

Chemical dynamics

CHEM674

From macroscopic observables to a microscopic description

Andrew Teplyakov

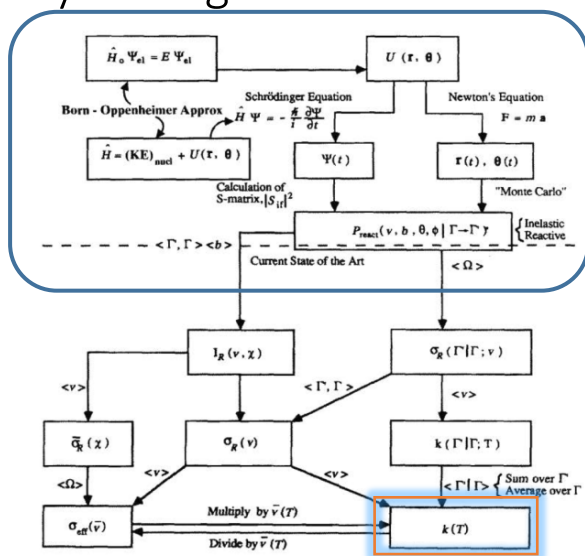
University of Delaware

2020

Outline

- From macroscopic observables to a microscopic description of chemical reactions (suggested reading Steinfeld et al. Chapter 6 & 7)
 - Potential energy surfaces
 - Long-range potentials
 - Empirical potentials
 - Molecular bonding potentials
 - Internal coordinates and Normal Modes of vibration
 - Ab Initio calculation of potential energy surfaces
 - Analytic potential energy functions
 - Reaction path and introduction to transition state theory
 - Potential energy surfaces of electronically excited molecules

From the intermolecular potential energy surface to thermally averaged rate coefficients.

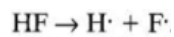


Potential energy curve

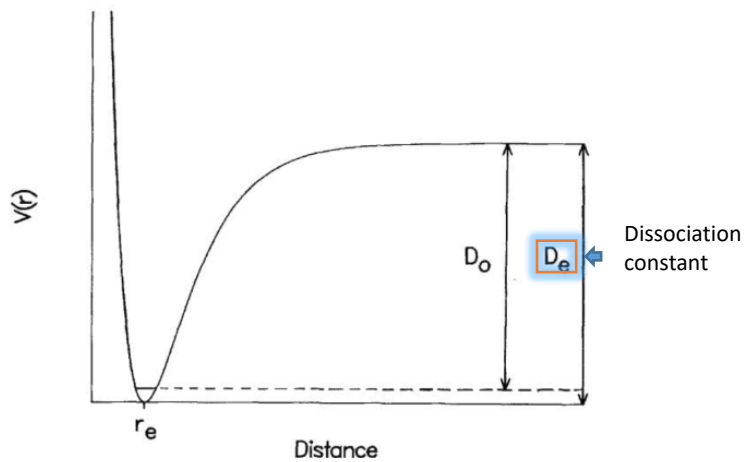
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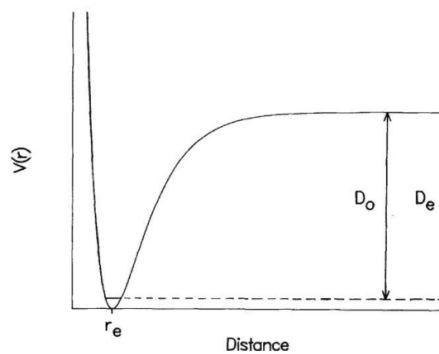
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Potential between two charges $Z_1 e$ and $Z_2 e$.



Long-range potentials

For N atoms, the potential energy surface depending on 3N-6 independent coordinates.

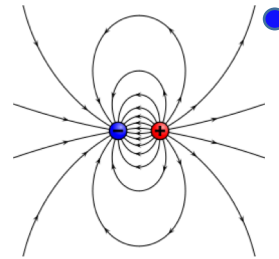
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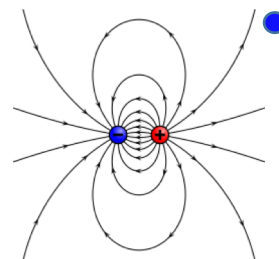
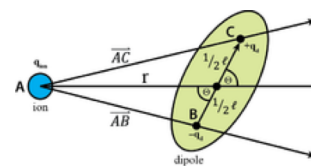
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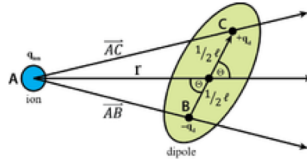
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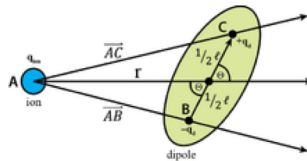
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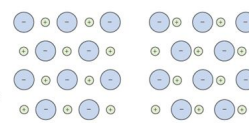
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Electronic Polarization



