

Lesson 3: the Potential Energy Surfaces (PES)

Potential Energy Surface

- The Potential Energy Surface (PES) is a mathematical function that gives the internal energy of a molecule as a function of geometrical modulations as it stretches, bends, torsions, breaks, etc.

The PES of a molecule is obtained by the total interactions of:

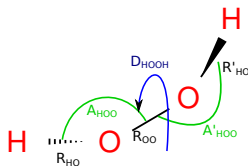
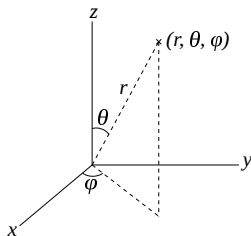
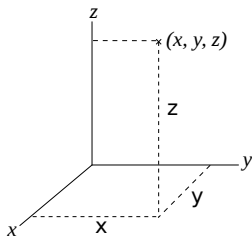
- nuclear-nuclear repulsion
- electron-electron interaction
- electron-nuclear attraction

The topology (surface) of the PES is dependent on what methods it is derived from

- Molecular Mechanics is based in some classical parameters and can provide approximate results.
- Quantum Mechanics is more accurate and exact and in principle and works for any molecule but computationally expensive.

Geometry Description

Coordinates	Notation	Degrees of freedom
Cartesian	x, y, z	$3N$
Spherical	r, θ, ϕ	$3N$
Internal	R, A, D	$3N-6$ ($3N-5$)



The Born-Oppenheimer Approximation

- the Born-Oppenheimer Approximations allows separation of electronic and nuclear degrees of freedom "simplifies things" even though they are coupled by the electron-nuclear potential energy $V_{eN}(\mathbf{r}, \mathbf{R})$.
Electrons are much lighter than the nuclei, thus with respect to electrons, the nuclei are almost stationary.
 - fix the nuclei at some chosen configuration \mathbf{R}_a
 - solve for the motion of the electrons for this nuclear configuration, giving an electronic energy $\mathbf{E}_e(\mathbf{R}_a)$
 - repeat for other nuclear configurations \mathbf{R}_b of interest, building up a Potential Energy Surface $\mathbf{E}_e(\mathbf{R}_b)$.

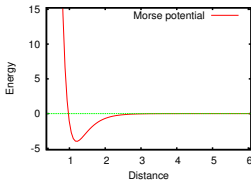
PES of a Diatomic Molecules

- can be visualized as function of energy versus internuclear distance (single internal coordinate)
- Morse potential:

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2 \quad (1)$$

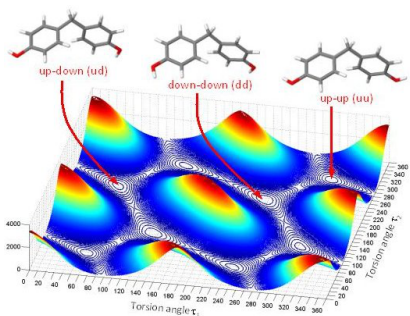
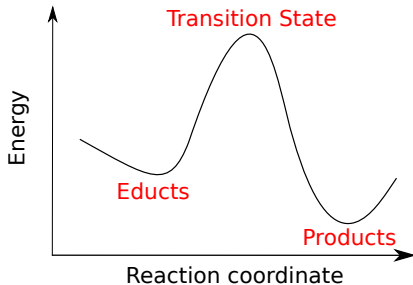
where

- D_e , is the depth of potential well
- a , controls the width of the potential
- r , is the internuclear separation
- r_e , is the equilibrium distance



PES of Multiatomic Systems

- impossible to visualize more than 2 variables and 1 energy dimension
- cuts from multidimensional space (hyperspace) where all other degrees of freedom are kept fixed



Important Points on the PES

- stationary points:

$$\frac{\partial E}{\partial q_i} = 0 \quad (2)$$

- local minimum:

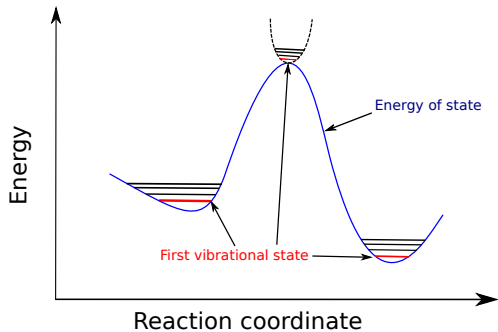
$$\frac{\partial^2 E}{\partial q_i^2} > 0 \text{ for all degrees of freedom} \quad (3)$$

- n^{th} order saddle point:

$$\frac{\partial^2 E}{\partial q_i^2} < 0 \text{ for } n \text{ degrees of freedom} \quad (4)$$

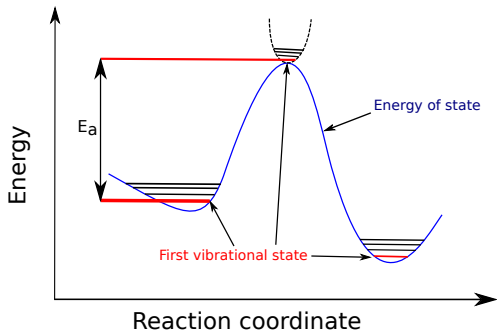
Zero-Point Energy (ZPE) Corrections

- Vibrational corrections for 0K (ground vibrational state)
- “Cancel out” for energy differences



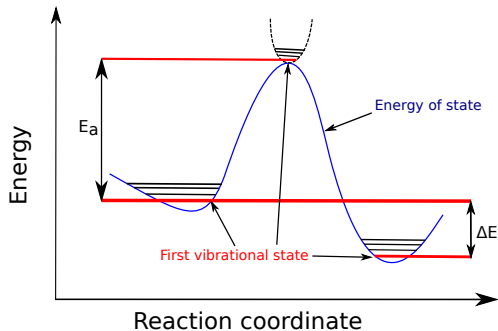
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Hessian Index

- a calculated optimized geometry needs a vibrational analysis to verify its location in the PES via the Hessian index
- the Hessian index is the number of negative eigenvalues of the force constant matrix (i.e. imaginary frequencies). For a stationary point, this corresponds to the number of internal degrees of freedom along which that point is a potential energy maximum. The Hessian index is:
 - 0 for minima
 - 1 for transition states
 - > 1 for higher-order saddle points

Relaxed vs Rigid PES

- there are two types of mapping the PES namely Rigid and Relaxed scanning
 - RIGID, means scanning the energetics of the molecule by only changing specific angle while all the bond lengths at their fixed position
 - RELAXED, means scanning the energetics while holding the dihedral angle constant at a series of values, and relaxing the remainder of the coordinates.
- the second method (RELAXED Scan) will give us the true minimum energy path while the first method is merely an approximation to the minimum energy path.

ACTIVITY

- Activities related to Potential Energy Surface scans will be included in

Lesson 7 : PES Scan, Reaction Coordinates, and Transition State Search

Introduction to Computational Quantum Chemistry

END