Introduction: What is Computational Chemistry?

Lecture Material: Lectures will be based on the following texts.

Lewars EG (2011) *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics*, 2nd edn. Springer, London New York.

Cramer CJ (2004) Essentials of *Computational Chemistry: Theories and Models*, 2nd edn. Wiley, Chichester, UK.

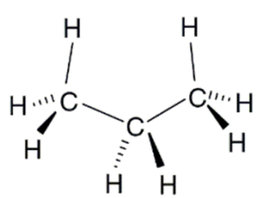
Reading Material: Lewars; Ch1; Ch 2, pg 9-35

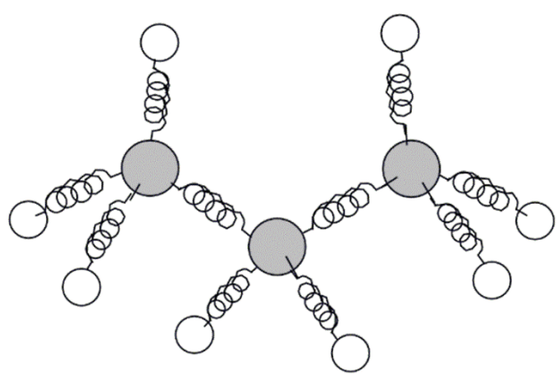
Models of Computational Chemistry

- Molecular Mechanics

– Ball-and-spring model of molecules

energy is expressed as a function of its resistance toward **bond-stretching**, **bond-bending**, and **Van der Waals overlap** (atom crowding).





- *Ab-Initio* Methods (from first principles)

– Based on approximate solutions to the Schrodinger equation ***without*** fitting to experiment, through optimization of a molecular wavefunction.

$$\hat{H}\psi = E\psi$$

- Semiempirical Methods

– Based on approximate solutions to the Schrodinger equation ***with*** fitting to experiment, through optimization of a molecular wavefunction.

- Density Functional Theory

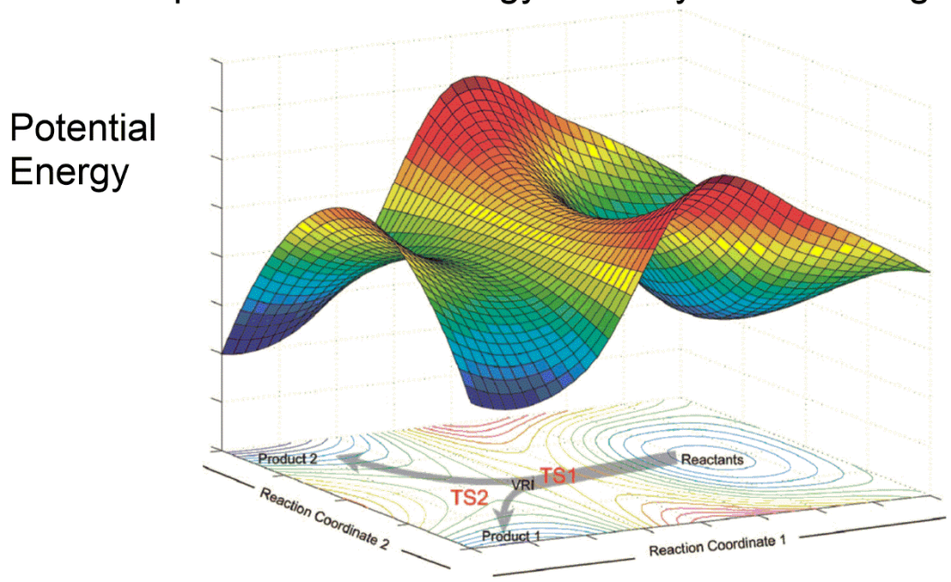
– Based on approximate solutions to the Schrodinger equation ***without*** fitting to experiment, through optimization of a molecular electron density.

Before introduction to the models, a firm understanding of potential energy surfaces is required, which is a central concept in computational chemistry.

Introduction to Potential Energy Surfaces

- Potential Energy Surface

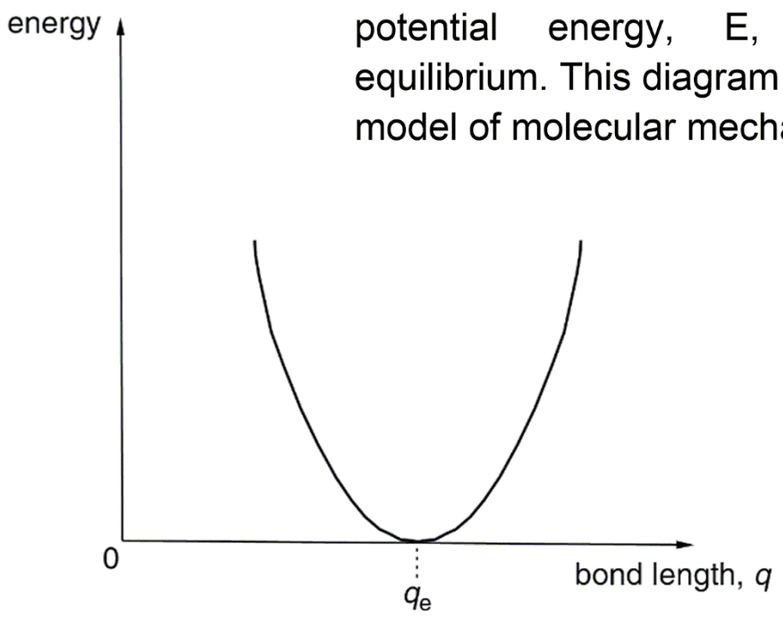
– The relationship between the energy of the system and its geometry



