Chapter #3

Potential Energy Surfaces Exploration

Coordinates, Scans, and IRC

Observables

[1] Structure.

[2] Energy.

[3] Properties.

Spectroscopy: MW, IR, UV/Vis, NMR, ESR,…

Thermochemistry and Kinetics.

Potential Energy Surface, PES

Energy = $E(x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_M, y_M, z_M)$

Nonlinear: M = 3N - 6

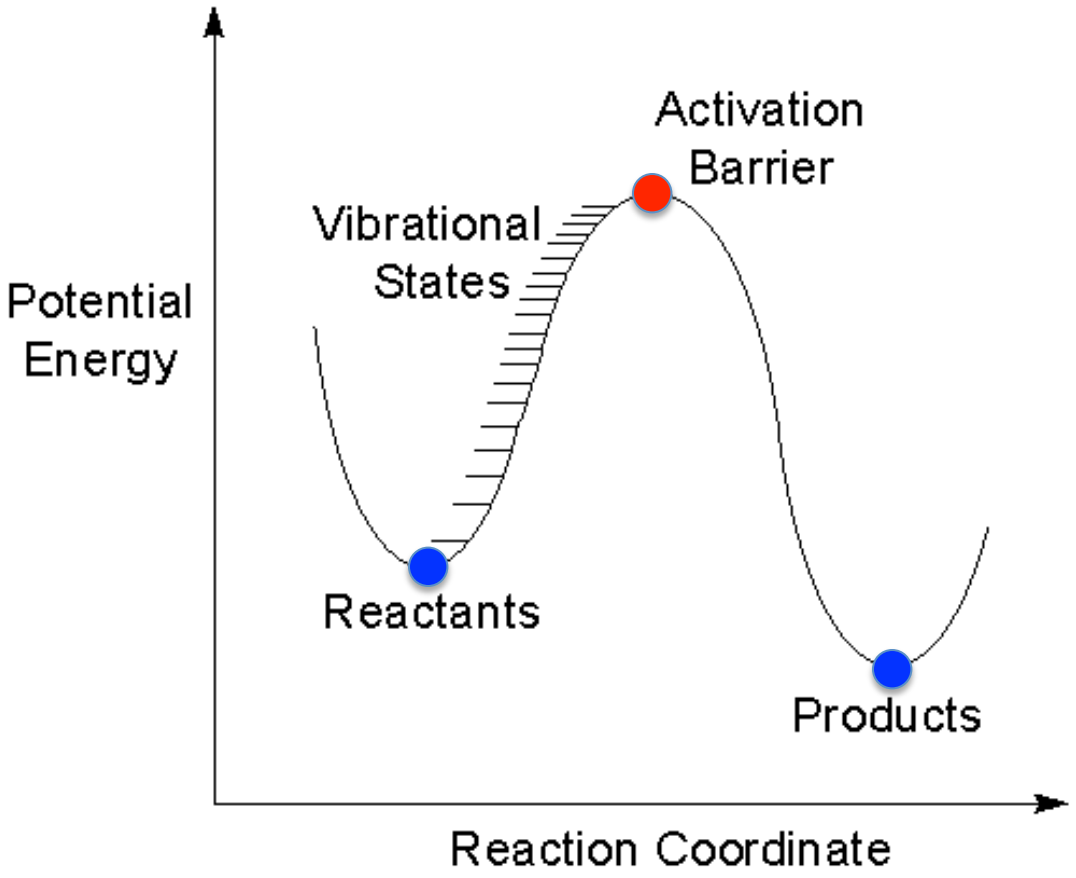
Linear: M = 3N - 5

N is the number of atoms. M is the number of internal coordinates.

The remaining coordinates describe the motion of the molecule as a whole.

VERY HARD TO VISUALIZE.

