Chapter 4 Quantum Chemistry Calculations in Gaussian Software

4.1 Single-Point Calculations (Gaussian Input & Output)

4.2 SCAN

4.3 Geometry Optimization

4.4 Frequency Calculations

4.5 NMR

4.6 UV-vis Spectrum

4.7 Transition State Search

4.1 Single-Point Calculations

➢Gaussian input file

✓Generation:

- Website search
- GaussView

✓Contents (take H_2O as an example)

```
%chk=H2O-single-point.chk
%mem=12000MW
%nprocshared=24
#p cam-b3lyp/6-31+g(d,p) geom=connectivity
 (black line)
single-point calculations
 (black line)
0 1
 O                    1.04492193   -0.44921874    0.00000000
 H                    2.00492193   -0.44921874    0.00000000
 H                    0.72446734    0.45571709    0.00000000

 1 2 1.0 3 1.0
 2
 3
```

4.1 Single-Point Calculations

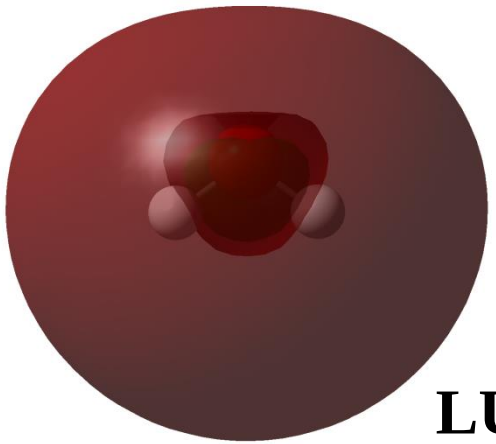
- Gaussian output file

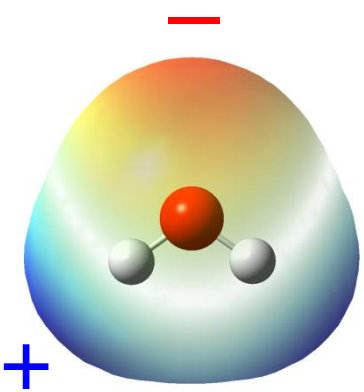
✓log file

- Text: copyright→citation→input→symmetry analysis (input/standard orientation)→basis sets→SCF (energy)→population analysis (orbital, charge (Mulliken), and dipole)→summary (HF=)
- GaussView: summary & charge

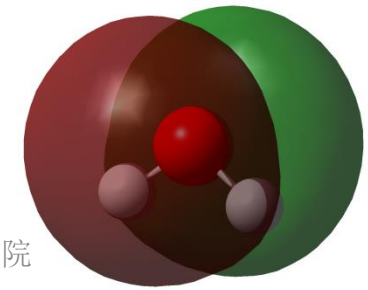
✓chk (fchk) file

```
**********************************************************************

          Population analysis using the SCF density.

**********************************************************************

Orbital symmetries:
      Occupied  (A1) (A1) (B2) (A1) (B1)
      Virtual   (A1) (B2) (A1) (B1) (B2) (A1) (B2) (A1) (B2) (B1)
                (A1) (A1) (A2) (A1) (B1) (B2) (A1) (B2) (B1) (A2)
                (A1) (A1) (B2) (A1)
The electronic state is 1-A1.
Alpha  occ. eigenvalues --  -19.23937  -1.09998  -0.61854  -0.45569  -0.38932
Alpha virt. eigenvalues --    0.07141   0.15470   0.19218   0.19389   0.26065
Alpha virt. eigenvalues --    0.28439   0.97836   1.05149   1.15368   1.17951
Alpha virt. eigenvalues --    1.18118   1.28895   1.56781   1.63338   1.71508
Alpha virt. eigenvalues --    2.29561   2.31107   2.59864   2.70083   2.73823
Alpha virt. eigenvalues --    3.11217   3.40553   3.57459   4.00604
```





LUMO EPS



HOMO

4.1 Single-Point Calculations

- Specific property: **charge** ↔ Keyword: **population**

  dipole

- ✓**pop = NPA/NBO** → output: 多出NBO一段的信息
- ✓pop = MK (ESP)

```
*****************************Gaussian NBO Version 3.1*****************************
         N A T U R A L   A T O M I C   O R B I T A L   A N D
      N A T U R A L   B O N D   O R B I T A L   A N A L Y S I S
*****************************Gaussian NBO Version 3.1*****************************
     /RESON  / : Allow strongly delocalized NBO set

 Analyzing the SCF density
 Job title: single-point calculations

 Storage needed:      2759 in NPA (  33554392 available)


 NATURAL POPULATIONS:  Natural atomic orbital occupancies

   NAO  Atom  No  lang   Type(AO)    Occupancy      Energy
  ---------------------------------------------------------
      1    0    1  S      Cor( 1S)     1.99990     -19.08929
      2    0    1  S      Val( 2S)     1.75005      -0.96111
      3    0    1  S      Ryd( 3S)     0.00116       1.07248
      4    0    1  S      Ryd( 4S)     0.00000       1.60707
      5    0    1  S      Ryd( 5S)     0.00000       2.95008
```