Potential Energy Diagram

– Energy as a function of bond length, bond angle, or dihedral angle

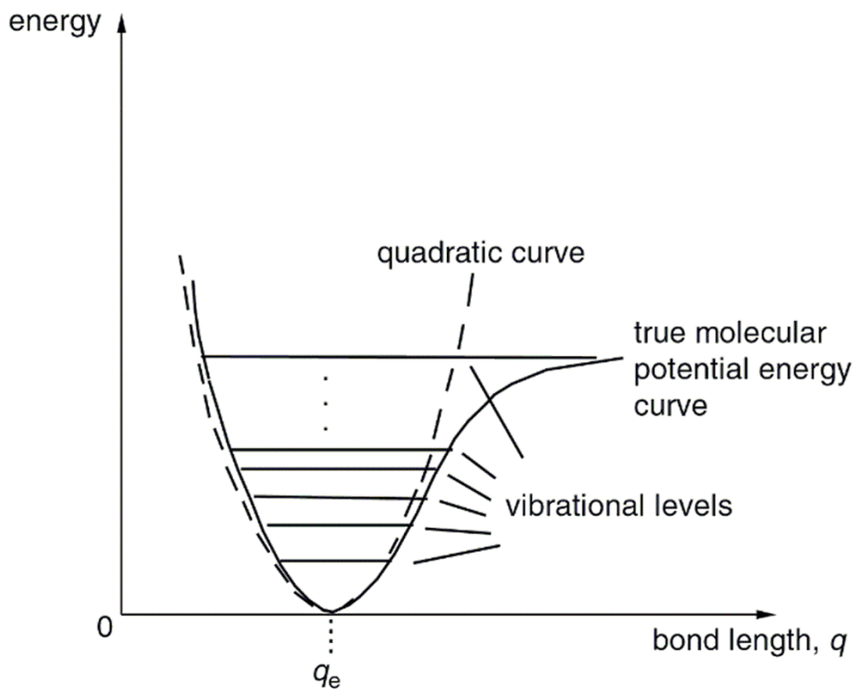
Consider a diatomic molecule A-B (with only one geometric parameter, q) distorted from the equilibrium bond length, q_e. It possesses some potential energy, E, when stretched from equilibrium. This diagram follows the ball-and-spring model of molecular mechanics.



In reality, molcules behave similar to the ball-and-spring model, but with some notable differences.

– Molecules are never stationary, and vibrately perpetually about the equilibrium bond length. A molecular does never has zero energy but rather occupies one of the available vibrational levels with some non-zero energy.

– Near the equilibrium bond length, q_e, the potential energy is accurately described by the quadratic equation $E=1/2k(q - q_e)^2$, where k is the bond/spring force constant. In real molecules, potential energy deviates from the quadratic form as q_e is deviated from. The region of deviation is the ***anharmonic*** region.



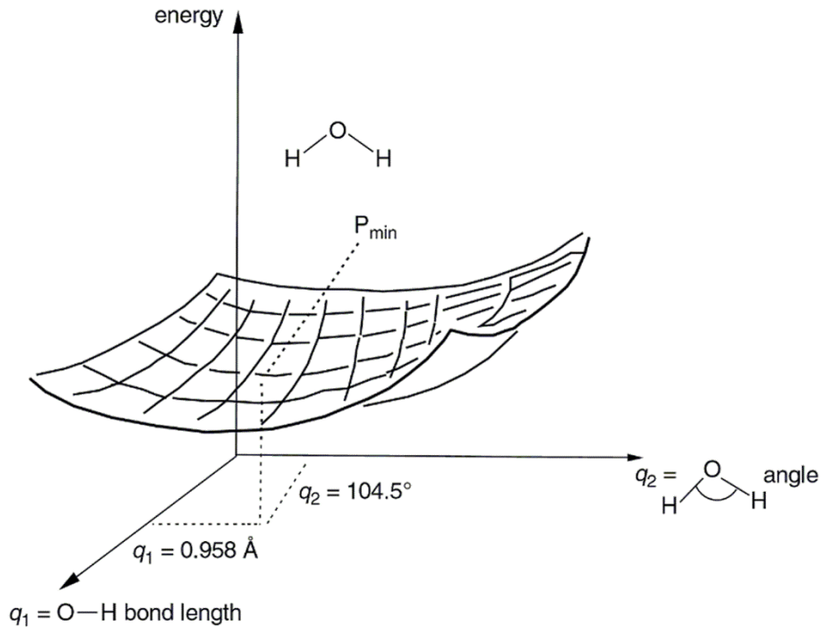
Introduction to Potential Energy Surfaces

A molecule with more than one geometric parameter provides a PES. Consider H_2O as an example.

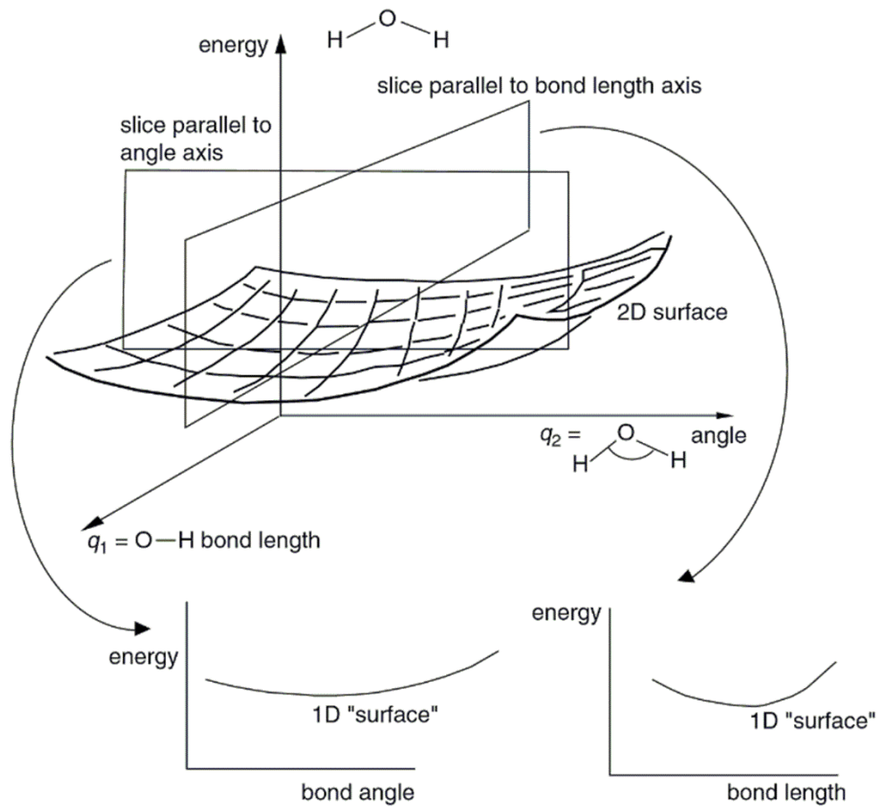
– If each O-H bond is the same, then the entire PES for H_2O contains two geometric parameters; O-H bond length (q_1), H-O-H bond angle (q_2).