PES and Stationary Structures



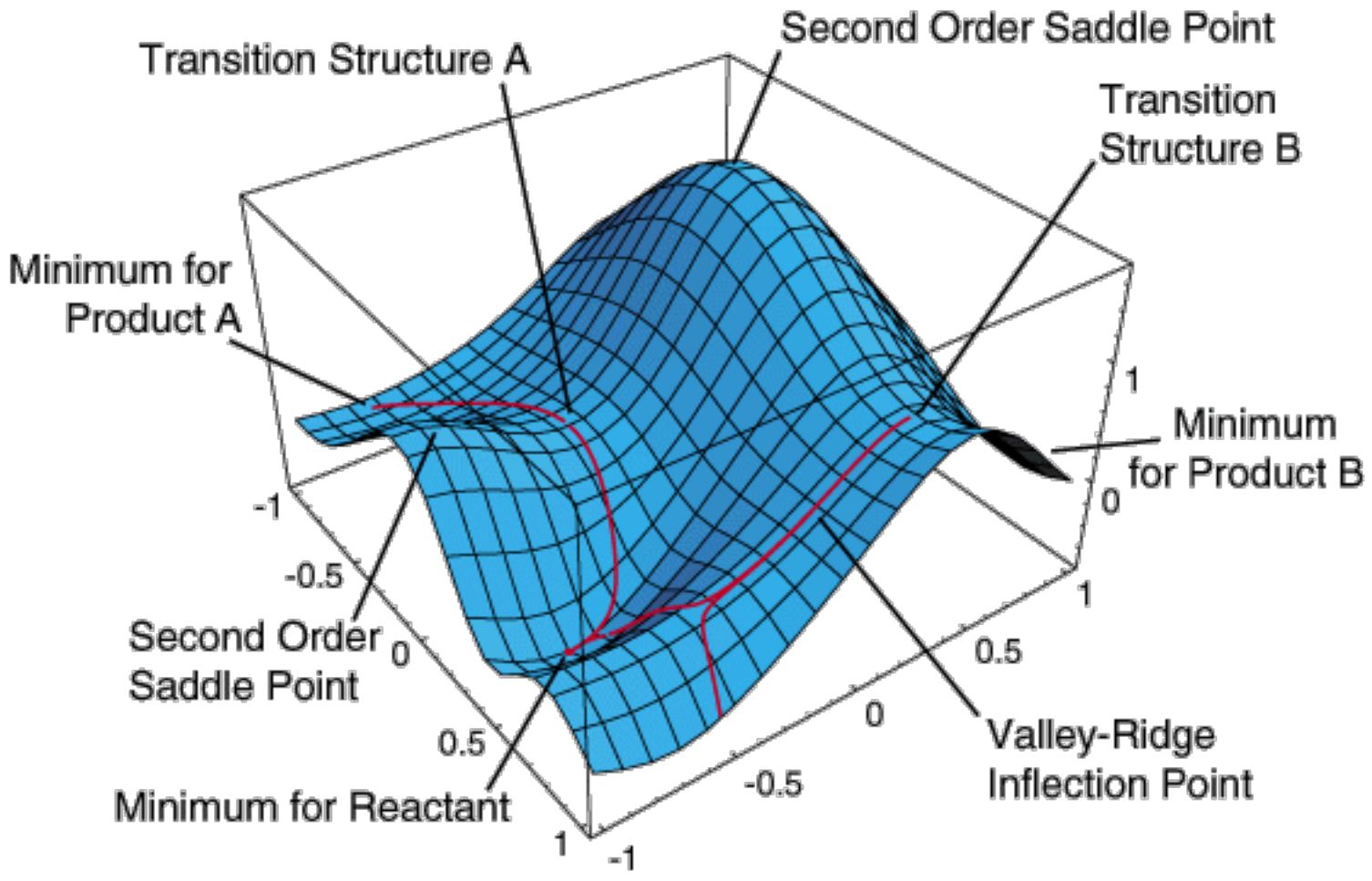
Stationary Structure
Gradient = 0

Minimum (pl.: Minima)
All curvatures are positive

Transition State Structure
ONE curvature is negative

Higher-Order Saddle Point
More than one curvature are negative

Potential Energy Surface, PES



www.chem.wayne.edu/ ~hbs/chm6440/PES.html

NH_3 Str. Opt.: Internal Coordinates

Draw NH_3 in Active Window without using Point Group

Save as internal coordinates from "File" menu

```
%chk=C:\Users\glaserr\Desktop\ammonia.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1           B1
 H                  1           B2     2            A1
 H                  1           B3     3            A2     2            D1     0

   B1             1.00000000
   B2             1.00000000
   B3             1.00000000
   A1           109.47120255
   A2           109.47125080
   D1          -119.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

NH_3 Str. Opt.: Cartesian Coordinates

Draw NH_3 in Active Window without using Point Group

Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")

```
%chk=C:\Users\glaserr\Desktop\ammonia_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    1.00000000
 H                  0.94280915    0.00000000   -0.33333304
 H                 -0.47140478   -0.81649655   -0.33333304

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

Optimization will still be performed in internal coordinates.

NH_3 Opt.: C_{3v}, Internal Coords.

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_C3v.chk
# opt=z-matrix hf/6-31G*

Ammonia in C3v

0 1
 N
 X    1         1.0
 H    1          b1    2          a1
 H    1          b1    2          a1     3   120.0     0
 H    1          b1    2          a1     3  -120.0     0

b1=1.
a1=110.
```

Opt=z-matrix: Optimization will be performed in internal coordinates.

NH_3 Opt.: D_{3h}, Internal Coords. I

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_D3h.chk
# opt=z-matrix hf/6-31G*

Ammonia in D3h

0 1
 N
 X    1        1.0
 H    1         b1    2        90.
 H    1         b1    2        90.    3  120.0    0
 H    1         b1    2        90.    3 -120.0    0

b1=1.
```

