there is no inverse of **B**, there is no direct way to convert kinetic energy description using **M** into internal coordinates.
- The **G** Matrix
  - The **G** matrix is the mass matrix in internal coordinates.
  - It is a $3K - L$ symmetric square matrix.
- The **K** Matrix
  - The **K** matrix is the inverse of the **G** matrix.
  - It is a $3K - L$ symmetric square matrix.

$$T(\dot{x}) = \frac{1}{2}\dot{r}^\dagger K \dot{r}$$

$$K = G^{-1} = \left[BM^{-1}B^\dagger \right]^{-1}$$

Potential Energy in Internal Coordinates

- Potential Energy Description
  - 3K – L **r** elements.
- The **F** Matrix
  - The force constant matrix in internal coordinates.
  - 3K – L symmetric square matrix.
  - Each element is the 2nd derivative of the potential energy.

$$V(\mathbf{r}) = \frac{1}{2}\mathbf{r}^\dagger \mathbf{F}\mathbf{r}$$

$$\mathbf{F}_{ij} = \frac{\partial^2 V(\mathbf{r})}{\partial \mathbf{r}_i \partial \mathbf{r}_j}$$
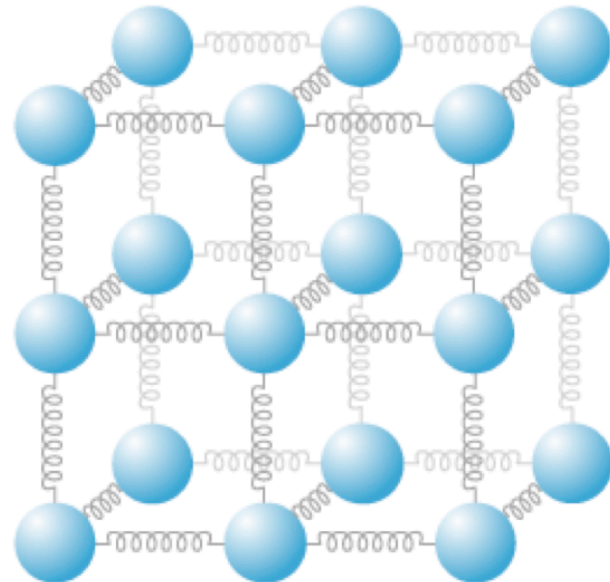
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The Euler-Lagrange Equation

- Lagrangian
  - The difference of the kinetic and potential energies.
  - The Lagrangian is a more kinetic and dynamic description versus the more potential and static based Hamiltonian description.

- Euler-Lagrange
  - The dynamics of the vibrating atoms in a molecule can be found by solving the system of Euler-Lagrange equations for i = 1,…,3K

$$L(\mathbf{x}, \dot{\mathbf{x}}) = T(\dot{\mathbf{x}}) - V(\mathbf{x})$$

$$\frac{d}{dt} \frac{L(\mathbf{x}, \dot{\mathbf{x}})}{d\dot{\mathbf{x}}_i} - \frac{L(\mathbf{x}, \dot{\mathbf{x}})}{d\mathbf{x}_i} = 0$$

Euler-Lagrange Example

Newton's Laws of Motion

1. A body in motion stays in motion until acted upon by an external force.

2. A body acted upon by a force accelerates proportionally, F = ma.

3. Forces between bodies are equal and opposite, $F_{a-b} = -F_{b-a}$

Lagrangian Mechanics

- Lagrangian mechanics is a different way of mathematically expressing Newtonian mechanics, but the physics stays the same.

- The primary advantage of using the Lagrangian is that it is not coordinate system dependent.
  - Changing from Cartesian coordinates to polar coordinates for some Newtonian problems can be tedious.
  - As the Lagrangian is not coordinate system dependent, changing coordinate systems for a particular type of problem are trivial.