– Equilibrium for H_2O is at q_{1e}=0.958Å and q_{2e}=104.5°. This equilibrium point is a minimum and must satisfy the criteria for a minimum of;

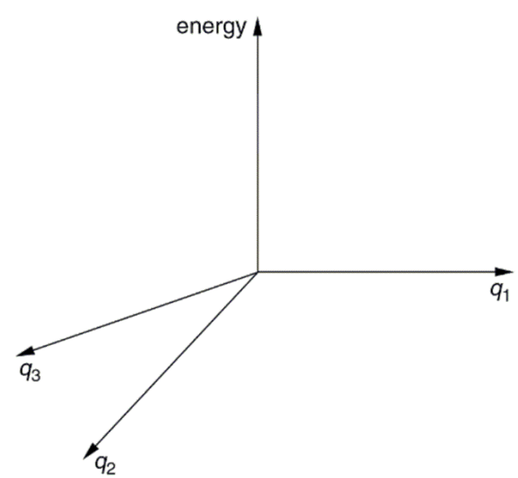
$$dE/dq_1 = dE/dq_2 = 0 \qquad @\ P_{min}$$



One dimensional surfaces can be obtained through slices of the along the exis for each parameter of a 3-D surface.



A system with more than two geometric parameters (q_1, q_2, q_3, ...) cannot be accurately visualized and is called a hypersurface. FOr example, the full potential energy surface for H-O-F is a hypersurface with three geometric coordinates; q_1 = H-O length, q_2 = O-F length, and q_3 = H-O-F angle. H-O-F would give a 4-D hypersurface.

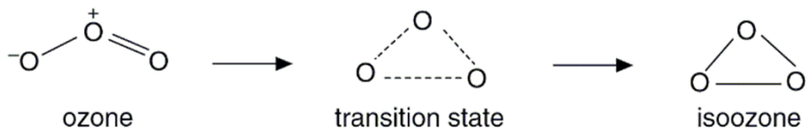


Introduction to Potential Energy Surfaces

• Stationary Points

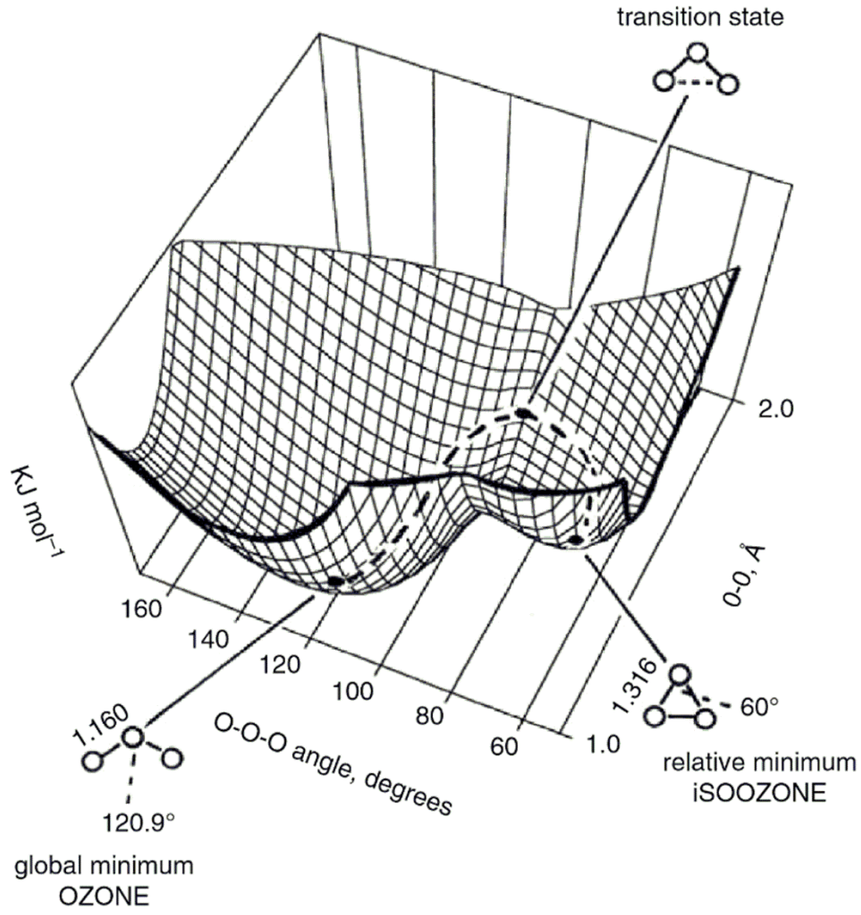
The stationary points on a PES are of particular interest in computational chemistry which include minima, maxima, and saddle points.

Consider the following three stationary points involving ozone isomerization.