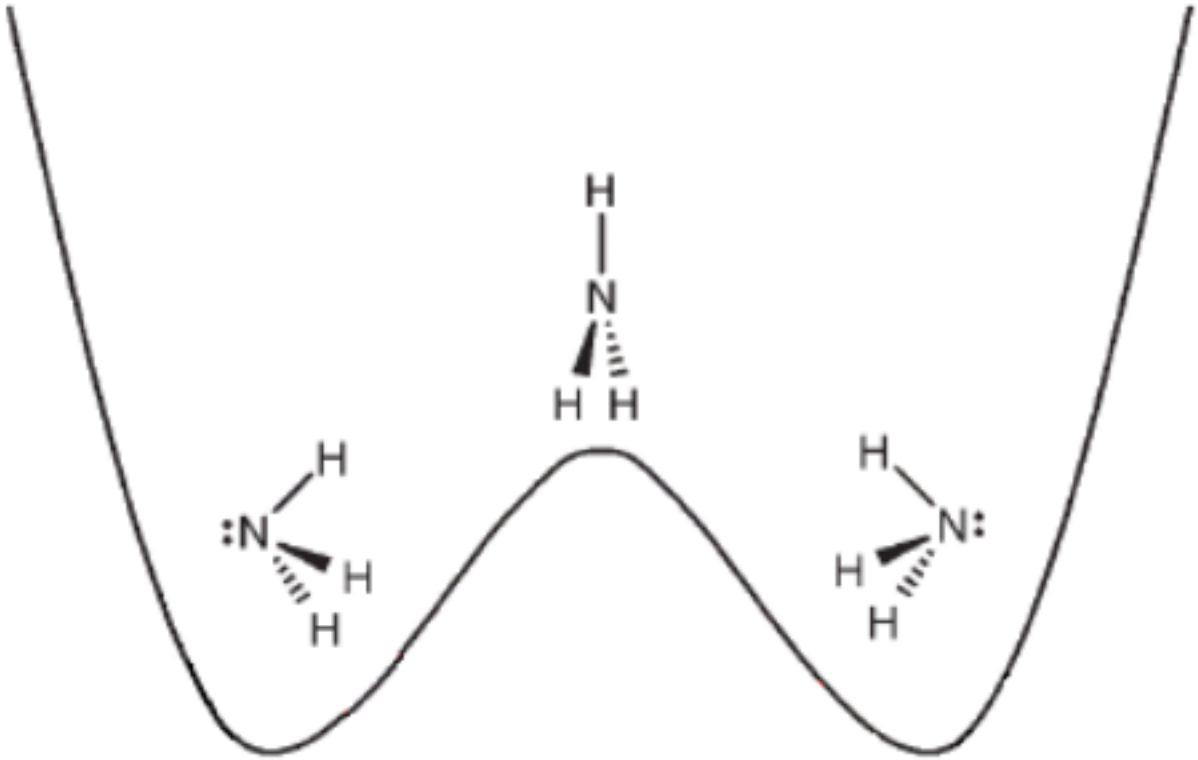
NH_3 Opt.: D_{3h}, Internal Coords. II

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_D3h_V2.chk
# opt=z-matrix hf/6-31G*

Ammonia in D3h

0 1
 N
 H    1         b1
 H    1         b1    2        120.
 H    1         b1    2        120.   3 -180.0    0

b1=1.
```

NH_3 Opt.: Locate TS

```
%chk=C:\Users\glaserr\Desktop\ammonia_TS.chk
# hf/6-31G* opt=(TS,calcfc) geom=connectivity

Title Card Required

0 1
 N