Euler-Lagrange Example

- Principle of Least Action
  - The path through configurational space as a function of time is such that "action" is minimized.
  - The Lagrangian is chosen such that the path taken is the path of least action according to Newton's Laws.

$$L(\mathbf{x}, \dot{\mathbf{x}}) = T(\dot{\mathbf{x}}) - V(\mathbf{x})$$

$$= \frac{1}{2} m \dot{\mathbf{x}}^2 - V(\mathbf{x})$$

Euler-Lagrange Example

$$L(\mathbf{x}, \dot{\mathbf{x}}) = \frac{1}{2} m\dot{\mathbf{x}}^2 - V(\mathbf{x})$$

$$\frac{d}{dt} \frac{L(\mathbf{x}, \dot{\mathbf{x}})}{d\dot{\mathbf{x}}_i} - \frac{L(\mathbf{x}, \dot{\mathbf{x}})}{d\mathbf{x}_i} = 0$$

$$\frac{d}{dt} \frac{\frac{1}{2} m\dot{\mathbf{x}}^2 - V(\mathbf{x})}{d\dot{\mathbf{x}}_i} - \frac{\frac{1}{2} m\dot{\mathbf{x}}^2 - V(\mathbf{x})}{d\mathbf{x}_i} = 0$$

Euler-Lagrange Example

$$\frac{d}{dt}\frac{\frac{1}{2}m\dot{\mathbf{x}}^2 - V(\mathbf{x})}{d\dot{\mathbf{x}}_i} - \frac{\frac{1}{2}m\dot{\mathbf{x}}^2 - V(\mathbf{x})}{d\mathbf{x}_i} = 0$$

$$\frac{d}{dt}m\dot{\mathbf{x}} - \frac{V(\mathbf{x})}{d\mathbf{x}_i} = 0$$

$$m\frac{d}{dt}\dot{\mathbf{x}} - \frac{V(\mathbf{x})}{d\mathbf{x}_i} = 0$$

$$m\ddot{\mathbf{x}}_i + F_{V_i} = F_{T_i} + F_{V_i} = 0$$

$$F_{T_i} = -F_{V_i}$$

2nd Law: F = ma

3rd Law: $F_{a\text{-}b}$ = -$F_{b\text{-}a}$

Euler-Lagrange Equation

- Euler-Lagrange
  - The dynamics of the vibrating atoms in a molecule can be found by solving the system of Euler-Lagrange equations for $i = 1, \ldots, 3K - L$.

  - The vibrational Euler-Lagrange equation is found by substituting the vibrational Lagrangian into the equation.

$$L(\mathbf{r}, \dot{\mathbf{r}}) = T(\dot{\mathbf{r}}) - V(\mathbf{r}) = \frac{1}{2}\dot{\mathbf{r}}^{\dagger}\mathbf{K}\dot{\mathbf{r}} - \frac{1}{2}\mathbf{r}^{\dagger}\mathbf{Fr}$$

$$\frac{d}{dt}\frac{\partial L(\mathbf{r}, \dot{\mathbf{r}})}{\partial \dot{\mathbf{r}}_i} - \frac{\partial L(\mathbf{r}, \dot{\mathbf{r}})}{\partial \mathbf{r}_i} = 0$$

$$\frac{d}{dt}\frac{\partial T(\dot{\mathbf{r}}) + V(\mathbf{r})}{\partial \dot{\mathbf{r}}_i} - \frac{\partial T(\dot{\mathbf{r}}) + V(\mathbf{r})}{\partial \mathbf{r}_i} = 0$$

$$\frac{d}{dt}\frac{\partial T(\dot{\mathbf{r}})}{\partial \dot{\mathbf{r}}_i} - \frac{\partial V(\mathbf{r})}{\partial \mathbf{r}_i} = 0$$