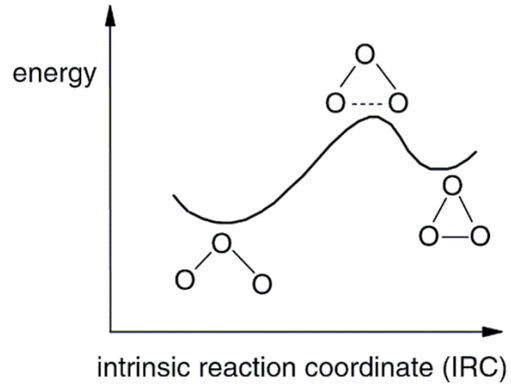


The minima ozone and isoozone may plausibly interconvert. The interconversion between minima requires the inclusion of at least one additional stationary point, one of which must be a saddle point (aka a transition state). Both ***Kinetic*** and ***thermodynamic*** data can be obtained from an understanding of the energetics of this interconversion.

The PES for this process can be visualized using the O-O bond forming length and the O-O-O bond angle (assuming that the other two O-O bond lengths remain roughly equal throughout the process). THe below sruface was computed using semi-empirical theory at the AM1 level.



The lowest energy path on the surface is called the ***intrinsic reaction coordinate*** (IRC). The IRC is some composite of the O-O-O angle and the O-O bond length.



Introduction to Potential Energy Surfaces

- Stationary Points

– What is the criteria for a stationary point?

The derivative of the energy with respect to all coordinates must be zero

$$\frac{\partial \boldsymbol{E}}{\partial \boldsymbol{q}_1} = \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{q}_2} = \cdots = 0$$

Curvature characterizes the nature of the stationary point.

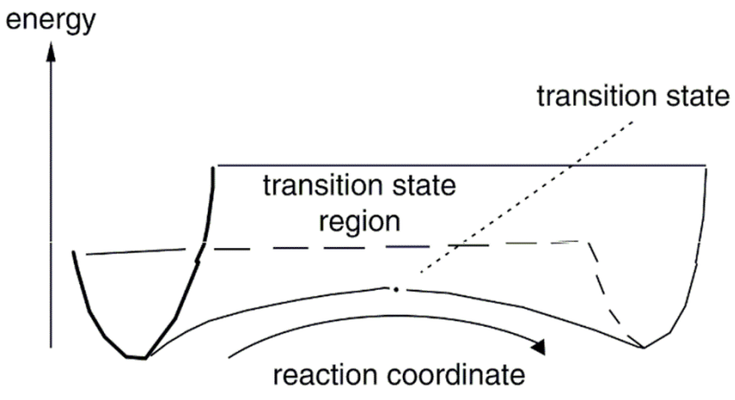
– Minimum $\quad \frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2} > 0$

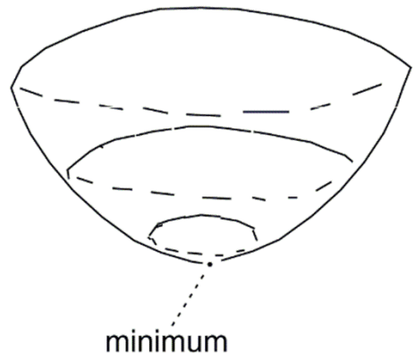
– Maximum (hilltop) $\quad \frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2} < 0$

– Saddle point

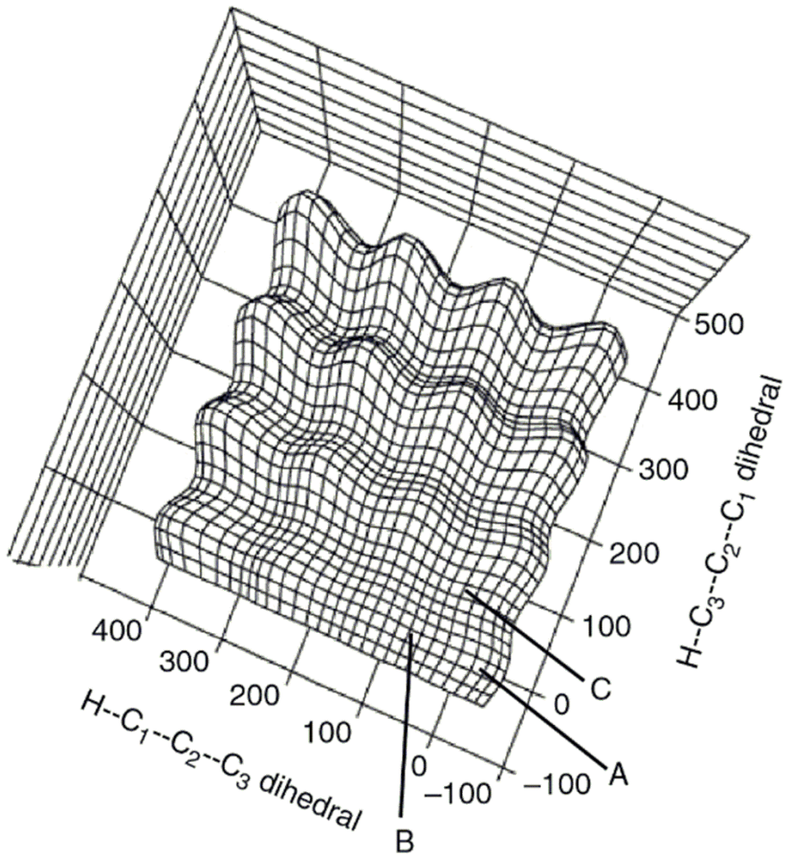
All second derivatives are negative except for that of the reaction coordinate.

