NWChem: Analysis of Potential Energy Surfaces

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- The Schrodinger equation is

$$H \left(r_i, \text{K}, R_I, \text{K} \right) \Psi \left(r_i, \text{K}, R_I, \text{K} \right) = E \Psi \left(r_i, \text{K}, R_I, \text{K} \right)$$

$$E = \int \text{K} \int \text{K} \, \Psi H \Psi \, d r_i \text{K} \, d R_I \text{K}$$

- 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
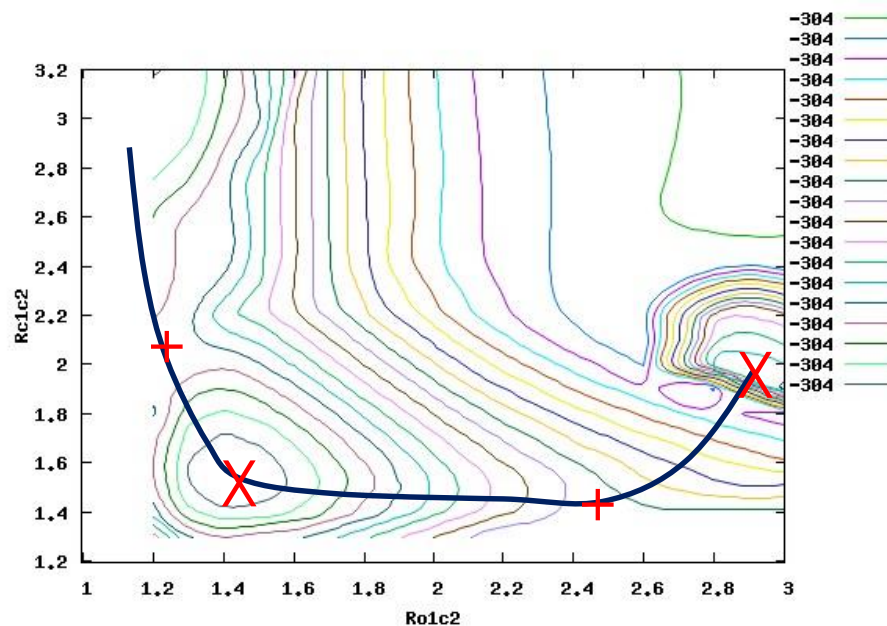
- The electronic energy then becomes

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

- 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)

EMSL

- 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

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```
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
```
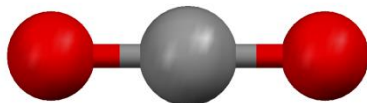
- Find a stable structure of a molecule

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

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- 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 Eigenvalue ||        Projected Infra Red Intensities
 Mode   [cm**-1]  || [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
```
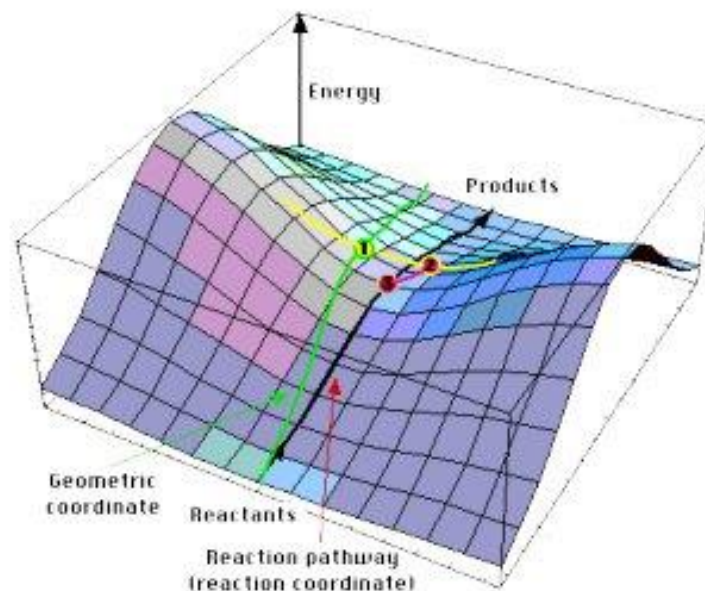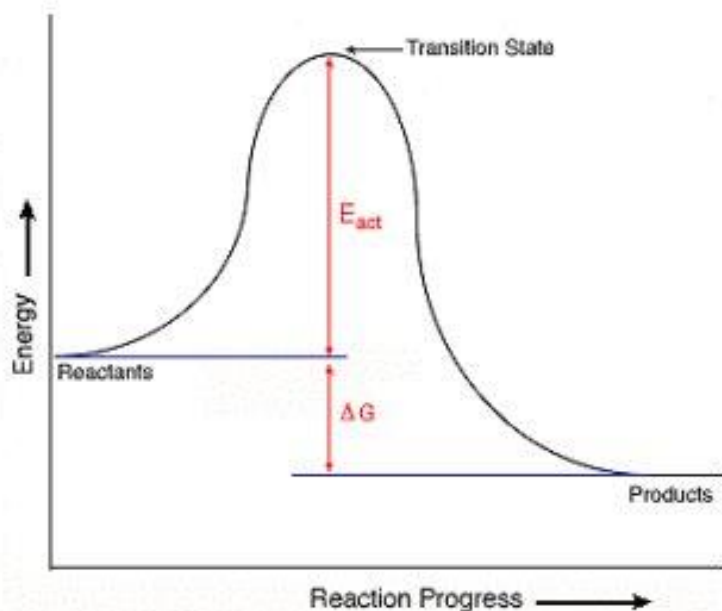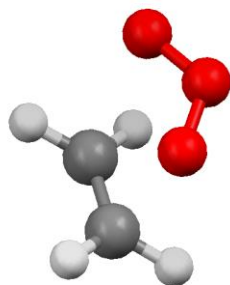
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Image source: http://ocikbws.uzh.ch/education/qmcourse/8-ts-theory.php

