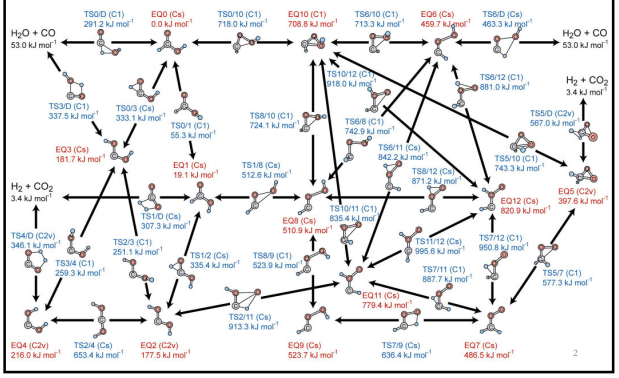
Effective usage of GRRM11

1. Automated Reaction Route Mapping
2. Quantum Chemical Synthon Analysis
3. Double-end Analysis
4. L-ADDF Search
5. Cluster Structure Sampling
6. Excited-State Analysis
7. Giant-System Analysis with ONIOM
8. Exploration of A + B type Reaction Routes

Example of GRRM : HCOOH



Exploration from HCOOH

GRRM/B3LYP/6-31G *This will be copied to the Root Section of a Gaussian Input.*

```
0 1
H    -0.452596548000    0.034871834140    -1.807771705495
O    -0.452596548000    0.643013717456    -1.034349518878
O    -0.452596548000   -1.276412777953     0.242743092264
C    -0.452596548000   -0.053534532177     0.147136623161
H    -0.452596548000    0.652061759532     0.979506709948
Options
GauMem=100
GauProc=4
```

Optimized geometries of HCOOH at B3LYP/6-31G

Exploration from a randomly generated initial structure

GRRM/B3LYP/6-31G *This will be copied to the Root Section of a Gaussian Input*

```
0 1
H    0.0    0.0    0.0    1
O    0.0    0.0    0.0    2
O    0.0    0.0    0.0    3
C    0.0    0.0    0.0    4
H    0.0    0.0    0.0    5
Options
NRUN=10
GauMem=100
GauProc=4
```

All atoms are randomly located, and an optimization generates an initial structure.

Start from 10 random structures

Output

- .log file : History, Amount of Compt., CPU time etc.
- EQ_list.log : List of Equilibrium Structures
- EQ*n*.log : History of ADDF from EQ*n*, Structure and Energy profiles along the ADDF path
- TS_list.log : List of Transition structures
- TS*m*.log : Details of IRC Traces from TS*m*
- DC_list.log : List of Dissociated Structures
- DC*m*.log : Meta IRC Traces from DC*m*

EQ_list.log

List of Equilibrium Structures

```
# Geometry of EQ 0, SYMMETRY = Cs
H    -0.452596548000    0.034871834140    -1.807771705495
O    -0.452596548000    0.643013717456    -1.034349518878
O    -0.452596548000   -1.276412777953     0.242743092264
C    -0.452596548000   -0.053534532177     0.147136623161
H    -0.452596548000    0.652061759532     0.979506709948
Energy   = -189.686345910766
Spin(**2) =   0.000000000000
ZPVE     =   0.033269502369
Normal mode eigenvalues : nmode = 9
  0.013844532  0.017705839  0.041505728  0.043865003  0.063830393
  0.075651074  0.114134257  0.376915991  0.486564365
```

Electronic Energy in hartree

Zero Point Vibrational Energy in hartree

Vibrational Eigenvalue f_i
*Vibrational frequency in cm^{-1} can be obtained by sqrt(f_i/1822.88853006256)*219474.638170777*

EQ*n*.log

PROFILE OF SHS-PATH 1

Initial geometry (negative direction of mode 1)

H	-0.273098290958	0.034871834140	-1.807771705495
O	-0.470810700199	0.643013717456	-1.034349518878
O	-0.461175866010	-1.276412777953	0.242743092264
C	-0.434217247418	-0.053534532177	0.147136623161
H	-0.425702172635	0.652061759532	0.979506709948