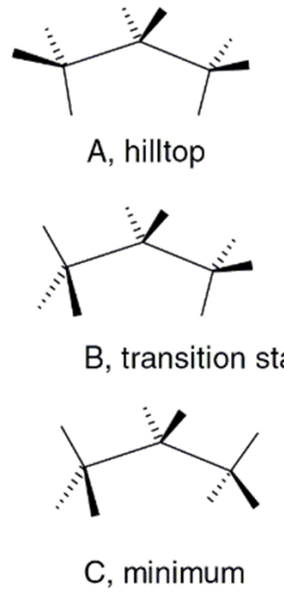
For all ***q*** except the IRC: $\frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2} > 0$ ***q*** of IRC: $\frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2} > 0$





Propane PES with varying dihedral angles computed at the AM1 semiempirical level of theory

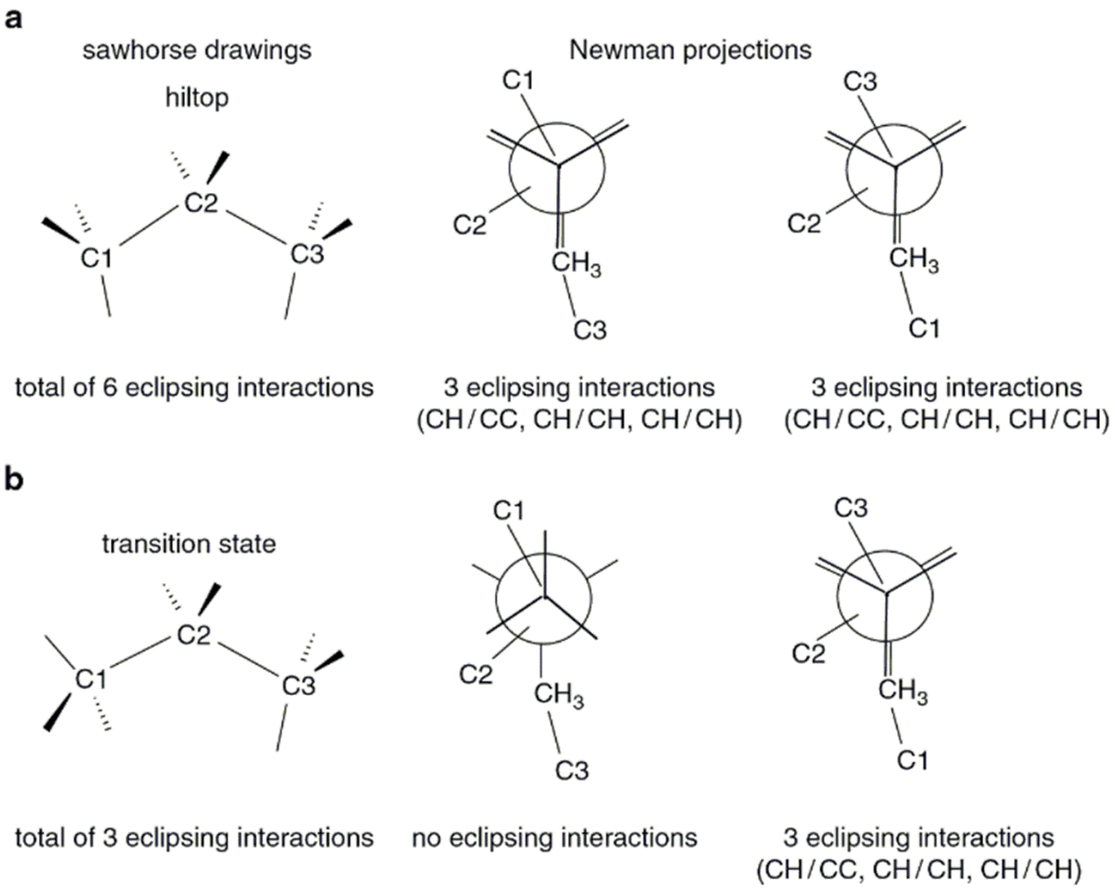




C is a hilltop or more specifically, a second order saddle point. Traversal of either dihedral coordinate exits the hilltop to a first order saddle point, **B**.

Introduction to Potential Energy Surfaces

– Stationary points on the propane surface



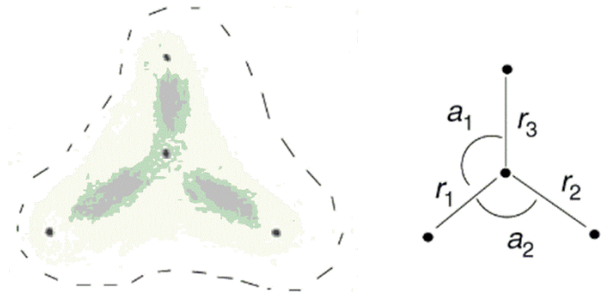
• Born-Oppenheimer Approximation

The motion and position of the nuclei and electrons are independent and the nuclei are stationary relative to the electrons.(m_p = 2000m_e)

Our undertanding of molecular structure relies on the B-O approximation.

The electrons are thus smeared out accross the nuclei. The nuclear coordinates define the molcular geometry.

time-averaged electron cloud



geometry based on nuclear positions

• Geometry Optimization

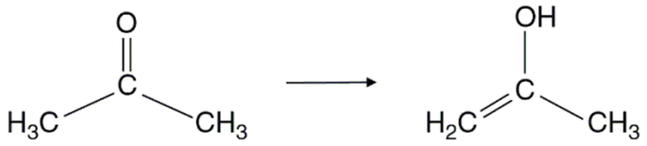
How do we efficiently locate stationary points from a given starting geometry?

Systematic geometric perturbations until criteria for a stationary point is met.

Chemists are mostly interested in mimina (local and global) and transition states.

