

Chemical dynamics

CHEM674

<https://www.slideshare.net/jahanghasemi/potential-energy-surface-molecular-mechanics-forcefield>

Ab Initio calculation of potential energy surfaces

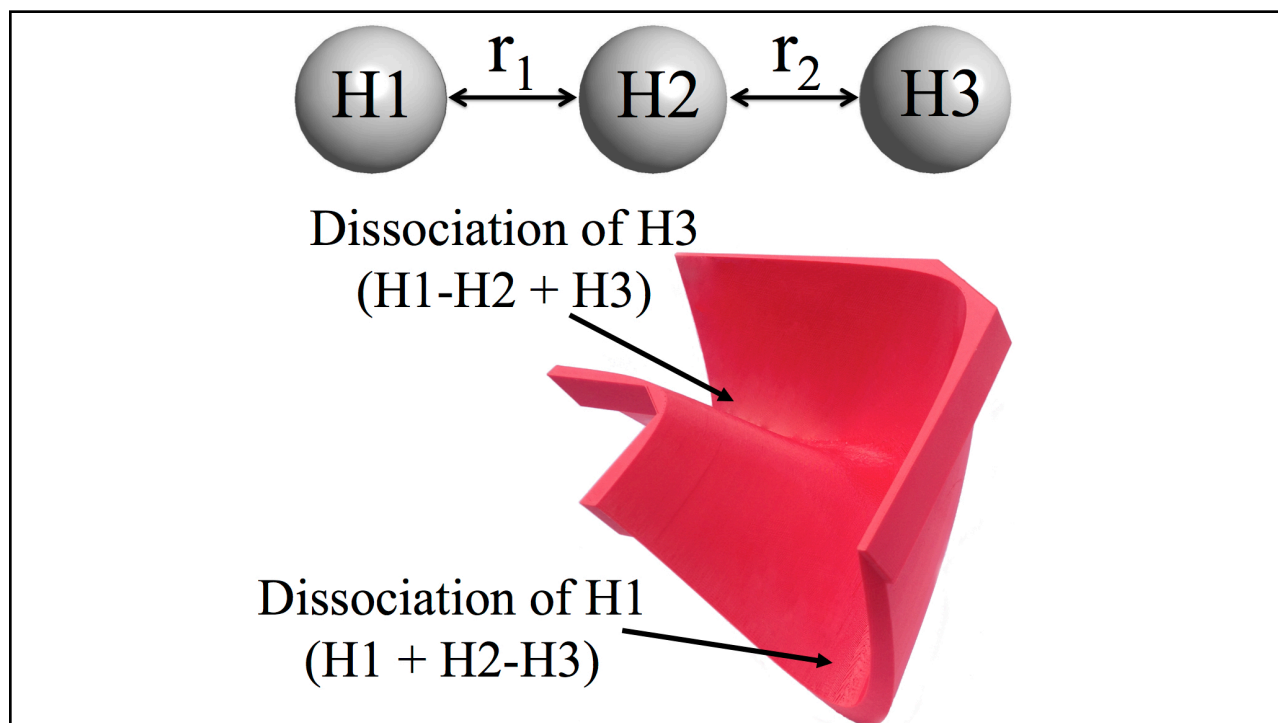
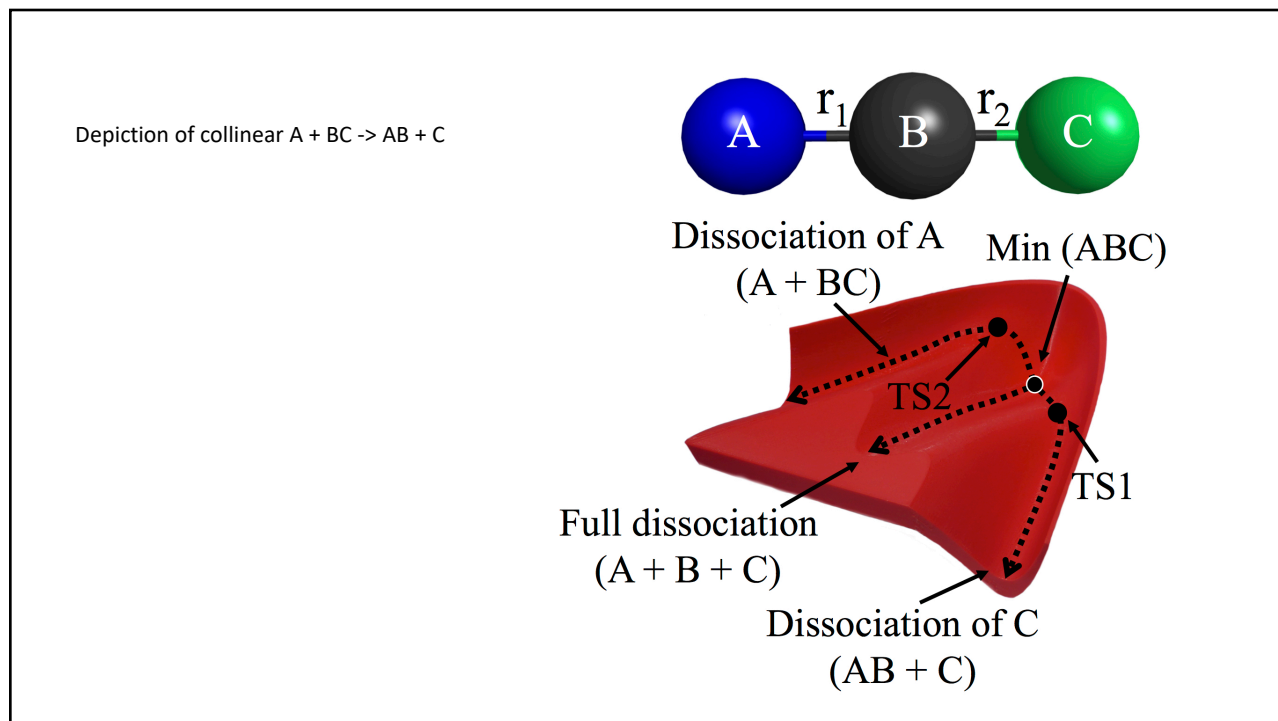
Andrew Teplyakov

