

# 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

```
%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=)

\*\*\*\*\*

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	

- GaussView: Summary & Charge

# 4.1 Single-Point Calculations

- Gaussian output file
  - ✓ chk (fchk) file

Surface/Contours →  
New Cube (Total Density)  
→ New Surface  
→ New Mapped Surface (EPS)  
→ Display Format (Transparent)

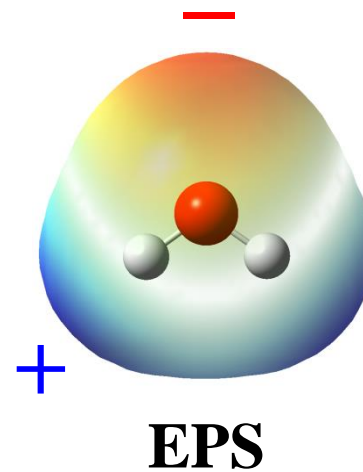
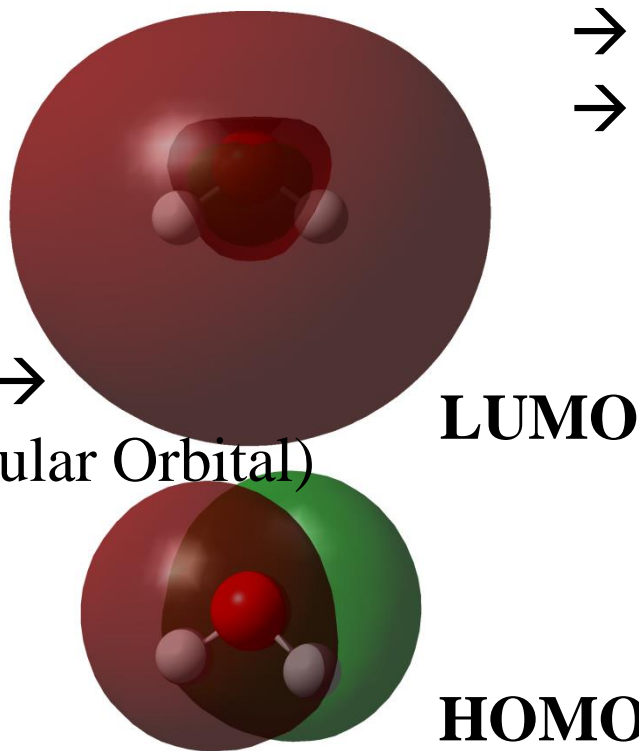
Surface/Contours →

New Cube (Molecular Orbital)

→ New Surface

→ Display Format

(Transparent)



# 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*****
      NATURAL ATOMIC ORBITAL AND
      NATURAL BOND ORBITAL ANALYSIS
*****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:

	Atom	No	Charge
1	O	1	-0.728645
2	H	2	0.364322
3	H	3	0.364322

Atom	No	Natural Charge	Core
O	1	-1.00789	1.99990
H	2	0.50395	0.00000
H	3	0.50395	0.00000
Sum of Mulliken atomic charges =		0.00000	
Total		0.00000	1.99990

Sum of Mulliken atomic charges = 0.00000

# 4.1 Single-Point Calculations

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

**energy**

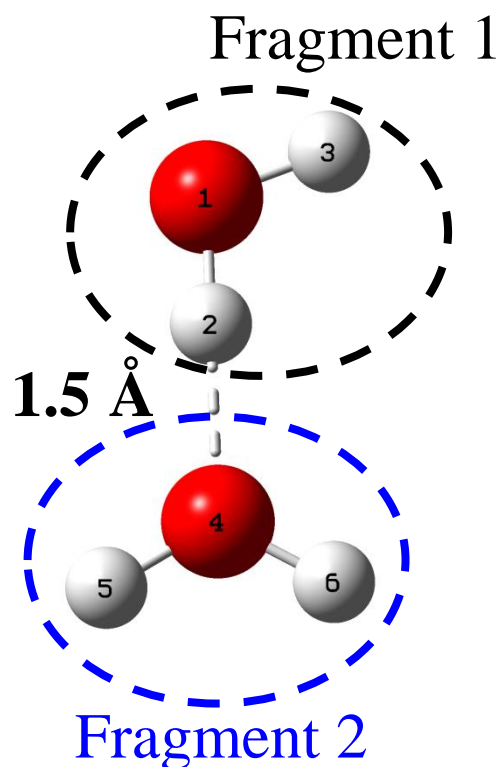
**Input**

✓ counterpoise=2 (number of fragments)