Ionic Polarization



Orientation Polarization



A dipole may be induced by the electric field of an ion.

$$\mu = \alpha_2 \mathbf{E}$$

Where α_2 is the polarizability of the nonpolar molecule. The magnitude of the ion's electric field is given by

$$E = -d[Z_1 e/r]/dr = Z_1 e/r^2$$

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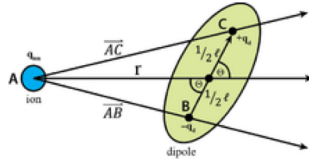
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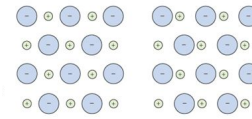
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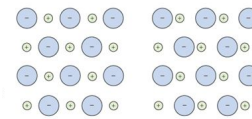
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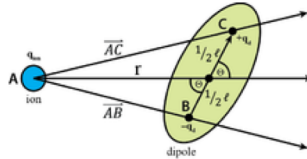
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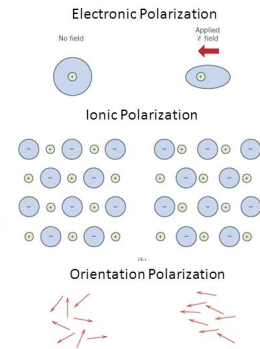
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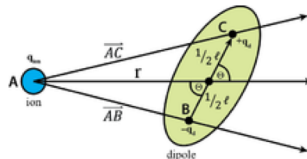
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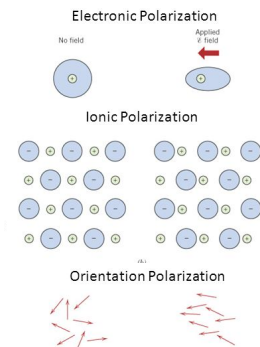
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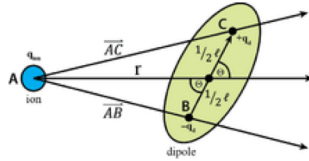
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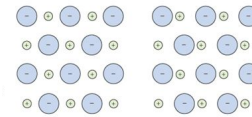
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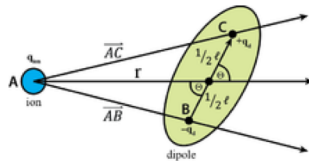
Similarly, a dipole μ_2 may be induced by a μ_1 dipole .

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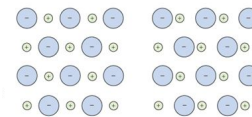
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For a large number of particles, the average interaction energy is obtained by averaging the interaction potential at a fixed r ; over all possible orientations.

Each orientation is weighted by the Boltzman factor: $\exp[-V(\theta_1, \theta_2; r)/k_B T]$

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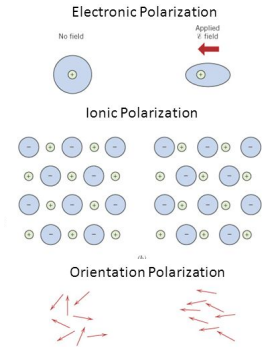
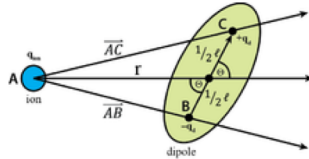
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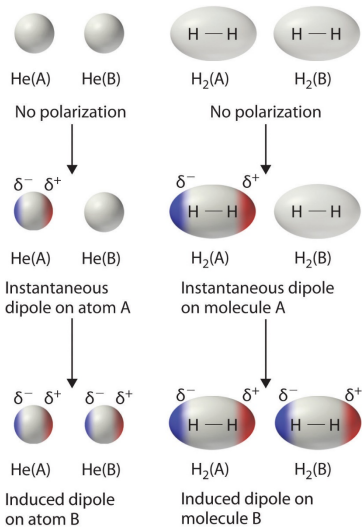