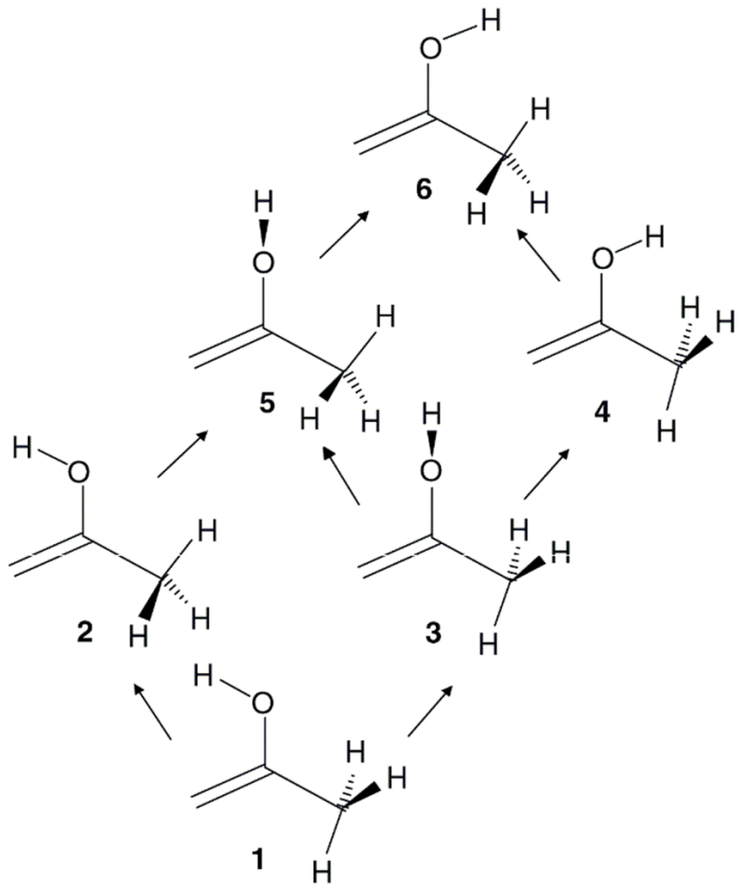
Introduction to Potential Energy Surfaces

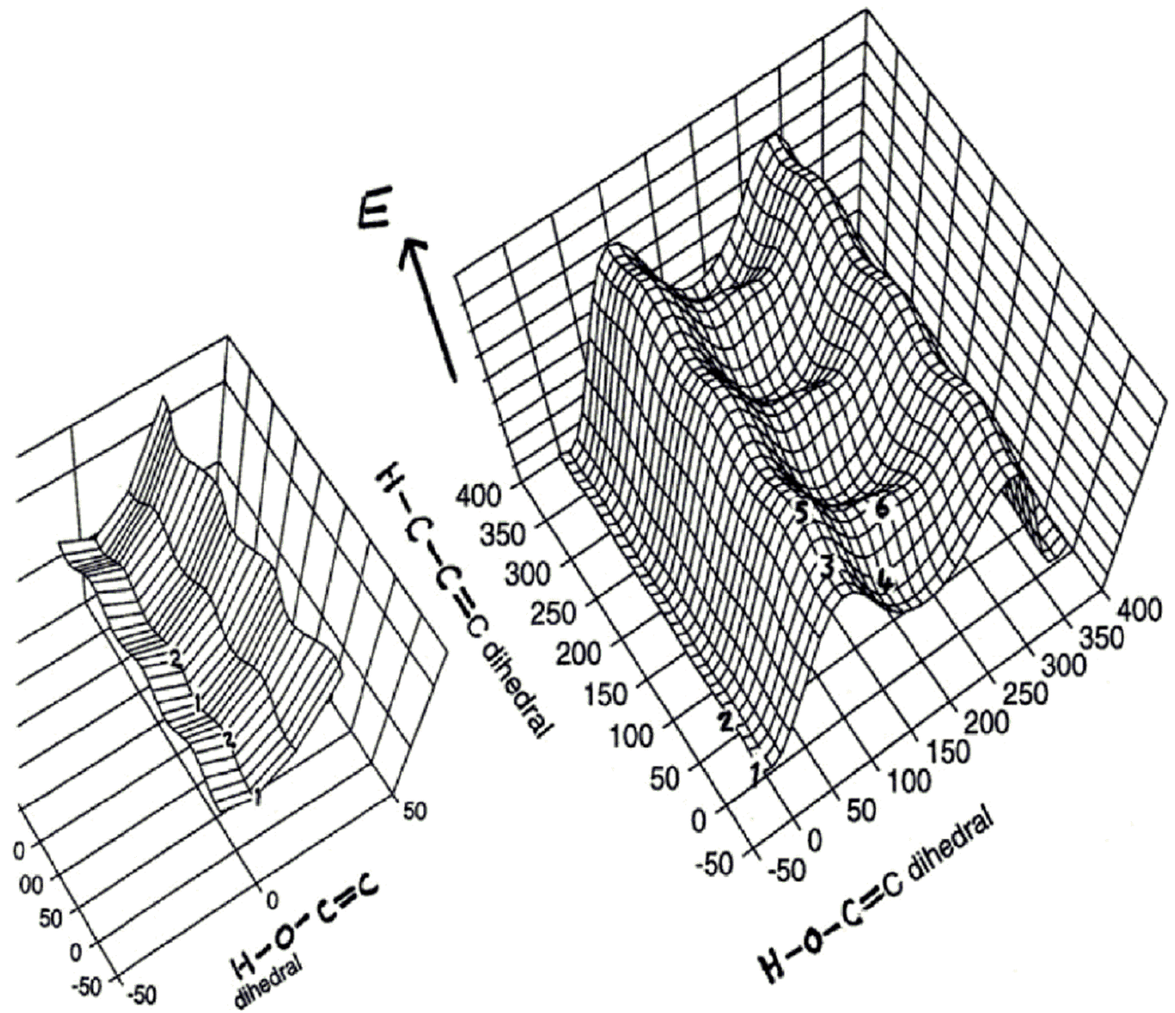
Example: keto-enol tautomerization



Which conformer of the enol should be focused on?

Rotation about the C-O bond and the C-C bonds creates 6 possible stationary points.