$$\mathbf{K}\ddot{\mathbf{r}} + \mathbf{Fr} = 0$$

Possible Solutions

- Possible solutions the Euler-Lagrange Equation
  - System of $3K - L$ solutions.
  - v_k and ρ are appropriately chosen constants.
  - λ_k are vibrational eigenvalues from which the harmonic frequencies can be determined.
- The **l** Vector
  - Contains $3K - L$ normal mode vectors.
- The possible solutions are substituted into the differentiated form of the Euler-Lagrange equation.
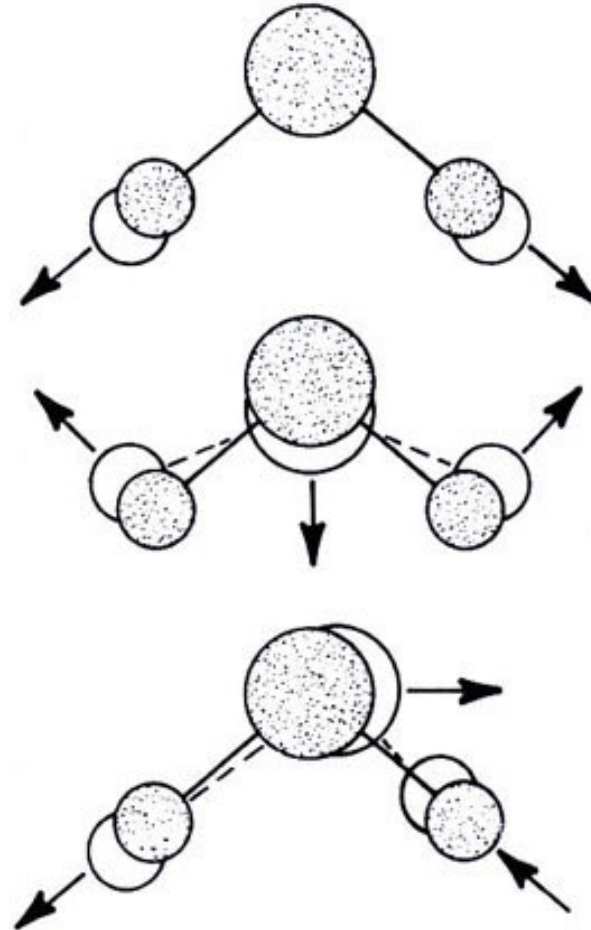
$$\mathsf{K\ddot{r} + Fr} = 0$$

$$\mathsf{r}_i = \mathsf{l}_{ik} \cos(2\pi v_k + \rho)$$

$$\mathsf{\ddot{r}}_i = -\lambda_k \mathsf{l}_{ik} \mathsf{r}_i$$

$$\left[\mathsf{F} - \lambda_k \mathsf{K}\right]\mathsf{l}_{ik} = 0$$

Normal Mode Vectors

- **Normal Mode Vectors**
  - Describe the motion of the vibrational normal modes.

- **Example: Normal Modes of Water**
  - Symmetric stretch.
  - Bending.
  - Asymmetric stretch.

Normal Coordinate

- Normal coordinates refer to the displacement of nuclei from their equilibrium positions during a normal mode vibration.
- A normal coordinate is a linear combination of mass weighted internal or Cartesian coordinate displacements.
- There is a single normal coordinate for each vibrational normal mode.
- Normal coordinates are required for a quantum mechanical versus classical description of molecular vibrations.
- The kinetic and potential energies are summed over i = 3K − L.

$$T(Q) = \frac{1}{2} \sum \lambda_i \dot{Q}_i^2$$

$$V(Q) = \frac{1}{2} \sum Q_i^2$$

Basic Equation of Vibrational Spectroscopy

- Basic Equation of Vibrational Spectroscopy
  - Provides connection between the 3K-L normal mode vectors l_i and their frequencies via Λ.
  - Λ is a matrix of which the diagonal elements are 3K-L vibrational eigenvalues from which the vibrational harmonic frequencies can be determined.
  - **E** is a unit matrix.
- Final Equation
  - Multiply from the left by **K**$^{-1}$ which is **G**.
  - The bracketed equations are equivalent.
  - The **L** matrix contains the normal mode eigenvectors.

$$\left[F - \lambda_k K \right] l_{ik} = 0$$
$$\left[GF - \lambda_k E \right] l_{ik} = 0$$
$$GFL = L\Lambda$$

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References

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Images
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Questions?