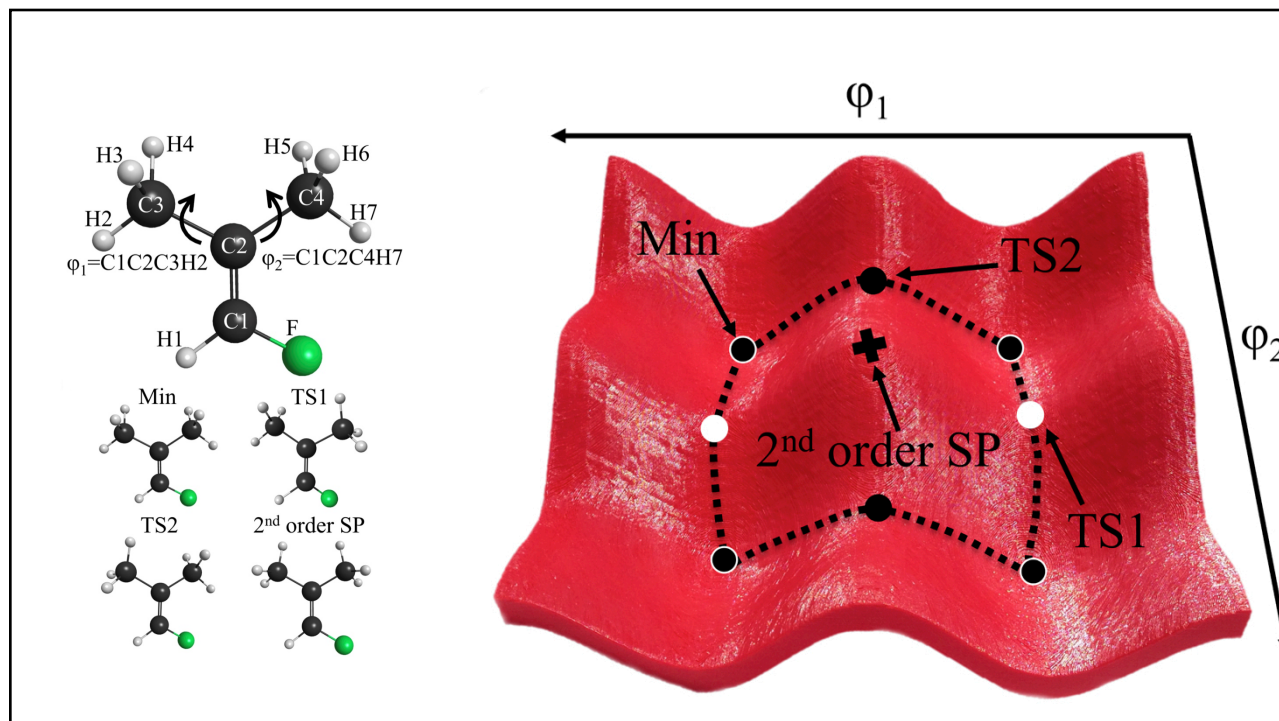
University of Delaware

Fall-2017

Outline

- From macroscopic observables to a microscopic description of chemical reactions (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





Ab initio calculation of potential energy surfaces

Using the Born-Oppenheimer approximation the molecular wave function is written as

$$\Psi = \Psi_e(\mathbf{r}, \mathbf{R})\Psi_n(\mathbf{R})$$

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Complexity grows as the number of electrons

Electronic Schrodinger equation :

$$(T_e + V_{ee} + V_{en})\Psi_e = E_e(\mathbf{R})\Psi_e$$

Electronic Schrodinger equation

$$(T_n + V_{nn} + E_e)\Psi_n = E\Psi_n$$