1 is the global minimum

2 is a transition state involving C-C bond rotation

3 is a transition state involving C-O bond rotation

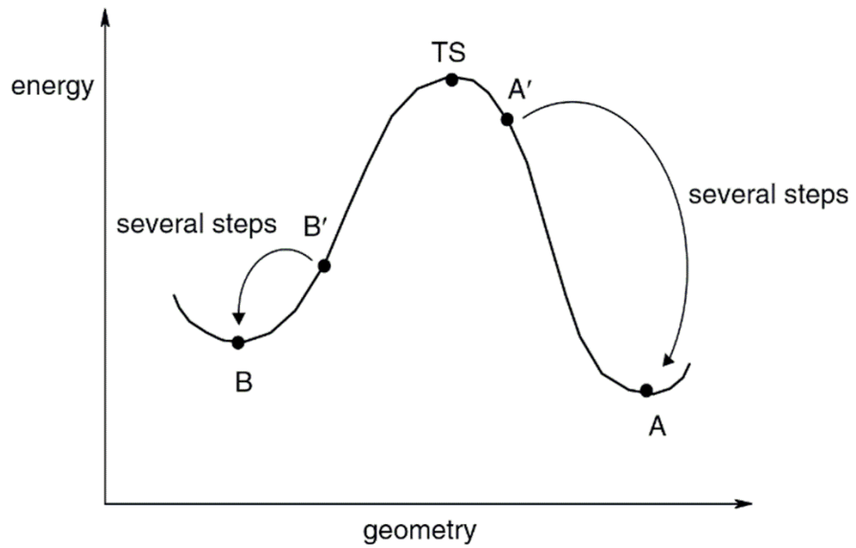
4 is a local minimum

5 is a hilltop, second order saddle point

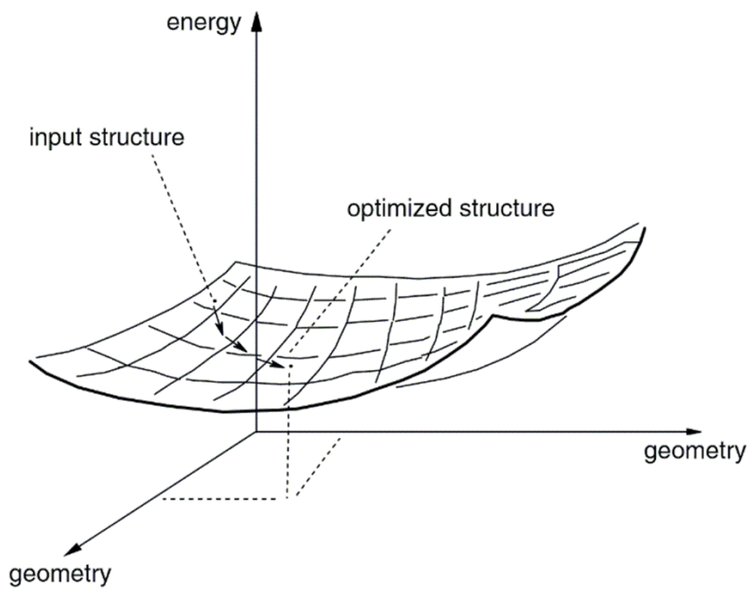
6 is a hilltop, second order saddle point

Introduction to Potential Energy Surfaces

The mimimum obtained in an optimization is that closed to the starting geometry. Obtaining the global minimum requires the exploration of all plausible mimima on the PES and determining the lowest energy minimum.

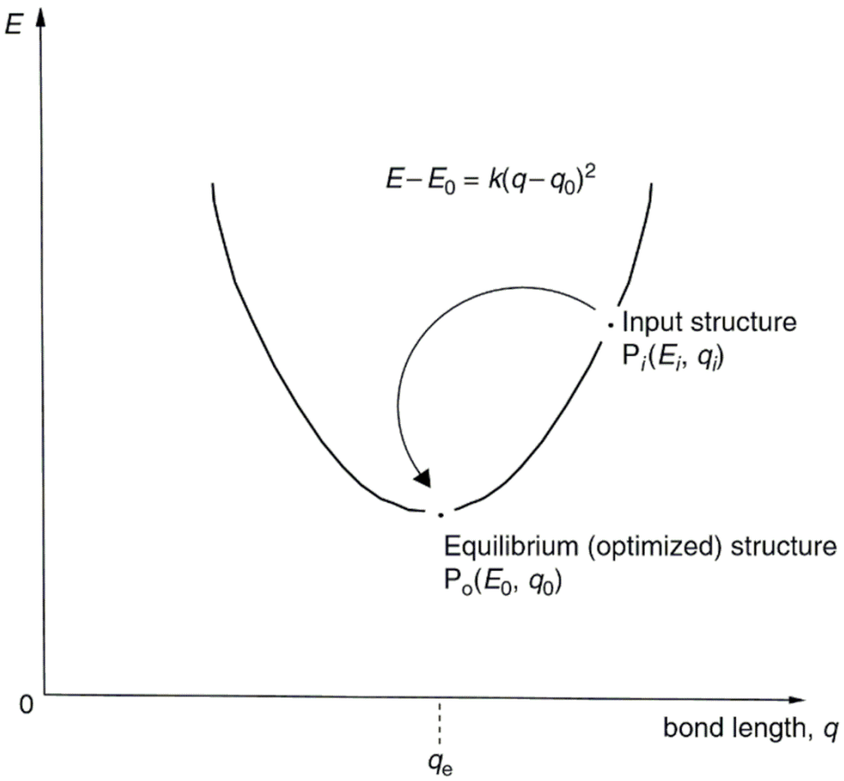


Optimization on a complex surface. An efficient optimization algorithm is that which reaches the optimized geometry from the input geometry in the fewest number of steps.



How is an optimized geometry obtained from an input geometry?

An example using a diatomic molecule with a spring potential.



$$E - E_{\mathrm{o}} = k\,(q - q_{\mathrm{o}})^2$$

$$\text{At the input point} \quad (dE/dq)_i = 2k(q_i - q_{\mathrm{o}})$$

$$\text{At all points} \quad d^2\mathrm{E}/dq^2 = 2k\,(= \text{force constant})$$

$$\text{From Eqs. (2.6) and (2.7),} \qquad (dE/dq)_{\mathrm{i}} = (d^2E/dq^2)\,(q_i - q_{\mathrm{o}})$$

$$\text{and} \quad q_{\mathrm{o}} = q_{\mathrm{i}} - (dE/dq)_{\mathrm{i}}/(d^2E/dq^2)$$

An improved geometry is obtained from knowledge of the slope (*dE/dq*) and local curvature (d^2E/dq^2) at the input geometry.

Introduction to Potential Energy Surfaces

Consider a more complex non-linear molecule H-O-F.