```
#p 6-31+g(d) counterpoise=2 geom=connectivity rm062x
hydrogen bond energy estimation
```

```
O 1 O 1 O 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**

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

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

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

$$4^{\text{th}} = E_A = -76.3833952727 \text{ a.u.}$$

$$5^{\text{th}} = E_B = -76.3792152769 \text{ a.u.}$$

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

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

$$E_A + E_B = -152.7626105 \text{ a.u.}$$

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

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

# 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,
  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.			

Second derivative matrix not updated.  
The second derivative matrix:

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 (Linear)	Delta X (Quad)	Delta X (Total)	New X
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

**opt=maxcycle=100**

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

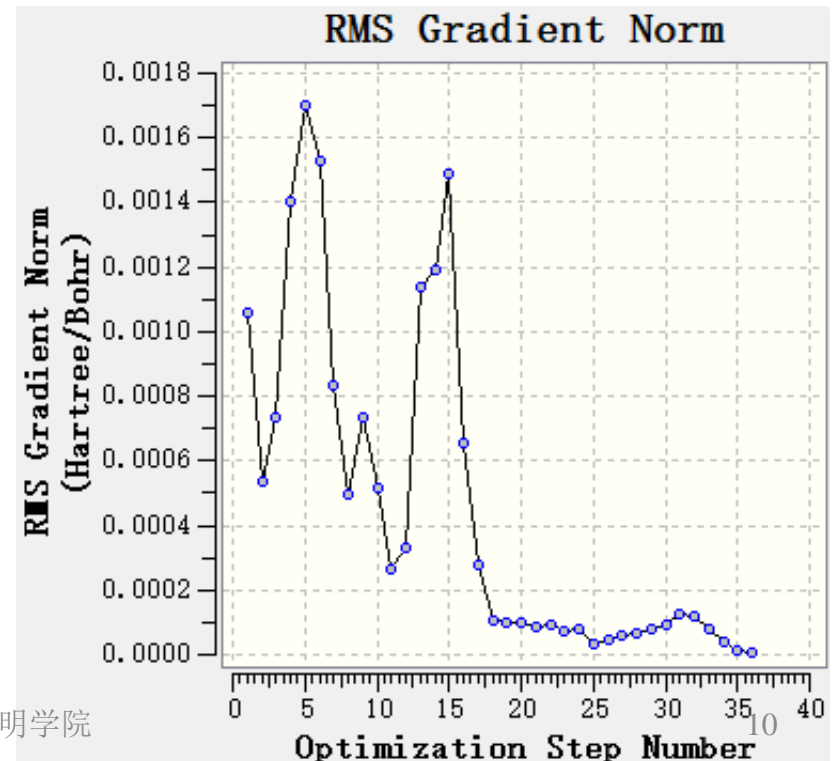
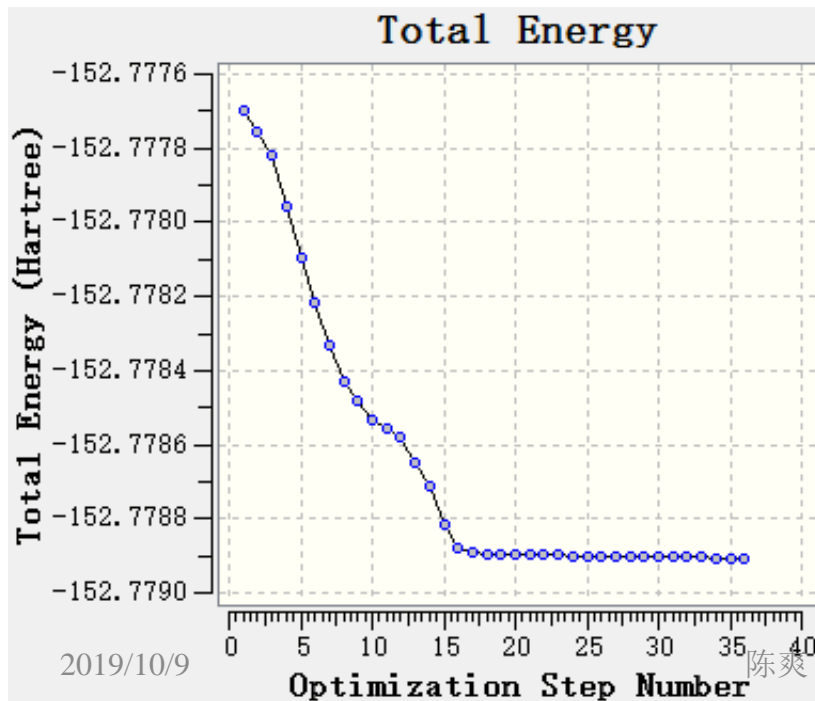
Optimization completed.  
-- Stationary point found.