Summary of Natural Population Analysis:

Mulliken versus NBO

Mulliken atomic charges:

		1
1	O	-0.728645
2	H	0.364322
3	H	0.364322

Sum of Mulliken atomic charges = 0.00000

Atom	No	Natural Charge	Core
O	1	-1.00789	1.99990
H	2	0.50395	0.00000
H	3	0.50395	0.00000
* Total *		0.00000	1.99990

4.1 Single-Point Calculations

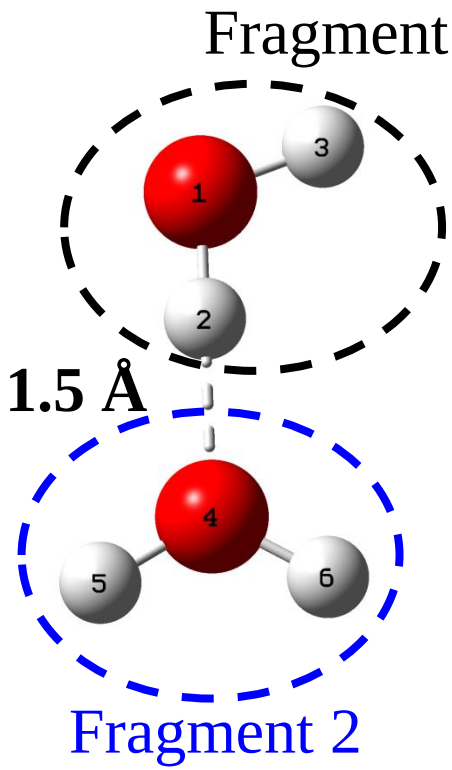
➢Specific property: **interaction** ↔ Keyword: **counterpoise**

energy

✓counterpoise=2 (number of fragments)

Input

```
#p 6-31+g(d) counterpart=2 geom=connectivity rm062x

hytrogen bond energy estimation

0 1 0 1 0 1
 O(fragment=1)        0.00000000      0.00000000      0.00000000
 H(fragment=1)        0.00000000      0.00000000      0.96000000
 H(fragment=1)        0.90493583      0.00000000     -0.32045458
 O(fragment=2)        0.00000000      0.00000000      2.46000000
 H(fragment=2)       -0.83138282      0.00161210      2.94000000
 H(fragment=2)        0.83138282     -0.00161210      2.94000000
```



Output

$1^{st} = E_{AB}$ = -152.763588415 a.u.

$2^{nd} = E_{A+}$ = -76.3842070395 a.u.

$3^{rd} = E_{B+}$ = -76.3808313376 a.u.

$4^{th} = E_{A}$ = -76.3833952727 a.u.

$5^{th} = E_{B}$ = -76.3792152769 a.u.

$E_{counter} = E_{AB} - E_{BSSE}$ = -152.761160587080 a.u.

$E_{BSSE} = (E_{A+} + E_{B+}) - (E_A + E_B)$ = 0.002427827421 a.u.

$E_A + E_B$ = -152.7626105 a.u.

E_I(raw) = $E_{AB} - (E_A + E_B)$ = -0.61 kcal/mole

E_I(corrected) = $E_{AB} - (E_A + E_B) - E_{BSSE}$ = -2.14 kcal/mole

4.1 Single-Point Calculations

- Specific property: Keyword:

  external electric field ↔ field

  background charges ↔ charge

  solvation ↔ SCRF

……

4.2 SCAN

- Specific property: **a potential energy surface (PES)**
  - ✓The molecular structure must be defined using Z-matrix (internal) coordinates.

Input

```
%chk=Fe-Fe-scan.chk
%mem=12000MW
%nprocshared=24
#p ub3lyp/6-31g scan nosymm

scan try

0 7
 Fe
 Fe                    1                 B1

   B1                 1.20000000 5 0.4
```

Output

```
Summary of the potential surface scan, energies are +2526 a.u.:
  N       B1           SCF
----  ---------  -----------
   1     1.2000     -0.06891
   2     1.6000     -0.90435
   3     2.0000     -1.02086
   4     2.4000     -0.98616
   5     2.8000     -0.93508
   6     3.2000     -0.89559
----  ---------  -----------
```