In a cartesian coordinate system, each atom has 3 coordinates (x, y, and z)

H-O-F therefore has 9 coordinates (q_1, q_2, q_3, ... q_9)

First and second derivatives of the energy with respect to all 9 coordinates are needed and can be expressed as matrices.

First derivate matrix is called the **gradient matrix**.

$$\mathbf{g}_i = \begin{pmatrix} (\partial \boldsymbol{E}/\partial \boldsymbol{q}_1)_i \\ (\partial \boldsymbol{E}/\partial \boldsymbol{q}_2)_i \\ \vdots \\ (\partial \boldsymbol{E}/\partial \boldsymbol{q}_9)_i \end{pmatrix}$$

Second derivative matrix (or the force constant matrix) is called the **Hessian matrix**.

$$\mathbf{H} = \begin{pmatrix} \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_1 q_1} & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_1 q_1} \cdots & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_1 q_9} \\ \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_2 q_1} & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_2 q_2} \cdots & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_2 q_9} \\ \vdots & \vdots \cdots & \vdots \\ \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_9 q_1} & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_9 q_2} \cdots & \partial^2 \boldsymbol{E}/\partial \boldsymbol{q_9 q_9} \end{pmatrix}$$

With input coordinates ($\mathbf{q_i}$) and optimized coordinates ($\mathbf{q_o}$).

$$\mathbf{q}_i = \begin{pmatrix} q_{i1} \\ q_{i2} \\ \vdots \\ q_{i9} \end{pmatrix} \qquad \mathbf{q}_o = \begin{pmatrix} q_{o1} \\ q_{o2} \\ \vdots \\ q_{o9} \end{pmatrix}$$

The matrix equation for obtaining the optimized geometry can be shown as:

$$\mathbf{q}_o = \mathbf{q}_i - \mathbf{H}^{-1}\,\mathbf{g}_i$$

analogous to:

$$q_o = q_i - (d^2E/dq^2)^{-1}(dE/dq)_i$$

A number of iterations is carried out until the new coordinates and energy change do not change relative to the previous iteration.

The Hessian matrix can be expensive to calculate analytically for each iteration and is often approximated as a ratio of finite increments.

$$\frac{\partial^2 E}{\partial q_i \partial q_j} \approx \frac{\Delta(\partial E/\partial q_j)}{\Delta q_i}$$

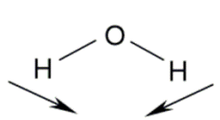
Introduction to Potential Energy Surfaces

• Stationary Point Characterization

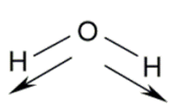
After an optimization, how is a minimum, hilltop, or saddle point identified?

– Check the ***Normal Modes*** of the system
– **Normal Modes**: fundamental vibrations of the sytstem involving synchronous motion of all atoms with the same frequency. All other molecular vibrations are a composition of normal modes
– A ***non-linear*** molecule has 3n-6 normal modes (n = # of atoms)
– A ***linear*** molecule has 3n-5 normal modes

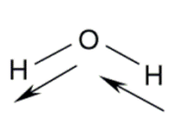
Normal modes for H_2O



1595 cm^{-1}
bend



3652 cm^{-1}
symmetric stretch



3756 cm^{-1}
asymmetric stretch

For a linear molecule, the singular normal mode is related to the force constant accoding to;

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

One we have the force constants, the normal modes can be obtained through mass-weighting (μ).

How do we obtain the force constants? From the **Hessian matrix**.

Matrix diagonalization of the Hessian furnishes information regarding the normal modes. Both **scalar** (force constants) and **direction** (normal mode vectors).

Matrix diagonalization of **A** produces, where **D** is a diagonal matrix with of-diagonal elements equal to 0.

$$\mathbf{A} = \mathbf{PDP}^{-1}$$

$$\mathbf{H} = \begin{pmatrix} \partial^2 E/\partial q_1 q_1 & \partial^2 E/\partial q_1 q_2 & \cdots & \partial^2 E/\partial q_1 q_9 \\ \partial^2 E/\partial q_2 q_1 & \partial^2 E/\partial q_2 q_2 & \cdots & \partial^2 E/\partial q_2 q_9 \\ \vdots & \vdots & \cdots & \vdots \\ \partial^2 E/\partial q_9 q_1 & \partial^2 E/\partial q_9 q_2 & \cdots & \partial^2 E/\partial q_9 q_9 \end{pmatrix}$$

$$= \underbrace{\begin{pmatrix} q_{11} & q_{12} & \cdots & q_{19} \\ q_{21} & q_{22} & \cdots & q_{29} \\ \vdots & & & \\ q_{91} & q_{92} & \cdots & q_{99} \end{pmatrix}}_{\mathbf{P}} \underbrace{\begin{pmatrix} k_1 & 0 & \cdots & 0 \\ 0 & k_2 & \cdots & 0 \\ \vdots & & & \\ 0 & 0 & \cdots & k_9 \end{pmatrix}}_{\mathbf{k}} \mathbf{P}^{-1}$$

P is the eigenvector matrix and **k** is the eigenvalue matrix from diagonalization of **H**.

Normal mode with force constant k_1, vibrates in the direction characterized by vector q_{11}, q_{21}, q_{21}, ... q_{91}.

k_1, k_2, k_3 correspond to the translational motion of the system

k_4, k_5, k_6 correspond to the rotational motion of the system

Introduction to Potential Energy Surfaces

The force constant matrix tells us the identity of the optimized stationary point.

– All $k > 0$; stationary point is a minimum (all frequencies are real)
– One $k < 0$; stationary point is a transition state (one imaginary frequency)
– More than one $k < 0$; stationary point is a hill top (more than one imaginary frequency)

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

*From the Hessian matrix, one can obtain an Infrared spectrum after mass-weighting.

The **zero point energy** (ZPE) can also be obtained from the frequencies. This energy is usually added to the electronic energy.

Example of adding the ZPE to the raw calculated electronic energy + nuclear replusion.