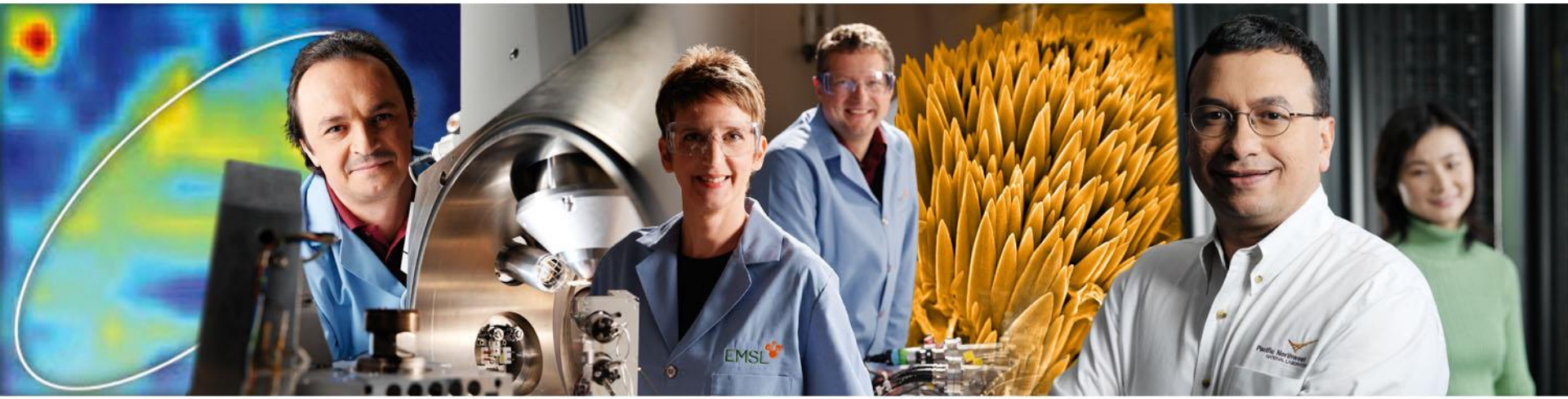
EMSL

NWChem: Analysis of Potential Energy Surfaces



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U.S. DEPARTMENT OF ENERGY

What is the Potential Energy Surface (PES)?

- The Schrodinger equation is

$$H\left(r_i,\cdots,R_I,\cdots\right)\Psi\left(r_i,\cdots,R_I,\cdots\right)=E\,\Psi\left(r_i,\cdots,R_I,\cdots\right)$$

$$E=\int\cdots\int\cdots\Psi\,H\,\Psi\,\mathrm{d}r_i\cdots\mathrm{d}R_I\cdots$$

- It includes all particle interactions as well as kinetic energies of both electrons and nuclei
- The Born-Oppenheimer approximation assumes that the nuclei are stationary
- The electronic energy then becomes

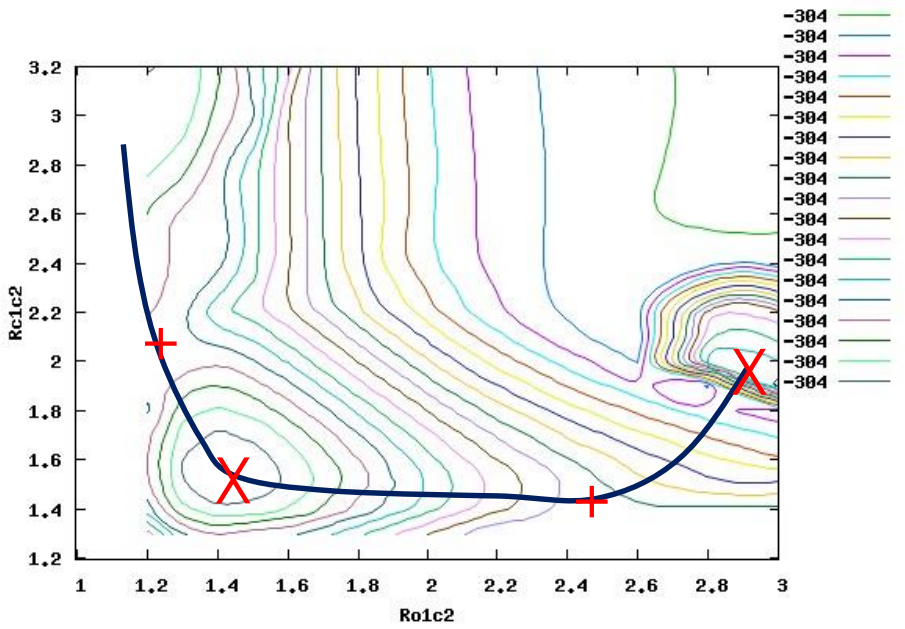
$$E\left(R_I,\cdots\right)=\int\cdots\Psi\,H\,\Psi\,\mathrm{d}r_i\cdots$$