4.3 Geometry Optimization

➢Keyword: **opt**

```
         Item               Value     Threshold  Converged?
Maximum Force            0.002219     0.000450     NO
RMS     Force            0.001045     0.000300     NO
Maximum Displacement     0.121942     0.001800     NO
RMS     Displacement     0.063003     0.001200     NO
Predicted change in Energy=-6.932877D-06
Optimization stopped.
   -- Number of steps exceeded,  NStep=  23
   -- Flag reset to prevent archiving.
```

opt=maxcycle=100

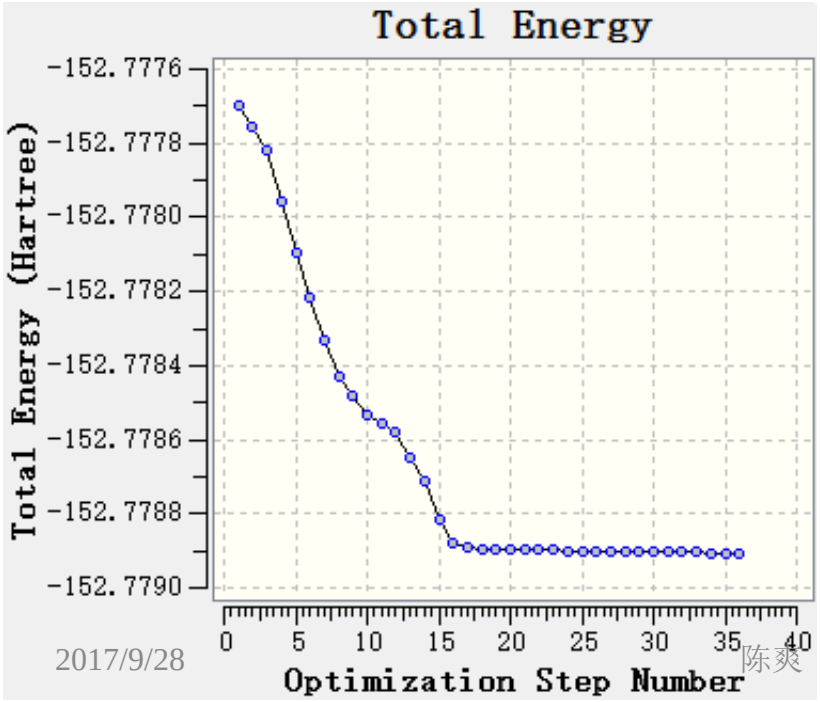
```
Second derivative matrix not upda
The second derivative matrix:
                          R1          R2          A1
          R1           0.54975
          R2          -0.00703     0.54975
          A1           0.02868     0.02868     0.15227
    Eigenvalues ---    0.14810     0.54689     0.55678
Angle between quadratic step and forces=  33.64 degrees.
Linear search not attempted -- first point.
Iteration  1 RMS(Cart)=  0.00003385 RMS(Int)=  0.00000000
Iteration  2 RMS(Cart)=  0.00000000 RMS(Int)=  0.00000000
ClnCor:  largest displacement from symmetrization is 2.68D-15 for atom     3.
Variable       Old X    -DE/DX   Delta X   Delta X   Delta X     New X
                                 (Linear)    (Quad)   (Total)
   R1         1.82045  -0.00001   0.00000  -0.00001  -0.00001   1.82044
   R2         1.82045  -0.00001   0.00000  -0.00001  -0.00001   1.82044
   A1         1.85404  -0.00001   0.00000  -0.00005  -0.00005   1.85398
         Item               Value     Threshold  Converged?
Maximum Force            0.000009     0.000450     YES
RMS     Force            0.000008     0.000300     YES
Maximum Displacement     0.000036     0.001800     YES
RMS     Displacement     0.000034     0.001200     YES
Predicted change in Energy=-2.977279D-10
Optimization completed.
   -- Stationary point found.
```

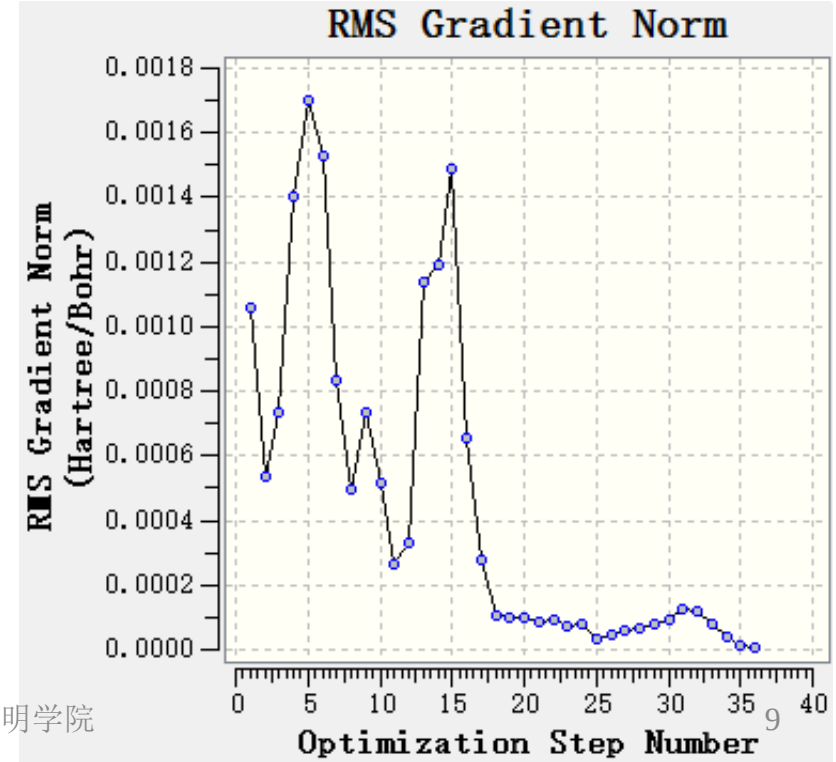
4.3 Geometry Optimization

➢Keyword: **opt**

✓Result presentation by virtue of GaussView

- Open "log" file
- Mark "Read Intermediate Geometries"
- Energy and force changes