Nuclear Schrodinger equation

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SCF (Hartree-Fock)
 GVB (Generalized valence bond)
 Multiconfiguration SCF (MCSCF)
 Density functional

Analytic potential energy functions

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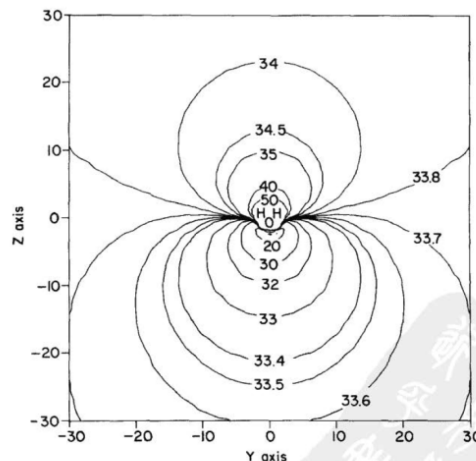
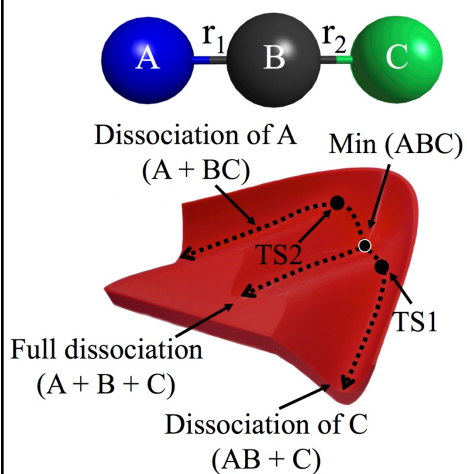
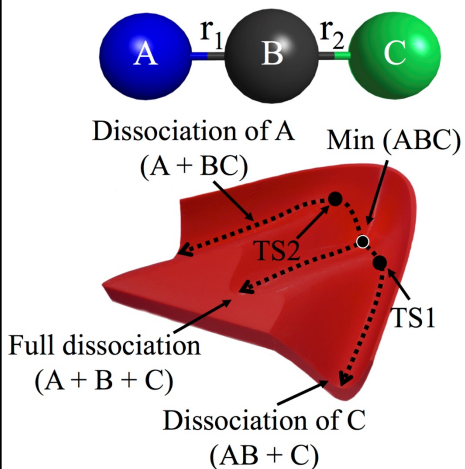


FIGURE 7-10 $\text{Li}^+ + \text{H}_2\text{O}$ potential energy contour diagram. The X and Y axes define the distance of Li^+ from O . The Li^+ ion is in the plane of H_2O molecule. Energy is in units of kcal/mol. [Adapted from W. L. Hase and D. -F. Feng, *J. Chem. Phys.* 75, 738 (1981)].