- The energy as a function of the nuclear coordinates is the **Potential Energy Surface (PES)**
  - Note: This excludes the kinetic energy of the nuclei (zero point correction)

Why is the PES important?

- The PES determines many important features
  - The minima a stable molecular structures
  - The saddle points are transition states
  - Energy differences are heats of reaction and barrier heights
  - The path of lowest energy connecting 2 minima is the reaction pathway

Ozone + Ethene



X – Minima

\+ – Transition states

Geometry Optimizations

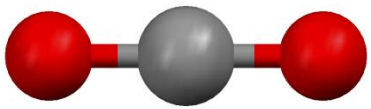
```
geometry
  o  0.0  0.0 -1.18
  c  0.0  0.0  0.00
  o  0.0  0.0  1.18
end
basis
  * library 6-31g*
end
dft
  xc pbe96
End

task dft optimize

task dft frequencies
```

- Find a stable structure of a molecule

Energy expression

Minimization wrt. Nuclear coordinates

Check on final point: All frequencies should be positive



Energy expressions and derivatives

- NWChem has a general approach to differentiation
  - If implemented analytic derivatives are used
  - Otherwise numerical differentiation is used
  - Convenient from "ease of use" point of view
  - But numerical differentiation is much more costly
- See table for analytic derivative availability

Method	Gradient	Hessian
SCF	Yes	Yes
DFT (LDA/GGA)	Yes	Yes
DFT (mGGA)	Yes	Yes/No
MP2	Yes	No
CC	No	No
EOM-CC	No	No

Frequencies at equilibrium geometry

- There should be 6 zero frequencies (translational and rotational modes)
- All other modes should have positive frequencies
- Does not always happen due to
  - Noisy numerics
  - Differences in convergence criteria (optimize & frequencies)

Normal Mode	Eigenvalue [cm**-1]	Projected Infra Red Intensities [atomic units]	[(debye/angs)**2]	[(KM/mol)]	[arbitrary]
1	0.000	0.003541	0.082	3.452	4.374
2	0.000	0.001074	0.025	1.047	1.327
3	0.000	0.000651	0.015	0.634	0.804
4	0.000	0.001154	0.027	1.125	1.426
5	0.000	0.000702	0.016	0.685	0.868
6	0.000	0.005578	0.129	5.438	6.890
7	127.797	0.004201	0.097	4.096	5.190
8	418.064	0.004610	0.106	4.494	5.694
9	735.938	0.002073	0.048	2.021	2.561
10	748.555	0.000768	0.018	0.749	0.949
11	798.461	0.042998	0.992	41.916	53.112
12	867.327	0.000350	0.008	0.341	0.432
13	959.498	0.000261	0.006	0.254	0.322
14	970.135	0.019309	0.445	18.824	23.851
15	1044.115	0.034880	0.805	34.003	43.084