## 4.3 Geometry Optimization

➤ Keyword: **opt**

✓ Result presentation by using GaussView

- Open “**log**” file
- Mark “**Read Intermediate Geometries**”
- Energy and force changes

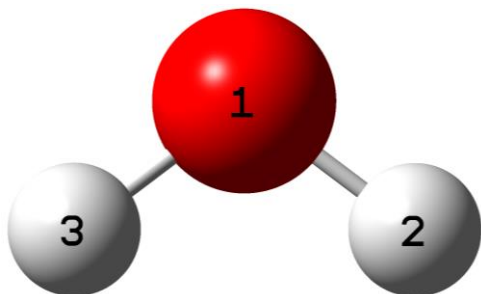


## 4.3 Geometry Optimization

➤ Keyword: **opt**

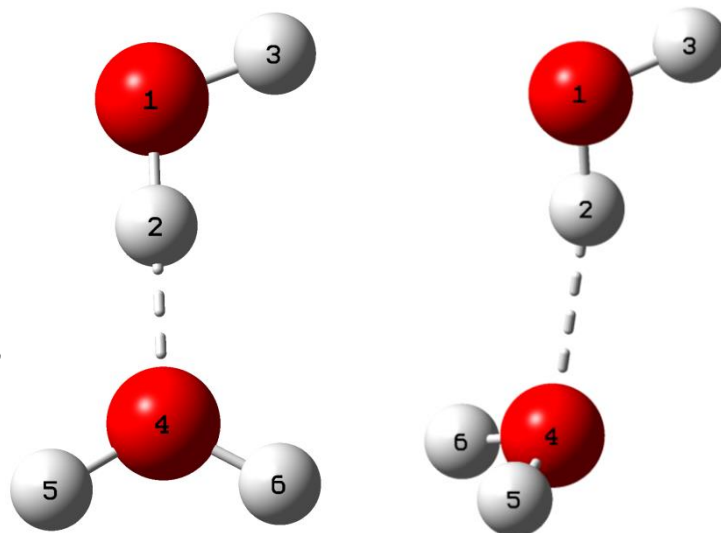
Before

O-H<sub>2</sub> 0.96 Å  
O-H<sub>3</sub> 0.96 Å  
∠H-O-H 109.5°



After

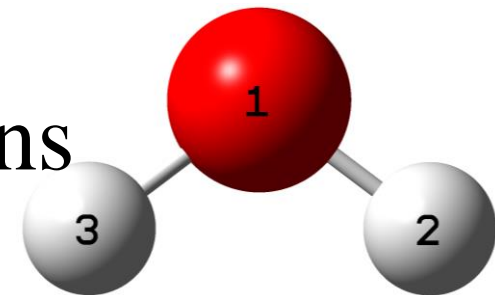
0.963 Å  
0.963 Å  
106.2°



O<sub>1</sub>-H<sub>2</sub> 0.96 Å  
O<sub>4</sub>-H<sub>2</sub> 1.5 Å  
∠O<sub>1</sub>-H<sub>2</sub>-O<sub>4</sub> 180.0°