Depiction of collinear $A + BC \rightarrow AB + C$



Depiction of collinear A + BC -> AB + C



London-Eyring-Polanyi-Sato (LEPS) potential

Q Coulomb Integral

J Exchange Integral

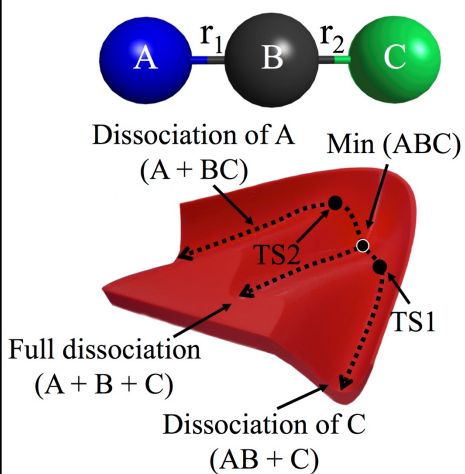
S Overlap Integral

$$V(r_{AB}, r_{AC}, r_{BC}) = \frac{Q_{AB}}{1 + S_{AB}} + \frac{Q_{BC}}{1 + S_{BC}} + \frac{Q_{AC}}{1 + S_{AC}} - \left\{ \frac{1}{2} \left[\left(\frac{J_{AB}}{1 + S_{AB}} - \frac{J_{BC}}{1 + S_{AB}} \right)^2 + \left(\frac{J_{BC}}{1 + S_{BC}} - \frac{J_{AC}}{1 + S_{AC}} \right)^2 + \left(\frac{J_{AC}}{1 + S_{AC}} - \frac{J_{AB}}{1 + S_{AB}} \right)^2 \right] \right\}^{1/2} \quad (7-35)$$

$$Q_{AB} + J_{AB} = D_{AB} \{ \exp[-2\beta_{AB}(r_{AB} - r_{AB}^0)] - 2 \exp[-\beta_{AB}(r_{AB} - r_{AB}^0)] \}$$

$$Q_{AB} - J_{AB} = \frac{1}{2} D_{AB} \{ \exp[-2\beta_{AB}(r_{AB} - r_{AB}^0)] + 2 \exp[-\beta_{AB}(r_{AB} - r_{AB}^0)] \}$$

Depiction of collinear A + BC -> AB + C



Bond energy-bond order (BEBO)

$$V = D_{BC} - D_{BC} (n_{BC})^{p_{BC}} - D_{AB} (n_{AB})^{p_{AB}} + V(r_{AC})$$

Dissociation of BC	Partially broken of BC	Partially formed of AB	AC repulsion
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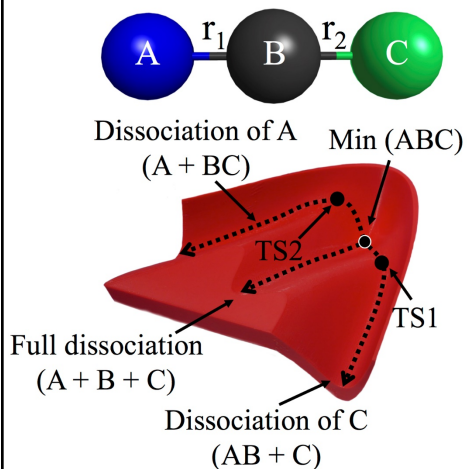
Pauling's relation for r_s (single bond length) and n , bond order