Finding Saddle Points I

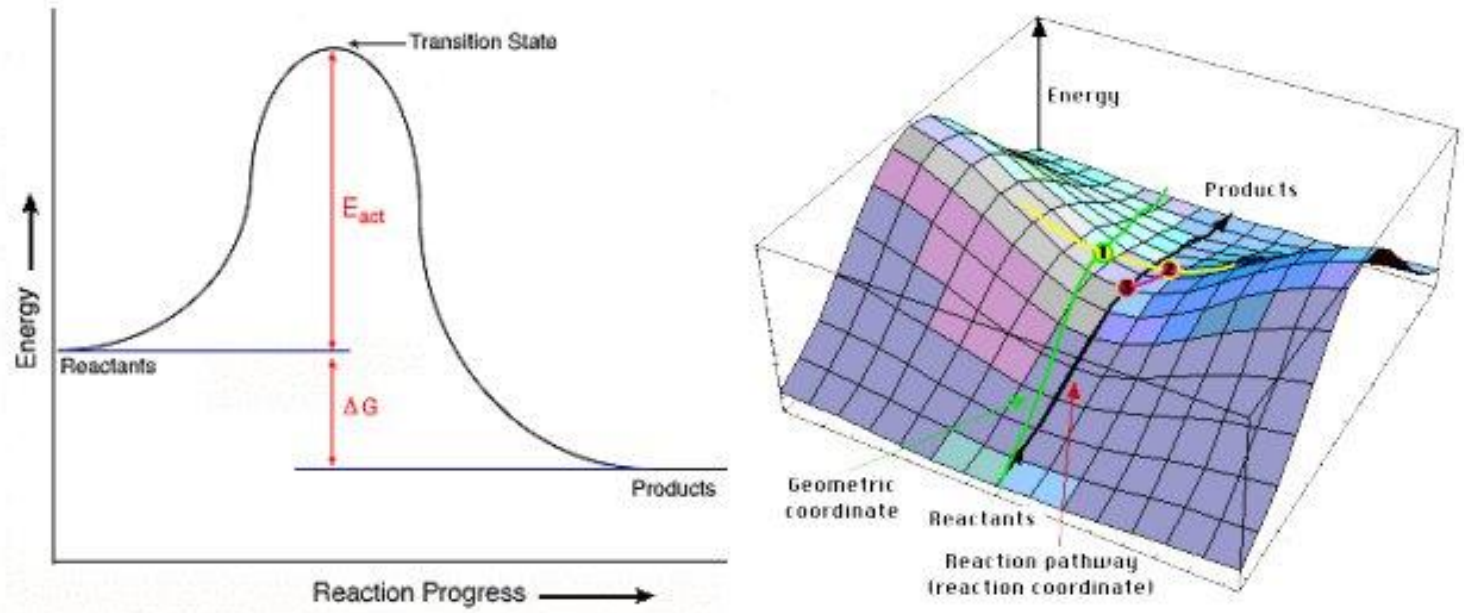
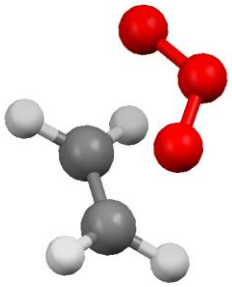


Image source: http://ocikbws.uzh.ch/education/qmcourse/8-ts-theory.php

Finding Saddle Points II

```
geometry
   …
   symmetry c1
end
…

driver
  clear
end

task dft saddle

task dft frequencies
```



- Saddle points are transition states
- For small molecules traditional search algorithms work
- Geometry needs to be close to the TS

Chemical intuition does not always work

Follows the negative frequency mode

Check what was found

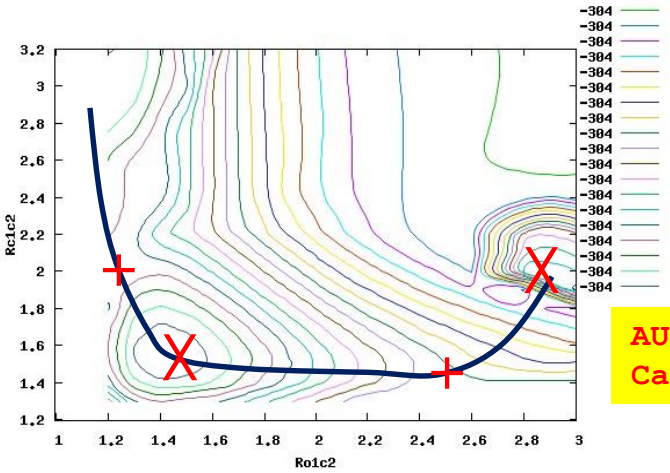
Frequencies at transition state

- There should be 6 zero frequencies (translational and rotational modes)
- The should be 1 negative frequency
- All other modes should have positive frequencies