# STEP 1 E(Harmonic) = 0.001382748031
GENERATION = 1

H	-0.427536180483	0.033981498650	-1.806811316248
O	-0.450816718537	0.643825451874	-1.035605196155
O	-0.448164828929	-1.276628047144	0.242624857766
C	-0.470612689786	-0.053172482437	0.150438437675
H	-0.361723584567	0.639174894802	0.961037157834

energy : -189.685073971923
Spin(**2) : 0.000000000000
STEP 2 E(Harmonic) = 0.015363867007
~~~~~~
Another EQ was reached over the TOP of SHS-PATH

Reached another EQ different from the started EQ

TS_list.log

List of Transition Structures

Geometry of TS 0, SYMMETRY = C2v

H	-0.452579896769	-0.739634023903	-1.194712914423
O	-0.452568723828	0.622484509496	-1.029441079169
O	-0.452556518725	-1.176022414821	0.106195948153
C	-0.452547834023	0.119374517004	0.165753891233
H	-0.452526289353	0.696601689310	1.079890807874

Energy = -189.621177046091
Spin(**2) = 0.000000000000
ZPVE = 0.028318278608
Normal mode eigenvalues : nmode = 9
-0.134645676 0.026856941 0.040118575 0.052256091 0.054695965
0.065556445 0.091473665 0.154739450 0.409107921

CONNECTION : 0 – 0 *A TS connecting EQ0 and EQ0*
~~~~~~
CONNECTION : 1 – 0 *A TS connecting EQ1 and EQ0*
~~~~~~
CONNECTION : 0 – DC *A TS connecting EQ0 and DC, whose structure can be found in TSn.log*
~~~~~~
CONNECTION : 0 - ?? *A TS connecting EQ0 and ??, which is described in TSm.log*

TS*m*.log

INITIAL STRUCTURE

H	0.299046126297	0.824914186341	-1.543088134585
O	-0.527191800919	0.602385717426	-1.071167510316
O	-0.483843412292	-1.274397964889	0.264284928724
C	-0.391162088155	-0.064922267476	0.144548168047
H	-0.276089959676	0.619520579434	0.994380478018

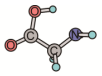
~~~~~~
IRC FOLLOWING (FORWARD) STARTING FROM FIRST-ORDER SADDLE
~~~~~~
IRC FOLLOWING ALONG BACKWARD DIRECTION
~~~~~~

- *Forward and Backward correspond to either reactant or product*
- *The last structure of Forward or Backward is EQ, DC, or ??*
- *DC or ?? in TS_list.log should be confirmed in the last structure of Forward or Backward in TSm.log*
- *?? Indicates an unsuccessful optimization or an imaginary frequency*

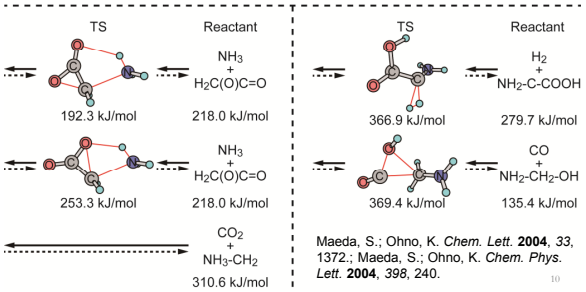
Quantum Chemical Synthon Analysis

(Synthon prediction from decomposition analysis)

The target (starting point of the search)



Glycine
0.0 kJ/mol



Maeda, S.; Ohno, K. *Chem. Lett.* **2004**, *33*, 1372.; Maeda, S.; Ohno, K. *Chem. Phys. Lett.* **2004**, *398*, 240.

Input

GRRM/B3LYP/6-31G

0 1

C	0.692268578114	-0.859602740672	-0.001060332460
H	0.677740993312	-1.514459597380	0.876536586179
H	0.678682736478	-1.510652355957	-0.881491724884
C	-0.611168011571	-0.040816289021	-0.000086983445
O	-0.394870440670	1.303201201109	-0.000453147261
O	-1.727513327852	-0.556298092642	0.000681594335
N	1.863759281644	0.033038180758	0.000826841830
H	2.433071741324	0.008847406074	-0.836395739236
H	0.603583762900	1.414439955155	-0.000747436209
H	2.429316521329	0.010021320926	0.840645157227

Options
GauMem=800
GauProc=8
FirstOnly *First step ADDF only*

Glycine Structure

TS_list.log

Geometry of TS 2, SYMMETRY = Cs

C	0.229022877916	-0.923253337269	0.358038127892
H	0.726068922113	-0.942691597054	1.319554214820
H	0.644845702569	-1.554721845183	-0.416706366822
C	-1.053219478319	-0.229836209480	0.173955228531
O	-0.513955621118	0.894468104516	-0.245975228151
O	-2.220201824375	-0.590109061205	0.354703370666
N	2.264782055458	0.403351849702	-0.207377902944
H	2.785759310501	0.105522928710	-1.023821667847
H	1.508553545021	1.051792813467	-0.402612865724
H	2.857103270848	0.669565839676	0.570429335491

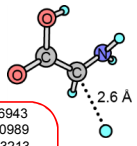
Energy = -284.231895209385
Spin(**2) = 0.000000000000
ZPVE = 0.073957342609
Normal mode eigenvalues : nmode = 24
-0.004846823 0.000187008 0.000440696 0.001744631 0.003440002
0.005361809 0.010240801 0.012068208 0.013136015 0.015585156
0.030332068 0.033688846 0.036637877 0.039287499 0.059837651
0.082224122 0.106827611 0.112198995 0.114951553 0.391070332
0.419509691 0.455191436 0.507963113 0.513310523

CONNECTION : 0 - DC *Structure of this DC is found in TS2.log*
~~~~~~