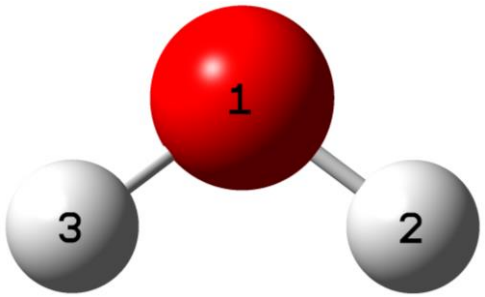




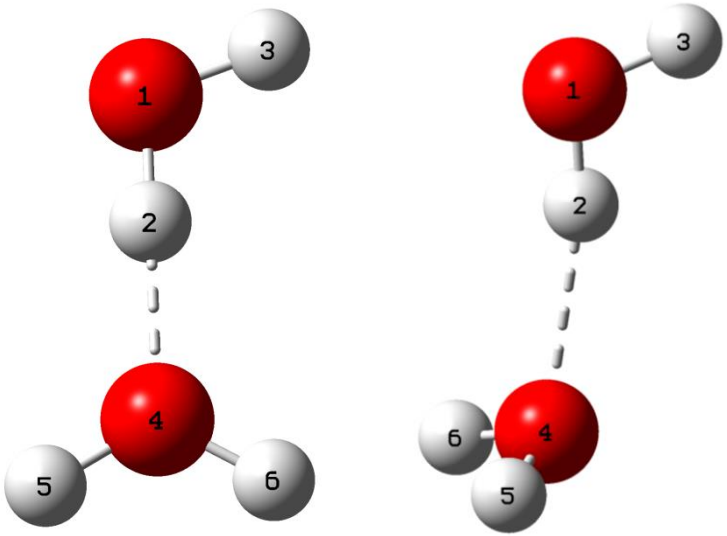
4.3 Geometry Optimization

➢Keyword: **opt**

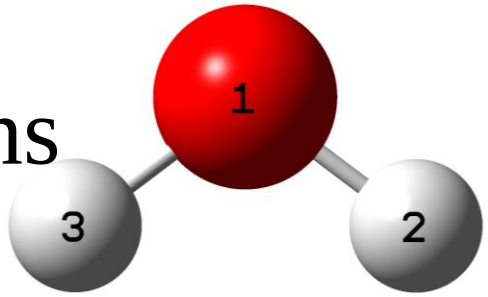
	Before	After
$O\text{-}H_2$	0.96 Å	0.963 Å
$O\text{-}H_3$	0.96 Å	0.963 Å
∠H-O-H	109.5°	106.2°



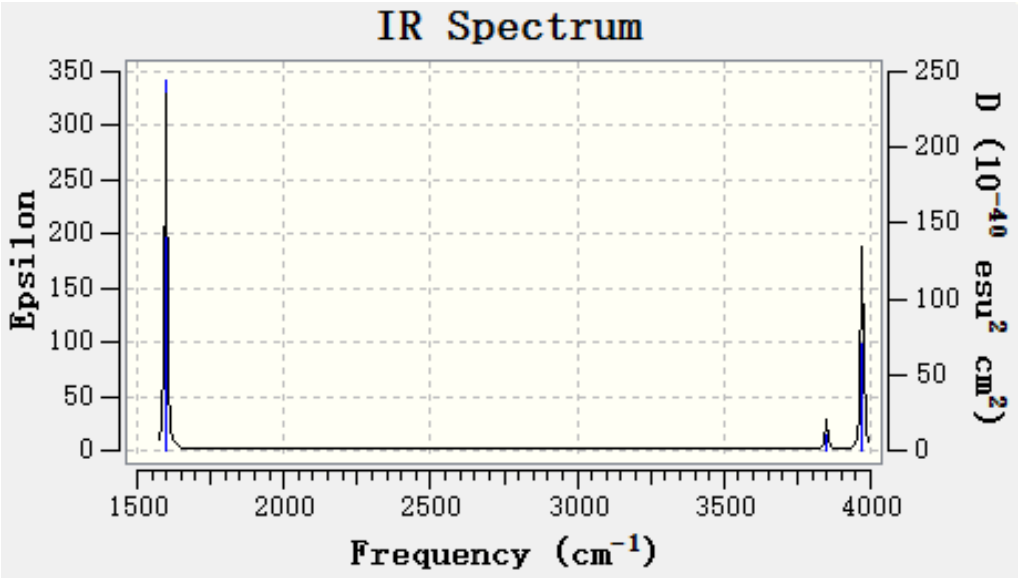
$O_1\text{-}H_2$	0.96 Å	0.973 Å
$O_4\text{-}H_2$	1.5 Å	1.896 Å
$\angle O_1\text{-}H_2\text{-}O_4$	180.0°	168.3°