Normal Mode	Eigenvalue [cm**-1]	Projected Infra Red Intensities [atomic units]	[(debye/angs)**2]	[(KM/mol)]	[arbitrary]
1	-212.571	0.056435	1.302	55.016	30.327
2	0.000	0.000126	0.003	0.123	0.068
3	0.000	0.000461	0.011	0.450	0.248
4	0.000	0.000129	0.003	0.126	0.070
5	0.000	0.000005	0.000	0.005	0.003
6	0.000	0.000227	0.005	0.221	0.122
7	0.000	0.000206	0.005	0.200	0.110
8	123.628	0.000728	0.017	0.710	0.391
9	250.414	0.008220	0.190	8.013	4.417
10	347.053	0.000139	0.003	0.135	0.075
11	413.274	0.001562	0.036	1.523	0.839
12	531.312	0.010232	0.236	9.975	5.498
13	777.688	0.010324	0.238	10.064	5.548
14	835.210	0.001279	0.030	1.247	0.687

Getting close to the TS

```
geometry "h2c2o3"
   …
   symmetry c1
end
geometry "h2c2o3" adjust
  zcoord
    bond 1 4 2.45 constant
    bond 4 5 1.50 constant
  end
end
set geometry h2c2o3
…

task dft optimize
```



- Identify 2 important internal coordinates
- Map out PES as function of these 2 coordinates
- Locate TS in contour plot
- Requires internal coordinates
  - Auto generated, but…
  - Constraints may be inconsistent with symmetry
  - May fail causing constraints to be ignored

```
AUTOZ failed to generate good internal coordinates.
Cartesian coordinates will be used in optimizations.
```

Path methods I

```
geometry
  …
end
geometry endgeom
  …
end
neb
  nbeads 10
  kbeads 0.1
  maxiter 10
  stepsize 0.1
end
…

task dft neb
```

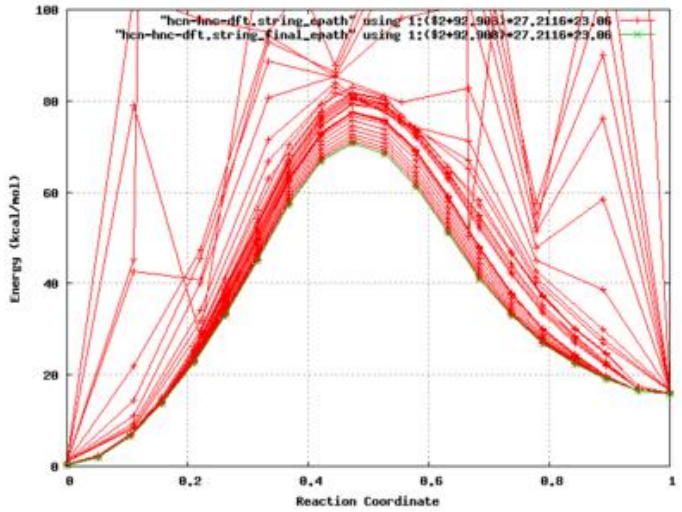
- Need to know reactant and product complex
- Use 2 or 3 point interpolation for guess structures along the path
- Consecutive geometries formally connected by a spring
  - Use nocenter noautoz noautosym
  - Atoms must be ordered identically
  - For 3 point interpolation add midgeom and hasmiddle

Path methods II

```
geometry
  …
end
neb
  …
  xyz_path path.xyz
end
…

task dft neb
```

- Interpolating an appropriate path can be tricky
- Alternative to load a file with geometries in XYZ format

```
3
E = -17.107
O 0.0 -0.02  0.00
H 0.0  0.55  0.75
H 0.0  0.55 -0.75
3
E = -17.095
O 0.0 -0.11  0.00
H 0.0  0.27  0.84
H 0.0  0.27 -0.84
…
```



Final remarks

- Characterization of the PES provides useful information about chemistry
- But it does not tell you everything…
  - The nuclear motion affects the thermodynamics
  - Real reactions do not follow minimum energy paths
  - Instead real reactive paths have to satisfy Newtonian laws of motion
  - Investigating this requires dynamics

Questions?