0.973 Å  
1.896 Å  
168.3°

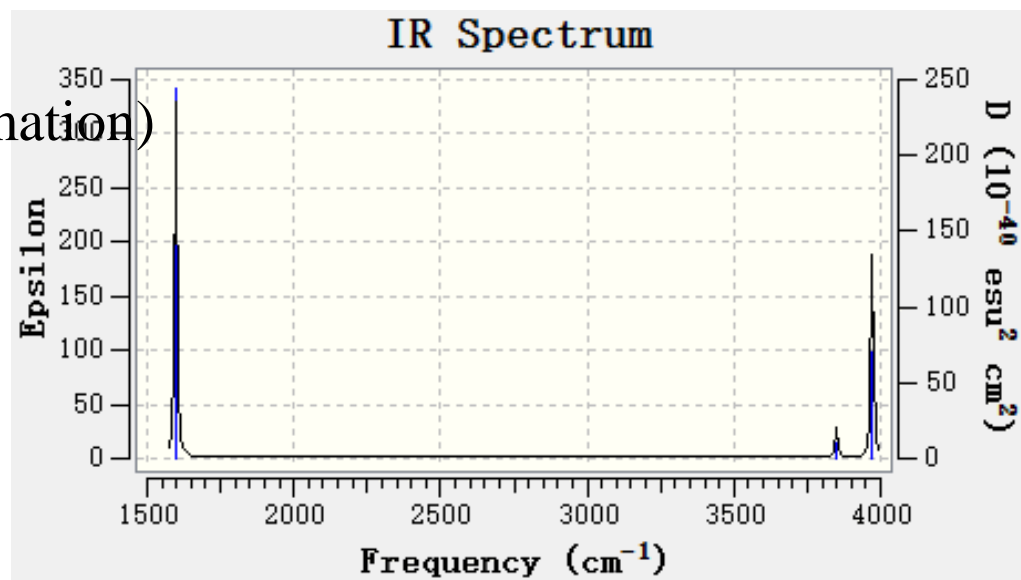
# 4.4 Frequency Calculations



➤ Keyword: **freq**

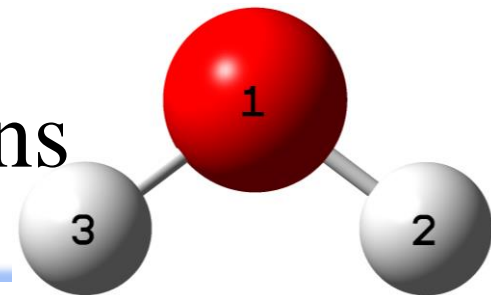
✓ Result presentation by using GaussView

- 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	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.		

**temperature = 350**

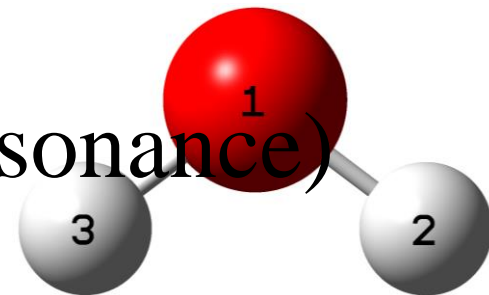
Zero-point correction=	0.021461 (Hartree/Particle)
Thermal correction to Energy=	0.024296
Thermal correction to Enthalpy=	0.025241
Thermal correction to Gibbs Free Energy=	0.003819
Sum of electronic and zero-point Energies=	-76.384257
Sum of electronic and thermal Energies=	-76.381422
Sum of electronic 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