4.4 Frequency Calculations

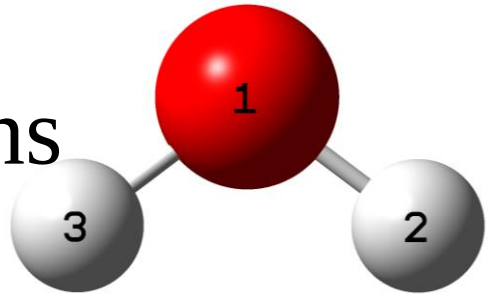


- Keyword: **freq**
- ✓Result presentation by virtue of GaussView
  - Open "log" file
  - Show vibration (animation)
  - IR spectrum



	1			2			3		
	A1			A1			B2		
Frequencies --	1597.4933			3850.6925			3971.9476		
Red. masses --	1.0839			1.0441			1.0836		
Frc consts --	1.6297			9.1213			10.0720		
IR Inten --	97.9611			9.7279			70.1623		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 8	0.00	0.00	0.07	0.00	0.00	0.05	0.00	0.07	0.00
2 1	0.00	-0.42	-0.57	0.00	0.59	-0.39	0.00	-0.56	0.42
3 1	0.00	0.42	-0.57	0.00	-0.59	-0.39	0.00	-0.56	-0.42

4.4 Frequency Calculations



- Keyword: **freq**

- Thermochemistry properties

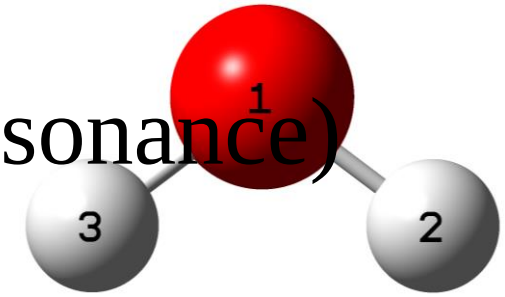
temperature = 350

```
 - Thermochemistry -
 -------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Atom     1 has atomic number  8 and mass  15.99491
Atom     2 has atomic number  1 and mass   1.00783
Atom     3 has atomic number  1 and mass   1.00783
Molecular mass:    18.01056 amu.
Zero-point correction=                           0.021461 (Hartree/Particle)
Thermal correction to Energy=                    0.024296
Thermal correction to Enthalpy=                  0.025241
Thermal correction to Gibbs Free Energy=         0.003819
Sum of electronic and zero-point Energies=            -76.384257
Sum of electronic and thermal Energies=               -76.381422
Sum of electronic and thermal Enthalpies=             -76.380477
Sum of electronic and thermal Free Energies=          -76.401899
```

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	15.246	6.015	45.085
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	34.608
Rotational	0.889	2.981	10.469
Vibrational	13.469	0.053	0.008

	Q	Log10(Q)	Ln(Q)
Total Bot	0.175116D-01	-1.756674	-4.044892
Total V=0	0.130171D+09	8.114515	18.684362
Vib (Bot)	0.134588D-09	-9.870995	-22.728805
Vib (V=0)	0.100045D+01	0.000195	0.000449
Electronic	0.100000D+01	0.000000	0.000000
Translational	0.300432D+07	6.477746	14.915562
Rotational	0.433086D+02	1.636574	3.768351

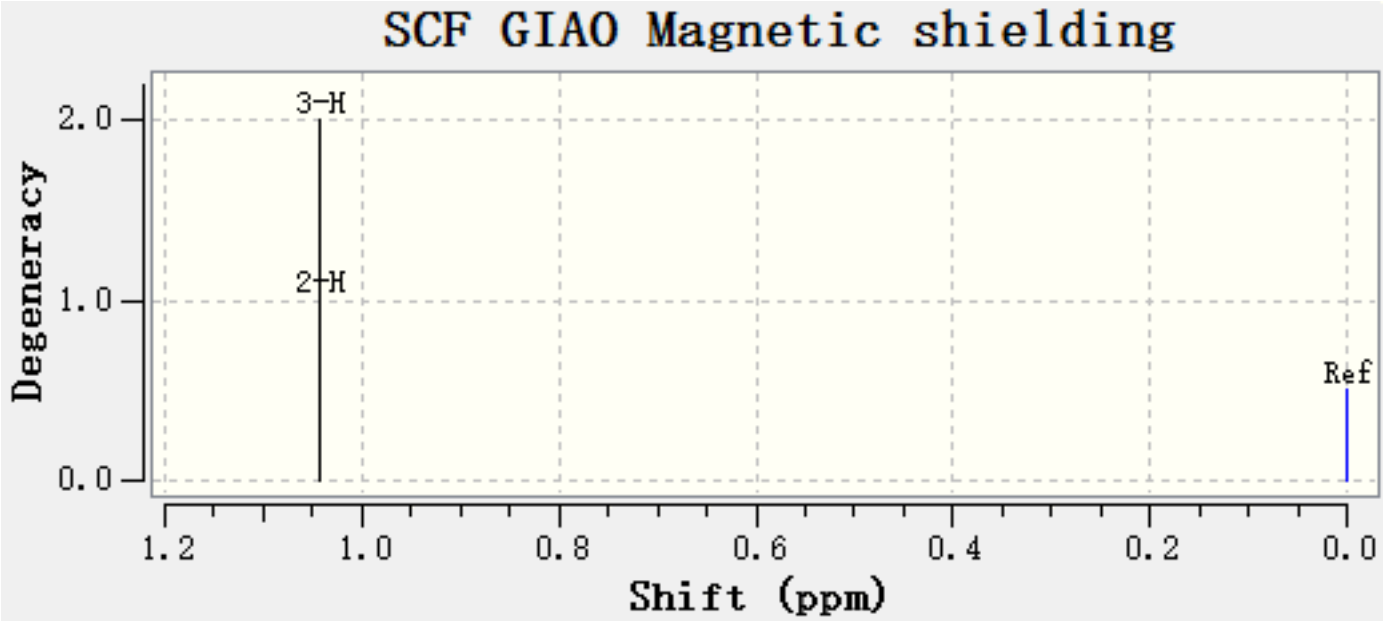
4.5 NMR (Nuclear Magnetic Resonance)



