Introduction to Computational Quantum Chemistry

Lesson 07: Reaction Coordinates and Transition State Calculations

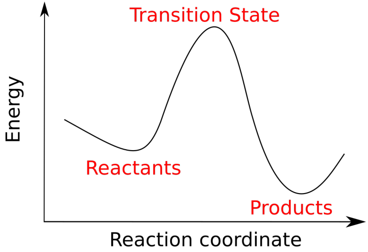
(Prepared by Radek Marek Research Group)

REVIEW: Potential Energy Surface

- the PES of a molecule is obtained by the total interactions of:
  - nuclear-nuclear repulsion
  - electron-electron interaction
  - electron-nuclear attraction
- important Points on the PES
  - stationary points:
    $$\frac{\partial E}{\partial q_i} = 0 \tag{1}$$
  - local minimum:
    $$\frac{\partial^2 E}{\partial q_i^2} > 0 \ \text{ for all degrees of freedom} \tag{2}$$
  - n^{th} order saddle point:
    $$\frac{\partial^2 E}{\partial q_i^2} < 0 \ \text{ for n degrees of freedom} \tag{3}$$

REVIEW: Potential Energy Surface (*Cont.)*

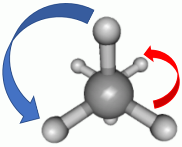
- a two-dimensional cut from a multidimensional PES illustrates one direction view of the reaction coordinates
- the energy differences of $TS - R$ is the activation energy while the $P - R$ is the reaction energy



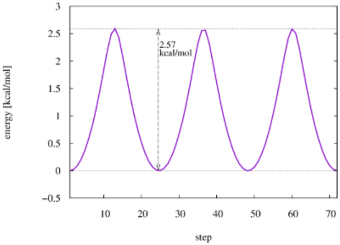
- however, these are only stationary points on a much larger potential energy surface (PES). The actual landscape of this surface can also be explored to see how the various stationary points connect.

Potential Energy Scan

- it is often useful to scan the potential energy surface (PES), optimizing all other degrees of freedom for each particular value of the scanned variable(s).
- possible to adjust distances as well as atomic and dihedral angles



Dihedral scan of ethane.



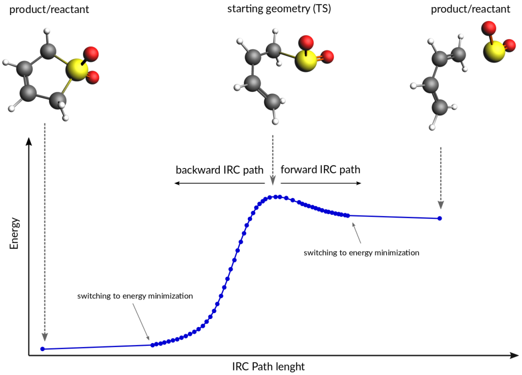
Energy diagram of the dihedral scan of ethane.

Potential Energy Scan, *Cont.*

- PES scan may provide a rough estimate of a pathway between reactants, TS, and products, assuming the coordinate(s) for the scan has been chosen wisely
- PES scan is often used in development of classical force fields

Intrinsic Reaction Coordinate (IRC)

- TS (transition state), the Hessian needs to display the required number of negative eigenvalues
- it is also necessary to confirm the TS connections to both sides (reactants and products).



Intrinsic Reaction Coordinate (IRC), *Cont.*

- the Intrinsic Reaction Coordinate (IRC) is the minimum energy reaction pathway (MERP) in mass-weighted cartesian coordinates between the **TS** to its reactants **R** and products **P**.
- the molecule takes moving down the product and reactant valleys with zero kinetic energy.
- the Gonzalez-Schlegel method for following the coordinate can be used in Gaussian using the IRC keyword, latest version using (HPC algorithm).

Transition State Methods

- mapping reaction coordinates and search of transition state (TS)
  - manual optimizations search for REACTANTS, TS, PRODUCTS (with aid from PES Scan)
  - advance methods such as QST2,QST3, etc

ACTIVITY 1: PES SCAN

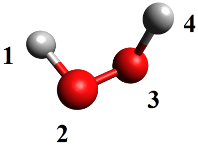
- rotational transition state in hydrogen peroxide (H-O-O-H) using Gaussian
  - (MANUAL) frozen optimization per angle:

```
#P HF/6-31G(d) opt=Z-Matrix

first step at d4=0.0

0 1
H1
O2   1   r2
O3   2   r3   1   a3
H4   3   r2   2   a3   1   d4

r2=1.0
r3=1.3
a3=110.
d4=0.0 F
```



  - the last line of the Z-Matrix describes a value of 0.0 degree for the H/O/O/H dihedral angle d4, the tailing character F indicating that this variable is frozen and **not to be varied** during the geometry optimization, then change it from 0.0 to 180