$$r = r_s - 0.26 \ln n \quad D = D_s n^P$$

$$n_{AB} + n_{BC} = 1.$$

Works well for C-C, C-O, O-O

Depiction of collinear A + BC -> AB + C

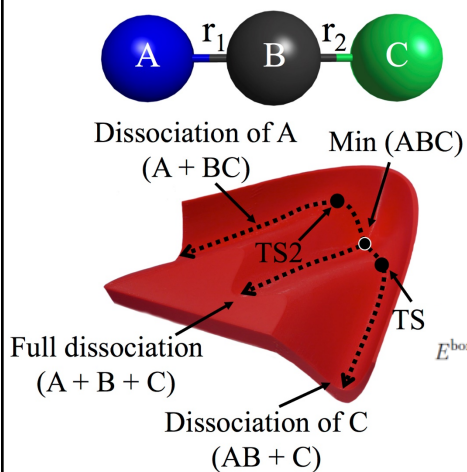


Blais and Buker surface based on Morse and a switching function

$$V = D_{AB}[1 - \exp[-\beta_{AB}(r_{AB} - r_{AB}^0)]]^2 + D_{BC}[1 - \exp[\beta_{BC}(r_{BC} - r_{BC}^0)]]^2 + D_{BC}[1 - \tanh(ar_{AB} + c)]\exp[-\beta_{BC}(r_{BC} - r_{BC}^0)] + D_{AC}\exp[-\beta_{AC}(r_{AC} - r_{AC}^0)].$$

First two terms are Morse potentials for A-B and B-C bonds
Third term attenuates the attraction between B and C, as A approaches (by means of switching function $1 - \tanh(ar_{AB} + c)$)
Final term is repulsive interaction between A and C

Depiction of collinear A + BC -> AB + C



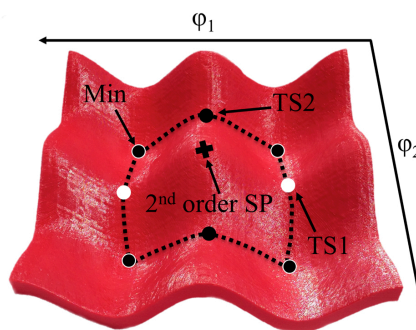
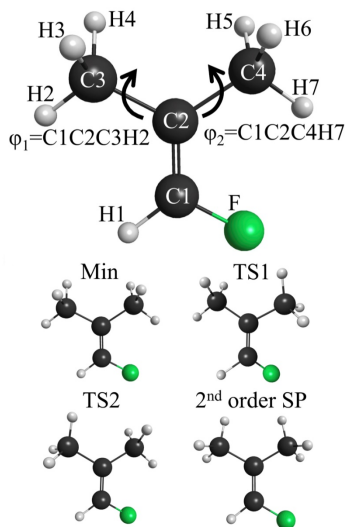
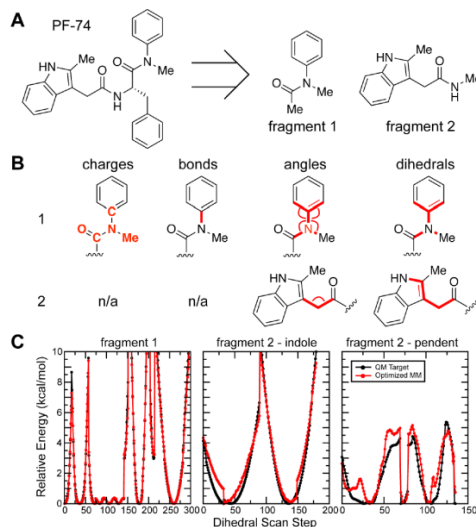
Charge-optimized many-body potentials (COMB)

$$E^{\text{COMB}} = E^{\text{self}} + E^{\text{Coul}} + E^{\text{polar}} + E^{\text{vdW}} + E^{\text{bond}} + E^{\text{others}}$$

$$E^{\text{bond}} = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V^R(r_{ij}, q_i, q_j) - (b^{\text{angle}} + b^{\text{coord}} + b^{\text{torsion}} + b^{\text{conjugation}}) \sum_{n=1}^3 V_n^A(r_{ij}, q_i, q_j) \right]$$

Analytic potential energy functions

$$\begin{aligned}
 U = & \sum_{i<j} \sum_{i<j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \\
 & + \sum_{i<j} \sum_{i<j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \\
 & + \sum_{\text{bonds}} \frac{1}{2} k_b (r - r_0)^2 \\
 & + \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2 \\
 & + \sum_{\text{torsions}} k_\phi [1 + \cos(n\phi - \delta)]
 \end{aligned}$$



There 3N degrees of freedom for the N-atom chemical system.