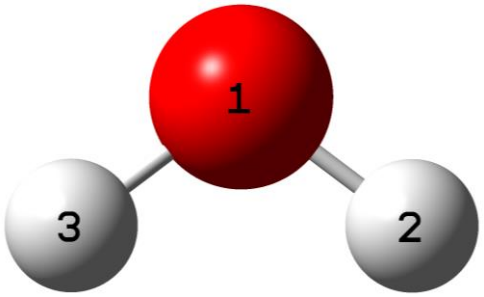
➢Keyword: **NMR test**

✓Result presentation by virtue of GaussView

- Open "log" file
- NMR chemical shift



4.6 UV-vis Spectrum

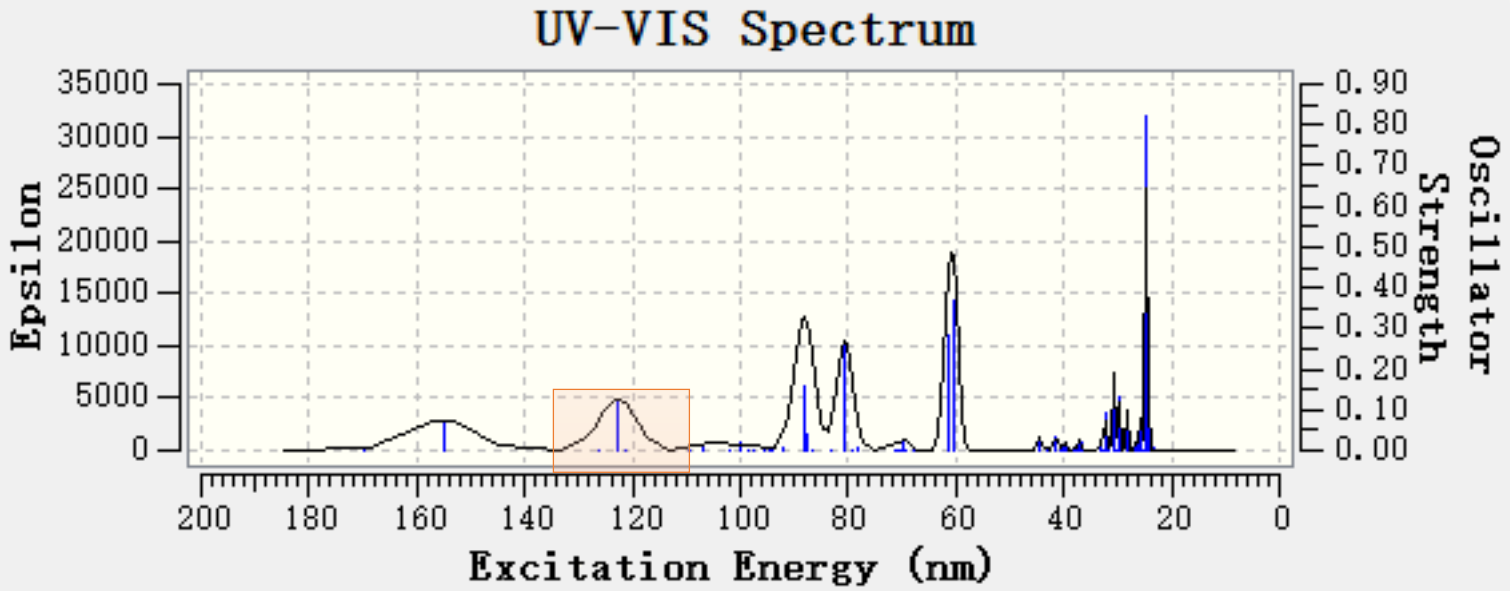


➢Keyword: **TD=(50-50,nstates=50)**

✓Result presentation by virtue of GaussView

- Open "log" file
- UV-vis spectrum (GaussSum)

```
Excitation energies and oscillator strengths

Excited State   1:      Triplet-B1     7.305
      5 ->  6         0.67895
 This state for optimization and/or second-or
Total Energy, E(TD-HF/TD-DFT) =  -76.13723096
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:      Singlet-A1     8.0015 eV  154.95 nm  f=0.0755  <S**2>=0.000
      5 ->  6         0.70364

Excited State   3:      Triplet-A1     9.3012 eV  133.30 nm  f=0.0000  <S**2>=2.000