ACTIVITY 1: PES SCAN, *Cont.*

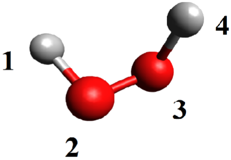
- (FULL SCAN) can be achieved in a single job:

```
#P HF/6-31G(d) opt=Z-Matrix nosymm

H2O2 rotational potential


0 1
H1
O2  1  r2
O3  2  r3  1  a3
H4  3  r2  2  a3  1  d4

r2=1.0
r3=1.3
a3=110.
d4=0.0 S  18  +10.0
```



- initial value of 0.0 degree for the H/O/O/H dihedral angle d4 but also specifies a scan of 18 steps, is varied by +10.0 degrees.
- in order to avoid problems caused through changes in the point group along the pathway, the nosymm keyword is added.

ACTIVITY 1: PES SCAN, *Cont.*

- examine the output file and look for the keyword "Summary of Optimized Potential Surface Scan", you can see the energy eigenvalues as d4 changes
- add module **gaussview**
- open the file using **gv** {*filename*}
- go to menu bar **Results** > **scan**, Energy and RMS values are presented
- you can visualize the molecular movements by clicking the animate play button

ACTIVITY 2: Reaction Coordinate and TS Search

- we will study a classic SN_2 reactions (known to have double well potentials), using Gaussian.
- SN_2 reaction: **Br^- + CH_3Cl** $\rightarrow$ **Cl^- + CH_3Br**
  - use B3LYP functional, the 6-31+G(d) basis set for all atom
  - first perform a geometry **Optimization** and **Freq** for all Reactants and Products
  - for an initial guess of transition state structure (TS), obtain it from PES scan by varying the both distances of **Br** and **Cl**, refer to this manual: $https://gaussian.com/scan/$
  - NOTE: to save time, use the coordinates provided in the next page, this structure is a good starting point for a PES SCAN
  - refer to this manual: $https://gaussian.com/scan/$

ACTIVITY 2: Reaction Coordinate and TS Search

- perform your SCAN from this structure (fucos on B1 and B2) bond lengths

  ```
  C
  Cl 1 B1
  Br 1 B2 2 A2
  H 1 B3 2 A3 3 D3
  H 1 B4 2 A4 3 D4
  H 1 B5 2 A5 3 D5
  variables:
  B1 2.0 9 0.1
  B2 2.0 9 0.1
  A2 179.13318
  B3 1.06210
  A3 89.25624
  D3 135.20467
  B4 1.06224
  A4 90.30745
  D4 352.54852
  B5 1.08241
  A5 91.90132
  D5 243.91238
  ```

ACTIVITY 2: Reaction Coordinate and TS Search, *Cont.*

- once you found a good TS candidate, be sure it has strongest imaginary frequency among others that refers to the bond breaking/forming of the **Br** · · · **C** · · · **Cl**, that's why it's necessary to perform a preliminary FREQ calculation
- if it's viable, proceed to Transition State Optimization
- for Transition State (TS) minimization use #P B3LYP/6-31G(d) opt(TS,ModRedundant,noeigentest) nosymm freq
- the option above only calculate freq once on the initial structure (calcfc), freq calculation for every step is also available (CalcAll) but is not typically necessary for this simple system

ACTIVITY 2: Reaction Coordinate and TS Search, *Cont.*

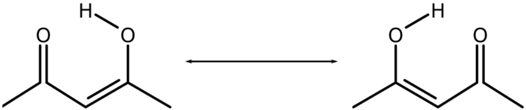
- after a successful TS Optimization, open the structure and examine the frequencies using Gabedit or Avogadro, if the frequencies are okay, you now got a **Transition State Structure**
- use the optimize TS structure and proceed with IRC calculation for the confirmation
  `#P B3LYP/6-31G(d) scf=(tight,direct) int=finegrid IRC(calcfc,maxpoints=500,maxcyc=500,stepsize=10)`
- by default IRC run examines every direction, you can also chose specific directions as Forward and Reverse options
- refer to this manual: $https://gaussian.com/irc/$

ACTIVITY 2: Reaction Coordinate and TS Search, *Cont.*

- once you have successful IRC calculation, open **Gaussview** for visualization
    - open the file using **gv** {*filename*}
    - go to menu bar **Results** > **IRC**, it allows you to view Total Energy and RMS Gradient along IRC values are presented
    - you can visualize the molecular movements by clicking the animate play button

ASSIGNMENT

- This process concerns the proton transfer in malonaldehyde, find the transition state geometry:



- use DFT methods PBE, B3LYP, and then try MP2. Be sure to use cc-pVDZ basis set. Verify your obtained transition state geometry.

END