EQ0.log

PROFILE OF SHS-PATH 12

Initial geometry (positive direction of mode 18)
~~~~~~
GENERATION = 1



C	0.704548498814	-0.741116935273	-0.126321896943
H	0.555038468712	-2.319903451614	1.976816850989
H	0.683372436623	-1.683165680060	-0.658432283213
C	-0.578949905598	-0.031018435066	-0.001789867057
O	-0.476352511700	1.359110857350	0.059088142868
O	-1.685407307918	-0.570704842910	-0.013677878776
N	1.897754907198	-0.073465480394	-0.036504634400
H	2.702162293155	-0.467051156845	-0.520529374586
H	0.374633193317	1.696818067805	-0.277459800688
H	2.129938359518	0.475165331871	0.791523766035

energy : -284.166219569826
Spin(**2) : 0.000000000000

This is a DC of $NH_2CHCOOH + H$

Old DC was reached

This is not listed in DC_list.log

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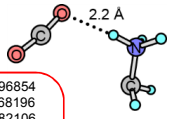
EQ0.log

PROFILE OF SHS-PATH 22

Initial geometry (positive direction of mode 20)
~~~~~~



C	2.085568310772	-1.555922826638	-0.227698296854
H	2.025909252773	-2.099175762747	0.735223768196
H	3.042414055749	-1.830570201822	-0.704432982106
C	-1.500160566931	0.453787226214	0.008435038057
O	-0.689606968874	1.324781529310	-0.089551191140
O	-2.445631699592	-0.293171875315	0.117873087918
N	2.220059624468	-0.023207551327	0.120360416317
H	2.693061080022	0.294589735679	-0.786965605219
H	1.316607948607	0.436826833210	0.225132094619
H	2.863884763055	0.271329193564	1.019953946341

energy : -284.203751045137
Spin(**2) : 0.000000000000
STEP 16 E(Harmonic) = 4.157448647915

This is $CH_2NH_3 + CO_2$

Minimum search on the final SH was failed

SHS optimization failed because of a flat PES in the DC region

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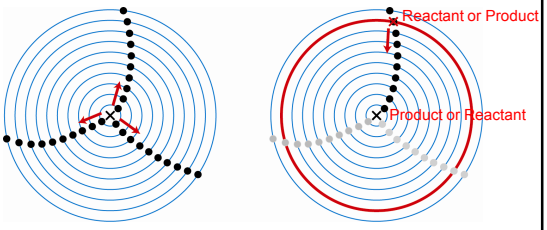
Double-end-ADDF (*d*-ADDF)

Sphere-Expansion-Mode

Sphere-Contraction-Mode



Quick search connecting a reactant and a product

15

d-ADDF-TS/EQ (2PSHS/SCW)

- *d*-ADDF-TS (2PSHS): Find a TS directly connecting two points
  - ADDF passes through a TS region as a sphere expansion
- *d*-ADDF-EQ (SCW): Find EQs between two points
  - A minimum on PES is a minimum on a hypersphere of a certain radius

Procedures finding a multi-step reaction path :

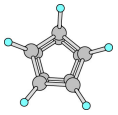
1. Exploration of intermediate EQ (EQs) by SCW
2. Exploration of TS between neighboring EQs by 2PSHS

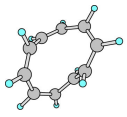
16

Ring ⇔ Cage ($C_{10}H_{10}$)

1. Optimization of Reactant and Product

Top view of the Cage
(Pentaprismane)

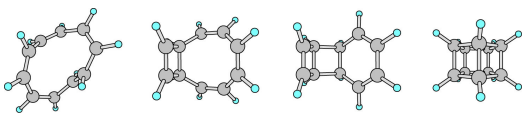




17

Ring ⇔ Cage ($C_{10}H_{10}$)