      4 ->  6         0.69540
      4 -> 11        -0.11425

Excited State   4:      Triplet-A2     9.8115 eV  126.37 nm  f=0.0000  <S**2>=2.000
      5 ->  7         0.66665
      5 -> 10         0.23092

Excited State   5:      Singlet-A1    10.1095 eV  122.64 nm  f=0.1216  <S**2>=0.000
      4 ->  6         0.69417
      5 ->  9         0.11337
```

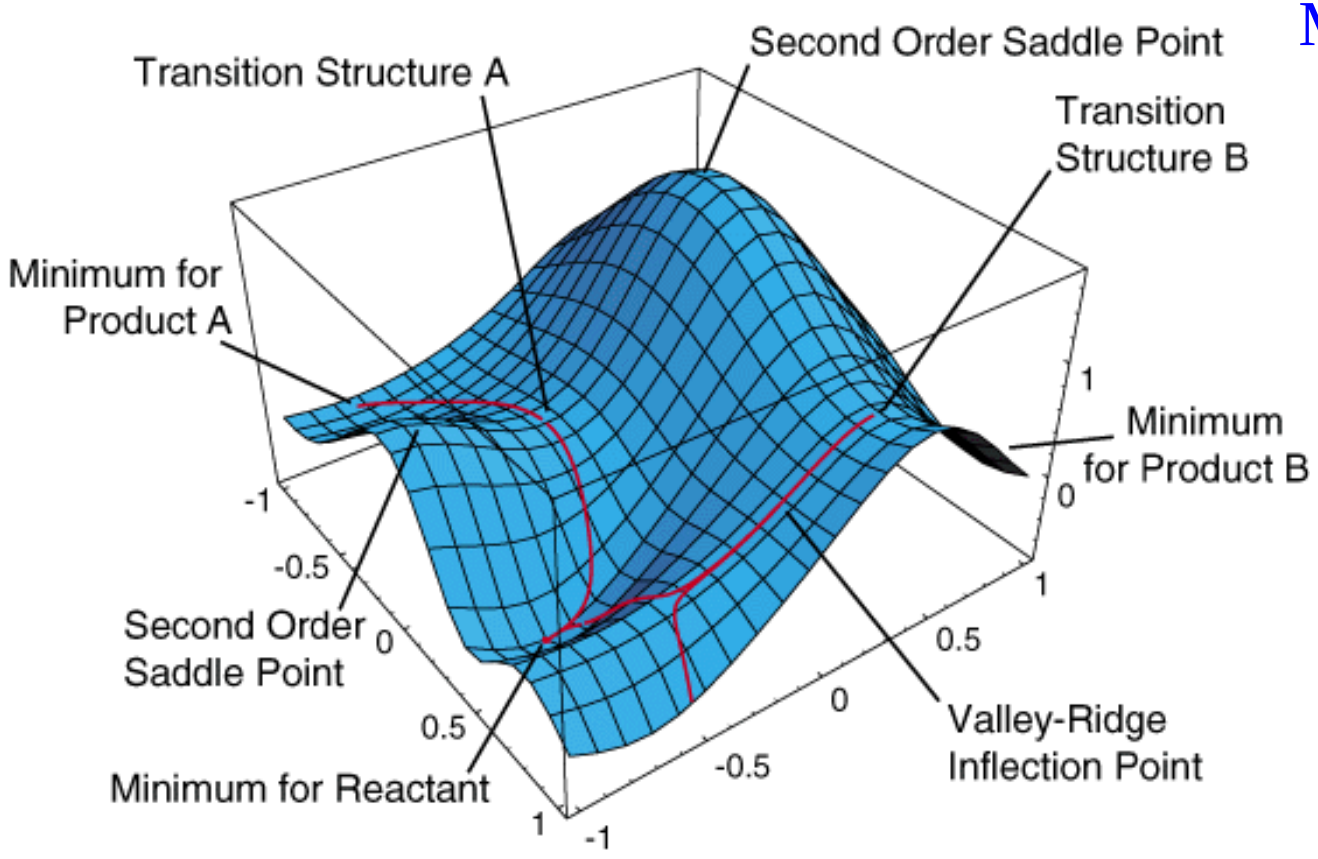


4.7 Transition State Search

- Potential energy surface

$$\frac{\partial E}{\partial R_i} = 0 \text{ and } \frac{\partial^2 E}{\partial R_i^2} > 0 \text{ for all } R_i$$

Minimum



4.7 Transition State Search

➢Transition state(the first-order saddle point)

✓a maximum with respect to one coordinate, and minima with respect to the rest of coordinates.