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$$V(r, \theta) = \frac{-\alpha_2 \mu_1^2 (3 \cos^2 \theta + 1)}{2r^6} \Rightarrow \langle V(r) \rangle = -\frac{2}{3} \frac{\mu_1^2 \mu_2^2}{k_B T r^6}$$

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Intermolecular potentials

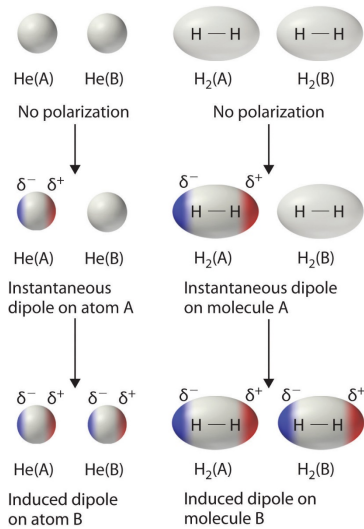


Dispersion and London forces are present even in the absence of net charges and permanent dipoles. The interaction energy from QM perturbation theory, is

$$V(r) = \frac{-3I_1 I_2}{2(I_1 + I_2)} \frac{\alpha_1 \alpha_2}{r^6}$$

I is first ionization potential of molecules 1 and 2
 α are polarizabilities

Intermolecular potentials



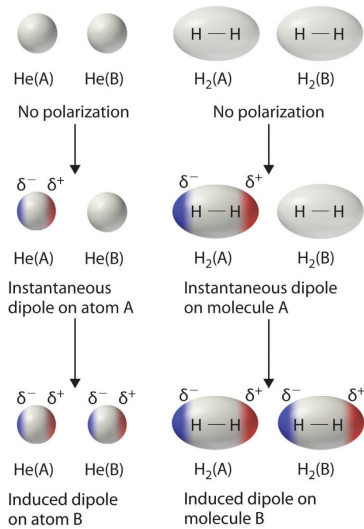
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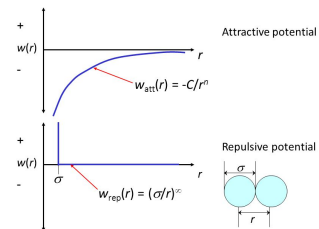
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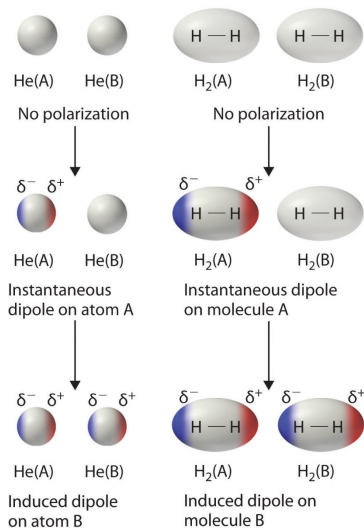
Hard sphere potential :

$$V(r) = 0 \quad r > \sigma$$

$$V(r) = \infty \quad r < \sigma$$



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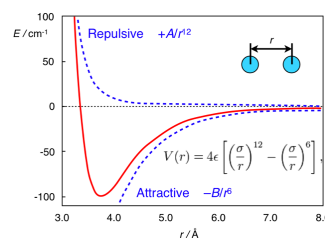
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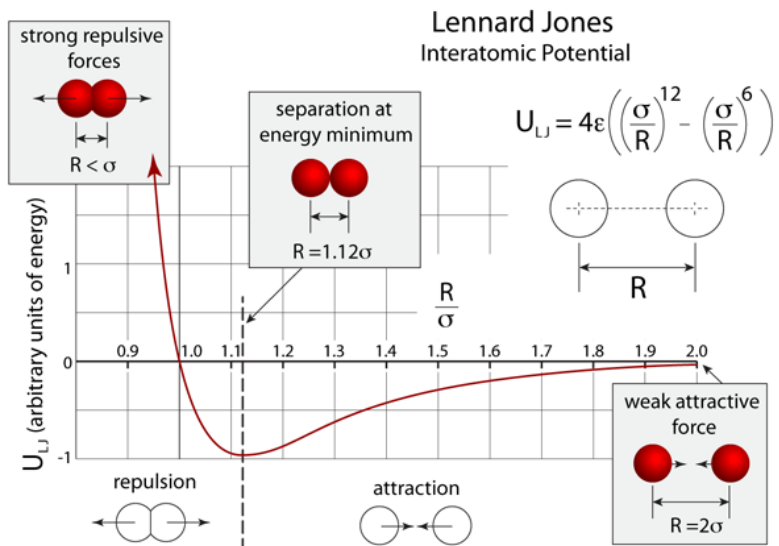
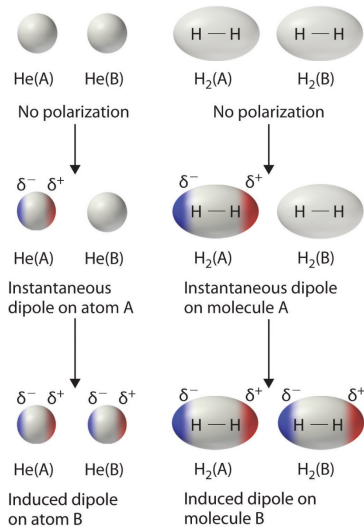
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Lennard-Jones potential (6-12) :