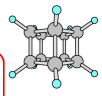
2. Exploration of EQs by SCW

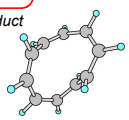


18

Input

```
# SCW/B3LYP/6-31G
                                   One Structure of Reactant or Product
0 1
C       2.445962211022   -5.078046387022   1.291611782326
C       2.313863867720   -3.896710330530   2.316180910401
C       0.785812904391   -3.622434879896   2.546590288136
~~~~~~
Reactant
C       2.200136081408   -6.095456140104   1.697094495718
C       2.071261719400   -5.039832830138   2.723796656501
C       1.136478821867   -4.070037184363   2.828097321401
~~~~~~
Options                            The Other Structure of Reactant or Product
GauMem=800
GauProc=8
```



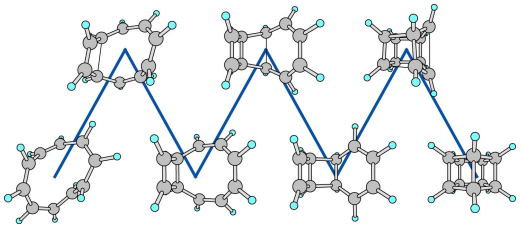


- *Structures of intermediates are listed in EQ_list.log*
- *EQs are listed in the reverse order in EQ_list.log*

19

Ring ⇔ Cage ($C_{10}H_{10}$)

3. Exploration of TSs by successive SCWs



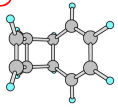
20

Input

```
# 2PSHS/B3LYP/6-31G
                                   One Structure of Reactant or Product
0 1
C       2.445962211022   -5.078046387022   1.291611782326
C       2.313863867720   -3.896710330530   2.316180910401
C       0.785812904391   -3.622434879896   2.546590288136
~~~~~~
Reactant
C       2.071278856174   -5.573029589518   1.732444377651
C       2.104963849879   -4.121231952680   2.114651850808
C       0.764704277745   -3.478859068434   2.679681180328
~~~~~~
Options                            Neighboring Structure
GauMem=800
GauProc=8
```


EQ0

EQ1

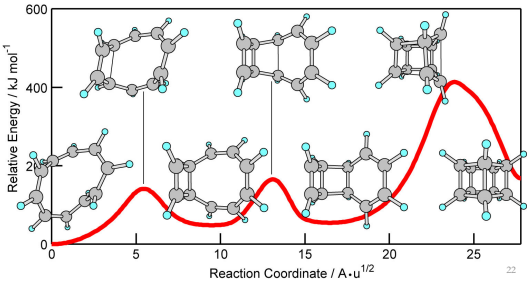


- *TS is listed at the end of the .log file*

21

Ring ⇔ Cage ($C_{10}H_{10}$)

4. IRC traces from each TS



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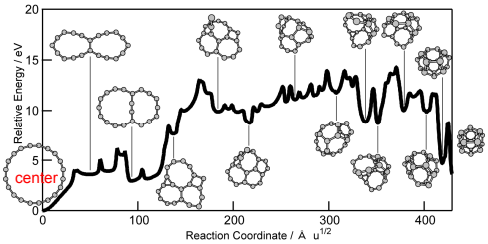
Important point 1

- All intermediate are not necessarily explored by one SCW.



1. SCW between the fullerene and the ring.
2. SCWs between neighboring intermediates
3. 2PSHS between neighboring EQs with no intermediates by SCW

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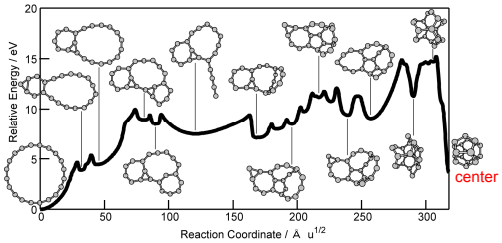
Important point 2

- Result depends on the choice of the center of the hypersphere



Reverse choice of the center should also be tested.

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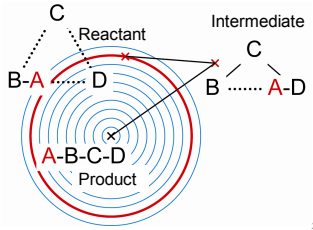
Important point 3

- Only two sets of multi-step pathways can be found between the reactant and the product.
- An intermediate not located linearly between reactant and product is difficult to be searched（ex. A-B + C + D → B-C-D-A → A-B-C-D）

To find many routes, several intermediates need to be assumed.



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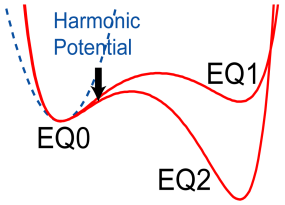
Large-ADDF (*l*-ADDF)

- Full-ADDF (*f*-ADDF): All ADDs are traced.
- *l*-ADDF: Only larger ADDs are traced.