 H          1       B1
 H          1       B2     2      A1
 H          1       B3     3      A2     2    D1     0

   B1              1.00000000
   B2              1.00000000
   B3              1.00000000
   A1            118.23587891
   A2            121.47125080
   D1           -115.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

PES and Scan of Inversion Path

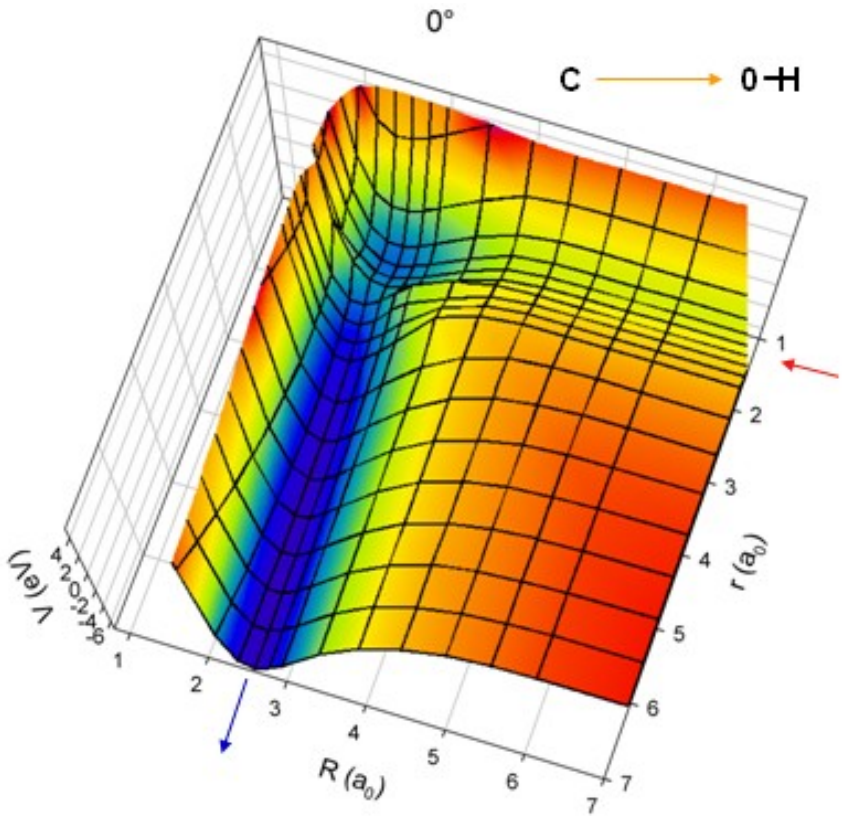


One internal coordinate suffices to define a “good path”