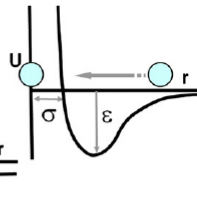
$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Intermolecular potentials

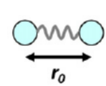


Molecular bonding potentials

$$U = \sum_{i < j} \sum 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$


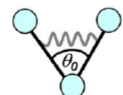
Harmonic potential for bonds



$$+ \sum_{\text{bonds}} \frac{1}{2} k_b (r - r_0)^2$$



Angles between 3 particles



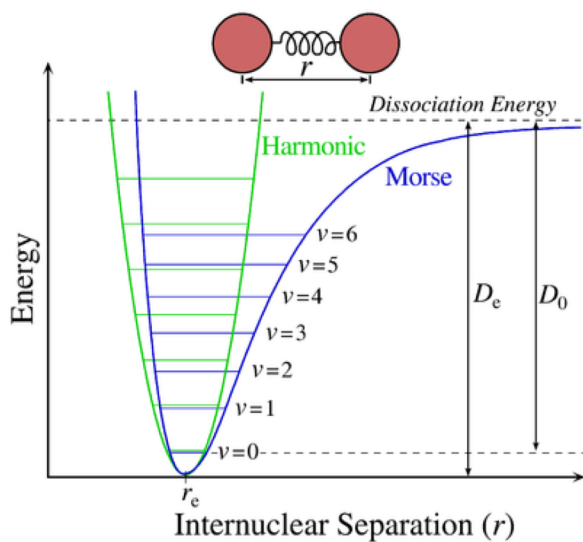
$$+ \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2$$


Torsion angles involving 4 particles



$$+ \sum_{\text{torsions}} k_\phi [1 + \cos(n\phi - \delta)]$$


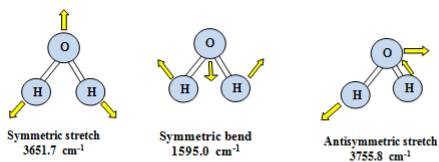
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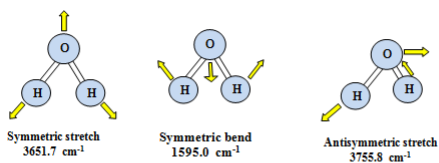
$$V(r) = D_e [1 - \exp\{-\beta_e(r - r_e)\}]^2$$

Morse potential are used to introduce anharmonicity.

Normal modes of vibration



Normal modes of vibration



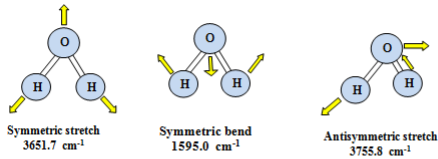
Consider the stretching vibration of a diatomic molecule with the harmonic potential:

$$V = f(r - r_e)^2/2$$



Let's make $r = x_2 - x_1$.

Normal modes of vibration



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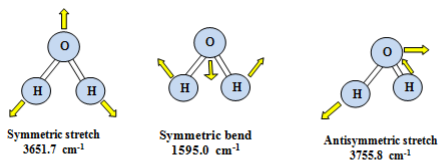


Let's make $r = x_2 - x_1$.