Our postulate: The larger ADD path has a TS at the shorter distance.
Hammond postulate: A TS at the shorter distance has the more stable product.
Bell-Evans-Polanyi principle: The more stable product has a TS at the shorter distance.



The larger ADD has the lower TS and the more stable product.

Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2007**, *111*, 4527.

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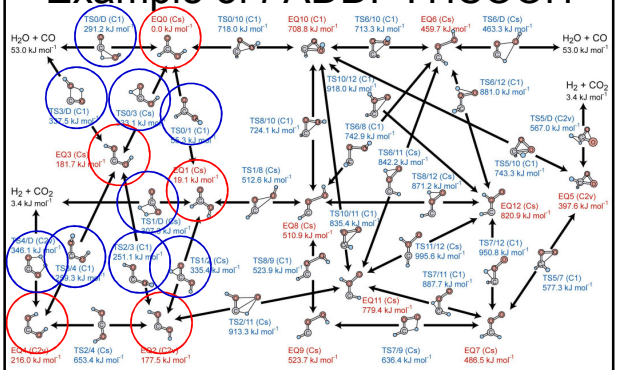
Example of *l*-ADDF : HCOOH



f-ADDF: 80,926 gradients and 2,672 Hessian (38 h on 4 CPU-cores)
l-ADDF (*N* = 5): 7,617 gradients and 314 Hessian (3.7 h on 4 CPU-cores)

27

Exploration from a HCOOH molecule

```
# GRRM/B3LYP/6-31G   This will be copied to the Root Section of a Gaussian Input.
0 1
H    -0.452596548000    0.034871834140   -1.807771705495
O    -0.452596548000    0.643013717456   -1.034349518878
O    -0.452596548000   -1.276412777953    0.242743092264
C    -0.452596548000   -0.053534532177    0.147136623161
H    -0.452596548000    0.652061759532    0.979506709948
Options                                   Optimized structure of HCOOH at B3LYP/6-31G
GauMem=100
GauProc=4
LADD=5   Trace five largest ADDs
```

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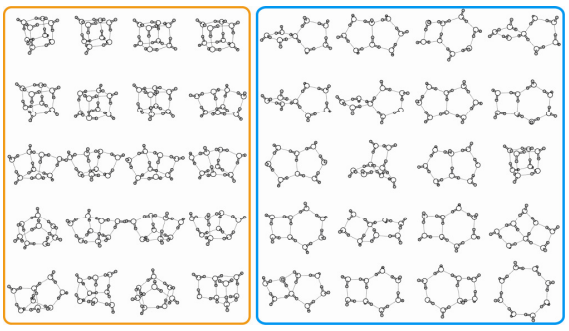
l-ADDF Exploration of $(H_2O)_8$



Lowest 20 minima at 0 K　　Lowest 20 minima at 400 K

29

Input

```
# GRRM/RHF/6-31G
0 1                                                    Water Monomer
O    -0.000000000000    0.010468354749    0.754819362610   1
H     0.000000000000    0.771670165130    1.319188188547   1
H    -0.000000000000   -0.747077150089    1.324086214974   1
O    -0.000000000000    0.010468354749    0.754819362610   2
H     0.000000000000    0.771670165130    1.319188188547   2
H    -0.000000000000   -0.747077150089    1.324086214974   2
~~~~~~
O    -0.000000000000    0.010468354749    0.754819362610   8
H     0.000000000000    0.771670165130    1.319188188547   8
H    -0.000000000000   -0.747077150089    1.324086214974   8
Options
NRUN=24   Start from 24 random structures
LADD=5
NLowest=24
Temperature=500.0   Apply ADDF to 24 lowest EQs in the EQ list for the Free energies at 0~500 K.
EQOnly   No search for TS
UpDC=12
DownDC=12
```

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Definition of DCs

- Upper limit of the bond length is assumed as

$$0.1 \times N \times (R_A + R_B)$$

1. For an upward search by ADDF: UpDC = *N* (Default = 10)
2. For a downward search by IRC: DownDC = *N* (Default = 8)

- Recommended value

1. Covalent bonds: UpDC = 10, DownDC = 8 (Default)
2. Hydrogen bonds: UpDC = 12, DownDC = 12
3. Dispersion forces : UpDC = 15, DownDC = 15

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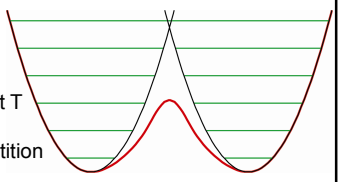
Thermodynamic simulation

- Superposition Approach

Eg. Wales, D. J.; et al. *Adv. Chem. Phys.* **2000**, *115*, 1.

- Population at Temperature *T*

$$P_i(T) = \frac{Z_i(T)}{\sum_{k=1}^{X} Z_k(T)}$$



- $Z_i(T)$: Partition function at T (Harmonic approx.)
- Denominator: Sum of partition functions of all structures

Thermodynamic simulation can be made on the basis of the data obtained by GRRM

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Thermodynamic analysis

List of Equilibrium Structures

Rotation