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```
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

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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 Eigenvalue ||          Projected Infra Red Intensities
  Mode    [cm**-1] || [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
```

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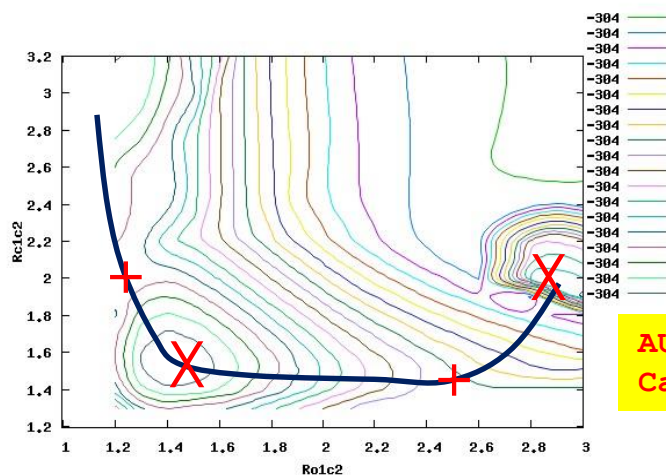
AUTOZ failed to generate good internal coordinates. Cartesian coordinates will be used in optimizations.

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```
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
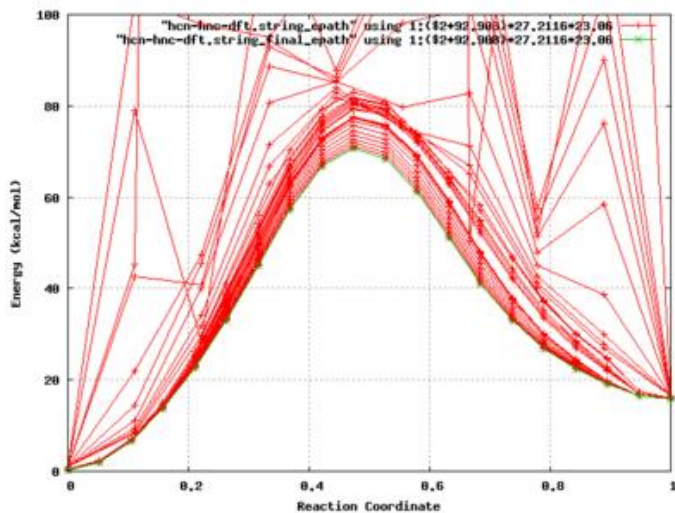 - For 3 point interpolation add midgeom and hasmiddle

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```
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

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