And calculating the second derivatives of the potential with respect to the Cartesian coordinates :

$$\partial^2 V / \partial x_1^2 = -f, \quad \partial^2 V / \partial x_2^2 = f, \quad \text{and} \quad \partial^2 V / \partial x_1 \partial x_2 = \partial^2 V / \partial x_2 \partial x_1 = -f.$$

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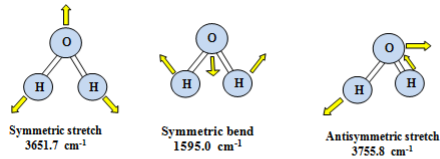
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$$\mathbf{F} = \begin{vmatrix} f/m_1 & -f/(m_1 m_2)^{1/2} \\ -f/(m_1 m_2)^{1/2} & f/m_2 \end{vmatrix}$$

Normal modes of vibration



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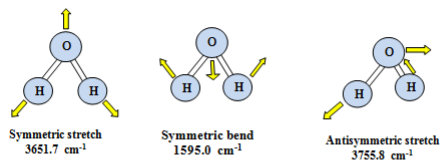
Hessian, second derivative matrix :

$$H f(x_1, x_2, \dots, x_n) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \frac{\partial^2 f}{\partial x_1 \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \frac{\partial^2 f}{\partial x_2 \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \frac{\partial^2 f}{\partial x_n \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

Thus, the mass-weighted Cartesian force constant matrix is (Hessian):

$$\mathbf{F} = \begin{bmatrix} f/m_1 & -f/(m_1 m_2)^{1/2} \\ -f/(m_1 m_2)^{1/2} & f/m_2 \end{bmatrix}$$

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And calculating the second derivatives of the potential with respect to the Cartesian coordinates :

$$\partial^2 V / \partial x_1^2 = f, \quad \partial^2 V / \partial x_2^2 = f, \quad \text{and} \quad \partial^2 V / \partial x_1 \partial x_2 = \partial^2 V / \partial x_2 \partial x_1 = -f.$$

Hessian, second derivative matrix :

$$H f(x_1, x_2, \dots, x_n) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \frac{\partial^2 f}{\partial x_1 \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \frac{\partial^2 f}{\partial x_2 \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \frac{\partial^2 f}{\partial x_n \partial x_3} & \dots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

Thus, the mass-weighted Cartesian force constant matrix is (Hessian):

$$\mathbf{F} = \begin{bmatrix} f/m_1 & -f/(m_1 m_2)^{1/2} \\ -f/(m_1 m_2)^{1/2} & f/m_2 \end{bmatrix}$$

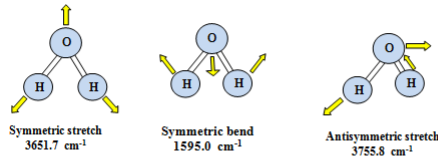
Solving the eigenvector problem :

$$(\mathbf{F} - \lambda \mathbf{I})\mathbf{L} = \mathbf{0}$$

We get :

$$\begin{bmatrix} f/m_1 - \lambda & -f/(m_1 m_2)^{1/2} \\ -f/(m_1 m_2)^{1/2} & f/m_2 - \lambda \end{bmatrix} = 0$$

Normal modes of vibration



Consider the stretching vibration of a diatomic molecule with the harmonic potential:

$$V = f(r - r_e)^2/2$$

Let's make $r = x_2 - x_1$.



And calculating the second derivatives of the potential with respect to the Cartesian coordinates :

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Thus, the mass-weighted Cartesian force constant matrix is (Hessian):

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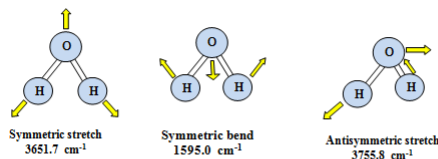
Solving the eigenvector problem :

$$(\mathbf{F} - \Lambda)\mathbf{L} = 0 \quad \mu = m_1 m_2 / (m_1 + m_2)$$

We get :

$$\begin{bmatrix} f/m_1 - \lambda & -f/(m_1 m_2)^{1/2} \\ -f/(m_1 m_2)^{1/2} & f/m_2 - \lambda \end{bmatrix} = 0 \quad \begin{matrix} \lambda_1 = 0 \\ \lambda_2 = f/\mu \end{matrix}$$

Normal modes of vibration



Consider the stretching vibration of a diatomic molecule with the harmonic potential:

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Solving the eigenvector problem :

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Translation $\longrightarrow \lambda_1 = 0$

Vibration $\longrightarrow \lambda_2 = f/\mu$