```
# Geometry of EQ 0, SYMMETRY = C1
O     -3.990749673348   0.812671330496   0.759596654549
H     -4.623998138945   1.477984504789   0.989567688782
H     -4.102553621535  -0.016833813104   1.233805951983
~~~~~~
```

Electronic energy

```
Energy   = -608.028031295279
Spin(**2) =  0.000000000000
ZPVE     =  0.215589990623
```

Vibration

```
Normal mode eigenvalues : nmode = 66
 0.000010181  0.000032843  0.000087596  0.000141739  0.000189141
 0.000289300  0.000410092  0.000619427  0.000760112  0.000883149
 0.001138962  0.001194830  0.001290467  0.001517249  0.001737303
~~~~~~
```

- *Partition functions can be computable at arbitrary temperature.*

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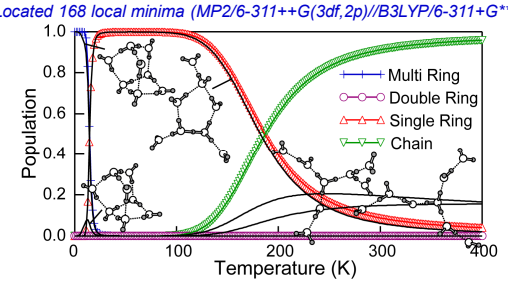
Thermal distributions of $H^+(H_2O)_8$

*Located 168 local minima (MP2/6-311++G(3df,2p)//B3LYP/6-311+G**)*



Population (by the superposition approach) on the basis of harmonic vibrational frequencies reproduced three (IR) observations at different temperatures

1. *JACS* **2000**, *122*, 1398: a mixture of chains and a Zundel single-ring, at ~170 K
2. *Science* **2004**, *304*, 1134: dominated by chains, at >> 170 K
3. *Science* **2005**, *308*, 1765: dominated by a Zundel single-ring, at <<170 K

Luo, Y.; Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2007**, *111*, 10732.

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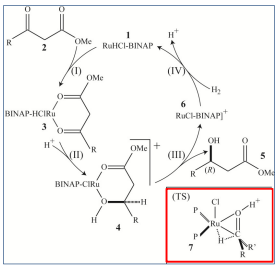
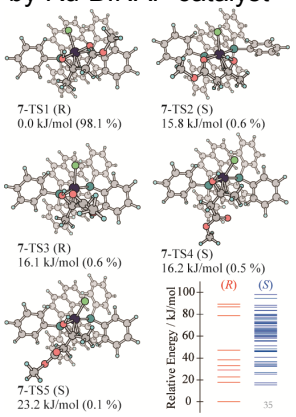
Asymmetric synthesis by Ru-BINAP catalyst





68 TSs leading to asymmetric selection were searched automatically. Among them an R type was found to be the lowest in agreement with the experiment. Right figures show five lowest TSs.
Maeda, S.; Ohno, K. *J. Am. Chem. Soc.* **2008**, *130*, 17228.

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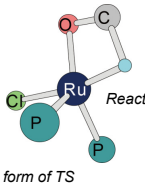
Input

```
# GRRM/PM6 EmpiricalDispersion=GD3

0 1                    90 atoms outside the reaction center
C     -0.128588   1.878776   3.239214
~~~~~~
H      1.027143  -4.484840   3.683857
Frozen Atoms
P      1.563807  -0.793743  -0.751263
P     -1.403001  -1.238551  -0.057742
Ru     0.135998  -2.368924  -1.238020
H      0.578221  -3.350460   0.067996
Cl    -0.285807  -1.341860  -3.384823
C      1.155131  -4.429632  -0.860073
O      0.985945  -4.096942  -2.110175
Options
GauMem = 400
GauProc = 8            Fix the reaction center at the form of TS
LADD=5
NLowest=5              Explore lower energy conformations
```



Reaction center

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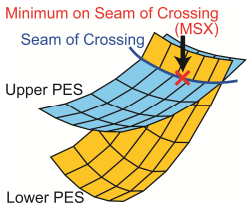
Application to crossings on potential surfaces

Exploration of minima on seams of crossings



Automated algorithm for MSX (Seam Model Function Method)

1. Approximate automated search for MSX based on penalty function
2. Further optimization yields more precise MSX structures.