✓The unique character of a transition state: an imaginary vibrational mode.

✓To identify whether a stationary point is a minimum or a transition state, one has to do vibrational frequency calculations.

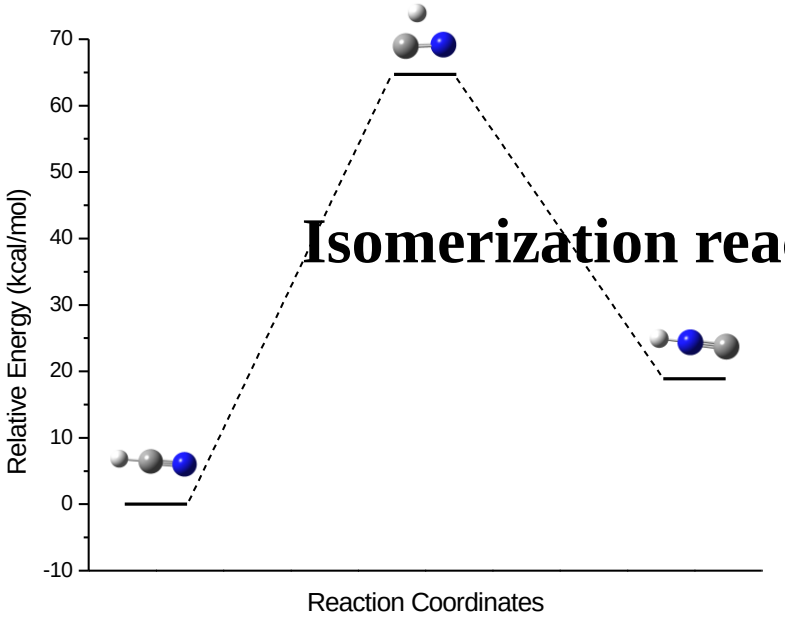
✓Intrinsic reaction coordinate (IRC): Along the IRC, a transition state should connect the reactants and the products.

✓To verify whether the transition state connects the reactants and products one should perform IRC calculations.

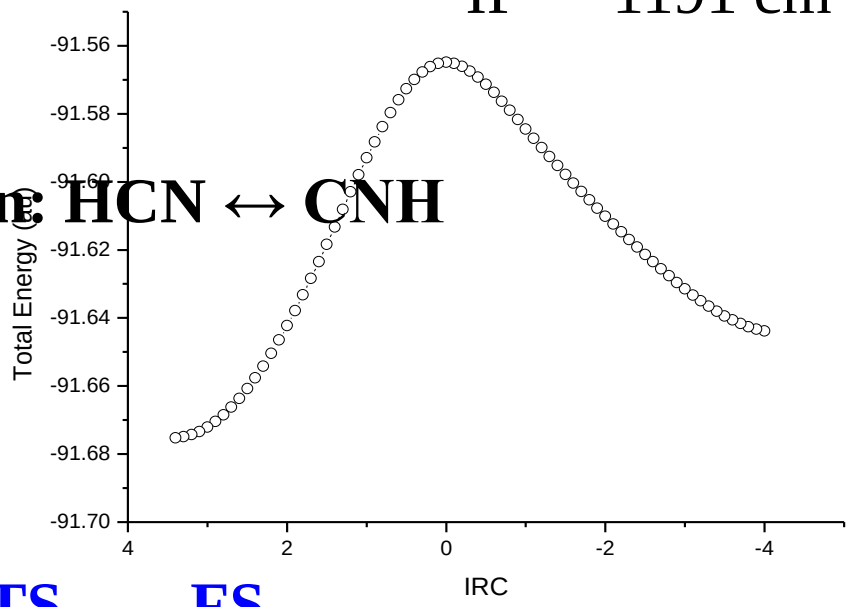
4.7 Transition State Search

➢Keyword: **opt=(ts,noeigentest,calcfc)**

IRC=(forward/reverse,calcfc)



IF = -1191 cm^{-1}



Isomerization reaction: HCN ↔ CNH

	IS	TS	FS
H-C (Å)	1.071	1.176	1.002 (N-H)
C-N (Å)	1.152	1.183	1.171
∠H-C-N (°)	180 .0	75.0	180.0

References

1. J. B. Foresman, *Exploring Chemistry with Electronic Structure Methods* (second Edition), Gaussian, Inc.
2. www.gaussian.com

10月9日Presentation

1. NBO分析，给出H_2O孤对电子的自然键轨道

2. 如何使用GaussSum结合Gaussian计算结果做出UV-vis Spectrum（可以H_2O为例）

3. NMR原理

4. 如何结合Gaussian的溶剂化模型计算特定溶剂下H_2O的NMR chemical shift