NH_3 Str. Opt.: Constrained

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\partd_80.chk
# opt=z-matrix hf/6-31G*

Ammonia with a1 angle 80 degrees

0 1
 N
 X    1         1.0
 H    1          b1    2         a1
 H    1          b1    2         a1    3  120.0    0
 H    1          b1    2         a1    3 -120.0    0

b1=1.          Variable will be optimized

a1=80.         Variable after the extra line with NOT be optimized
```

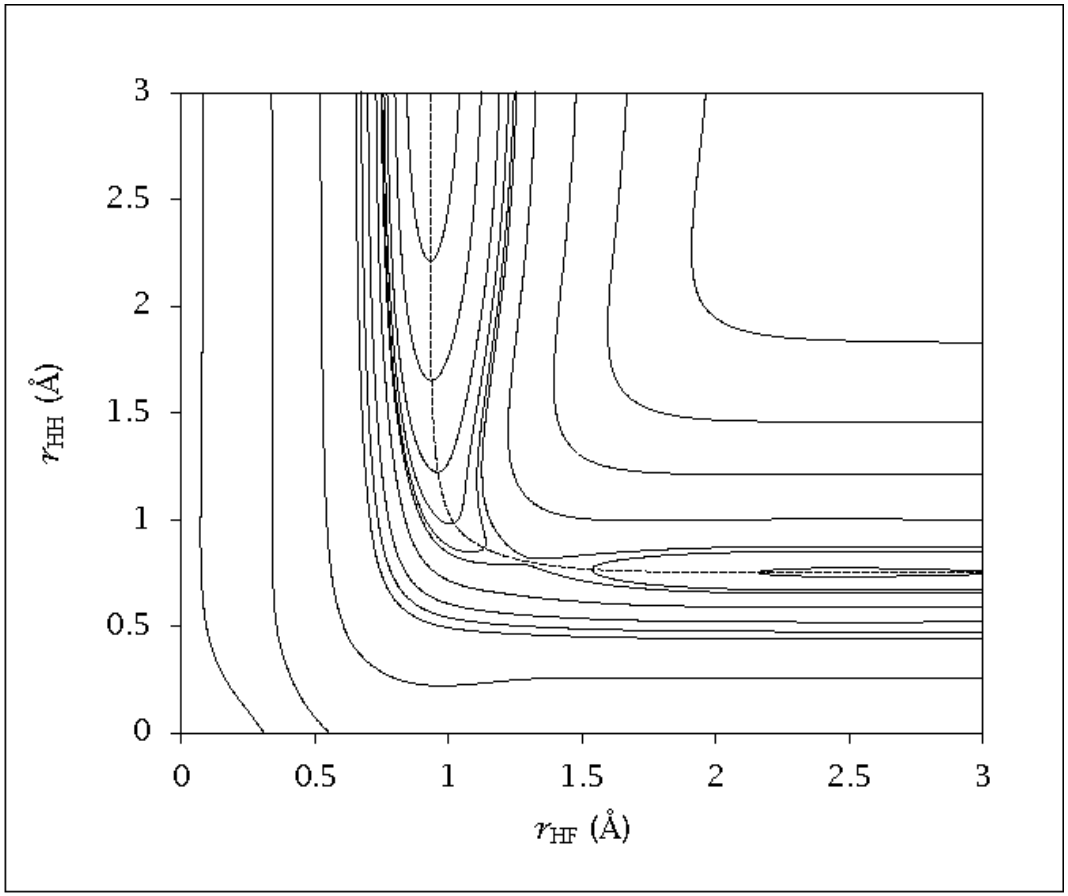
PES Scan: 2 of 3 Coordinates



C + OH ➔ CO + H

http://www.utinam.cnrs.fr/utinam/IMG/jpg/COHcol.jpg

PES: PES Scan *versus* IRC



http://jbrwww.che.wisc.edu/home/jbraw/chemreacfun/ch5/figures/hfc.png