A penalty function for automated MSX search:

$$X(\mathbf{Q}) = \frac{1}{2}\left(E^{\text{State1}}(\mathbf{Q}) + E^{\text{State2}}(\mathbf{Q})\right) + \frac{\left(E^{\text{State1}}(\mathbf{Q}) - E^{\text{State2}}(\mathbf{Q})\right)^2}{\alpha}$$

Mean potential energy | A penalty function

Maeda, S.; Ohno, K.; Morokuma, K. *J. Phys. Chem. A* **2009**, *113*, 1704.

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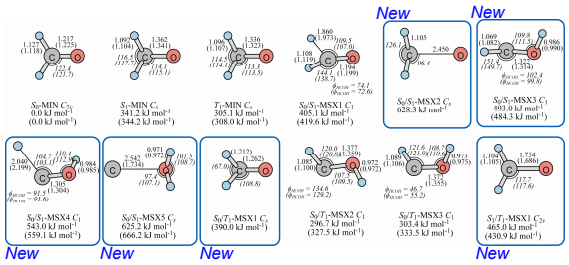
H_2CO (S_0, S_1, and T_1 PESs)



Initial search: (4e,3o)-CASSCF/6-31G and (2e,3o)-CASSCF/6-31G
(85,000 (4e,3o)-CASSCF gradients and 80,000 (2e,3o)-CASSCF gradients)
Optimization 1: (12e,10o)-CASSCF/aug-cc-pVDZ
Optimization 2: (12e,10o)-CASPT2/aug-cc-pVDZ (shown in parentheses)

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Optimization of MSX structures

Geometry optimization

```
# MIN UB3LYP/6-31G        Unify the calculation levels

0 1  Singlet state
C      -0.341655575913   -0.061830207285   -0.629143745161
O       0.051090096597   -0.153079538593    0.678261012364
H      -0.148111884773    0.634881653256    1.224415641392
H       0.344846324087   -0.329784658376   -1.435884114596
Options
OptX(Seam)  Within crossing regions
Second Input
UB3LYP/6-31G
0 3  Triplet state
END
MaxStepSize = 0.1   Stepsize should be smaller than the default value.
Stable=Opt
```

Without this option, the closed-shell singlet surface is explored with DFT.

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Automated search of *approximate* MSX structures

```
# GRRM/UB3LYP/6-31G

0 1                    Pre-optimized structure with an input using MIN
C      -0.341655575913   -0.061830207285   -0.629143745161
O       0.051090096597   -0.153079538593    0.678261012364
H      -0.148111884773    0.634881653256    1.224415641392
H       0.344846324087   -0.329784658376   -1.435884114596
Options
ModelF(Seam)   Use of model function placing EQ near MSX
Second Input
UB3LYP/6-31G
0 3
END
MaxStepSize = 0.1
Stable=Opt
```

- *GRRM options such as LADD and Nlowest are available.*
- *EQOnly is automatically assumed.*
- *Crude MSX is obtained as EQ, which needs to be refined by using OptX.*

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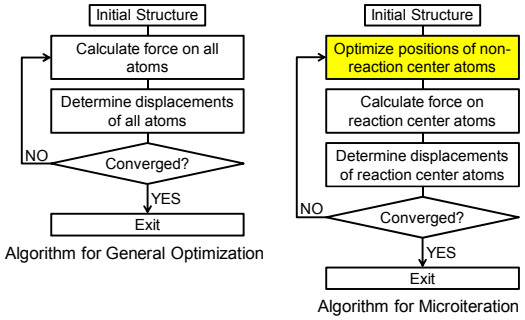
Geometrical Microiteration

- *Divide reaction center from the others in the Giant system.*
- *Always optimize for variables other than the reaction center*



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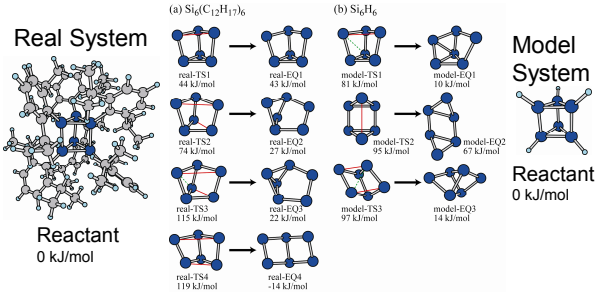
An Application to the Si_6-Prism



New channels open in the real system

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Input

```
# GRRM/ONIOM(B3LYP/6-31G*:UFF)

0 1                                   Reaction center including link atoms
Si-Si3-0.10182  -1.1881857   -0.9102208   -1.0465917   H
Si-Si3-0.09963  -1.2116703   -0.4296025    1.3210086   H
~~~~~~
C-C_R--0.09616  2.3999742   -0.7349068    2.7547234    L    H-H_--0.08955  5
C-C_R--0.09221  2.3697321    2.7146470   -0.8151322    L    H-H_--0.10701  6
External Atoms
C-C_R--0.09800  -4.5129210   -2.4126440   -3.1593396   L
~~~~~~
Options                               Atoms of every-step-optimization in Microiteration
GauMem=800
GauProc=8
FirstOnly
GauInpB
1    2    1.0  3    1.0  4    1.0  7    1.0   Connectivity matrix for UFF calc.,
2    3    1.0  5    1.0  8    1.0               to be copied at the end of the
~~~~~~                                          Gaussian input file .
180
END
```

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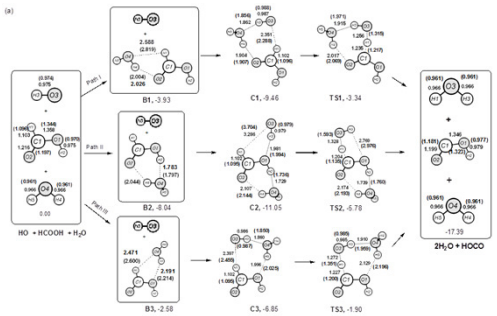
Application to complex reactions



- *Exploration of reaction precursors by l-*ADDF (cf. water cluster)
- Hand-making of product geometries and connecting reaction routes by *d-*ADDF

Luo, Y.; Maeda, S.; Ohno, K. *Chem. Phys. Lett.* **2009**, *469*, 57.

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*Precursor search by l-*ADDF

```
# GRRM/M062X/6-31+G*

0 2
H    0.279704309   -2.419095131   0.087118953   1
O    0.279704309   -1.767230166   0.810586808   1
O    0.279704309   -3.669699011   2.040431695   1      HCOOH
C    0.279704309   -2.467398098   1.960665441   1
H    0.279704309   -1.772053247   2.812917361   1
O    0.349449893   -2.139473528   0.851411182   2
H    0.349449893   -1.380136528   1.447454182   2      H2O
H    0.349449893   -2.898810528   1.447454182   2
O    0.349449893   -2.139473528   0.851411182   3
H    0.349449893   -1.380136528   1.447454182   3      OH
Options
DownDC=12
UpDC=12
LADD=3                                Similar to the search for water clusters
NLowest=3
NRUN=16
EQOnly
```

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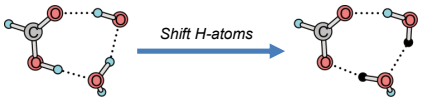
*Connecting reaction route by d-*ADDF

```
# 2PSHS/M062X/6-31+G*

0 2                                   Starting structure obtained by l-ADDF (Left Fig. bellow)
H    -0.462142232965   -1.064413231066   0.102466212778
O    -1.206875810840   -0.667073981701   0.642204190946
O    -0.096500753587    1.280103269769   0.399425908015
~~~~~~
Reactant
H    -0.084528637   -1.459791639   -0.466700719
O    -1.206875811   -0.667073982    0.642204191     Hand-made structure from a
O    -0.096500754    1.280103270    0.399425908     structure obtained by l-ADDF
~~~~~~                                               (Right Fig. below)
Options
GauMem=800
GauProc=8
DownDC=12
UpDC=12
```



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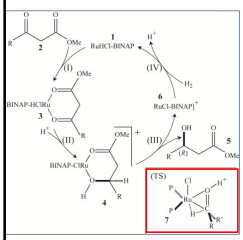
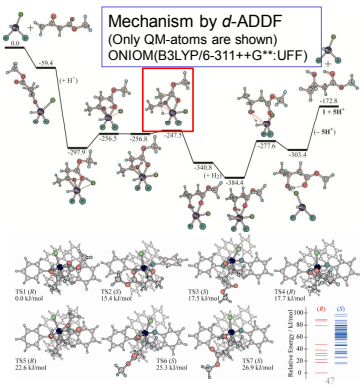
Ru-BINAP-catalyzed hydrogenation



*The whole cycle obtained by d-*ADDF
Ohno, K.; Maeda, S. *J. Mol. Catal. A: Chem.* **2010**, *324*, 133.



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