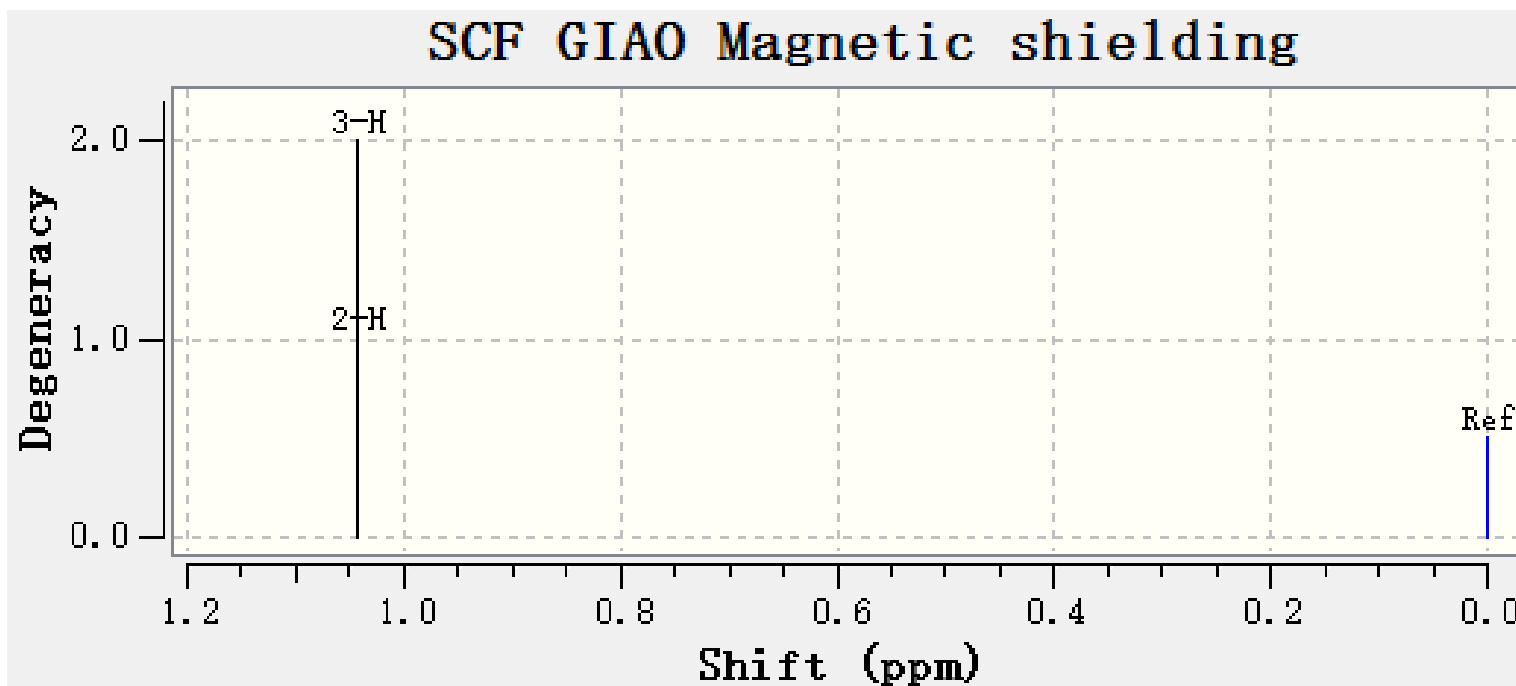
## 4.5 NMR (Nuclear Magnetic Resonance)



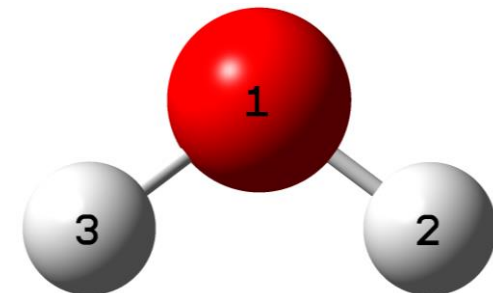
➤ Keyword: **NMR test**

✓ Result presentation by using GaussView

- Open “log” file
- NMR chemical shift



# 4.6 UV-vis Spectrum



➤ Keyword: **TD=(50-50,nstates=50)**

✓ Result presentation by using GaussView

- Open “log” file
- UV-vis spectrum (**GaussSum**)

Excitation energies and oscillator strengths:

Excited State 1: Triplet-B1 7.3059 eV 169.70 nm f=0.0000 <S\*\*2>=2.000  
5 -> 6 0.69899

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -76.1372309888

Copying the excited state density for this state as the 1-particle RhoCI density.

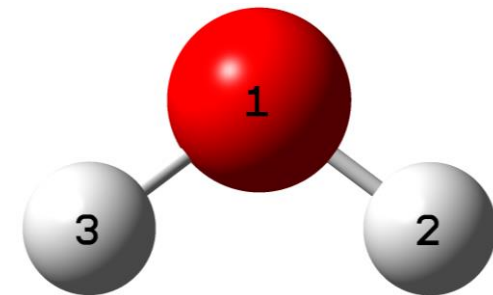
Excited State 2: Singlet-B1 8.0015 eV 154.95 nm f=0.0755 <S\*\*2>=0.000  
5 -> 6 0.70364

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

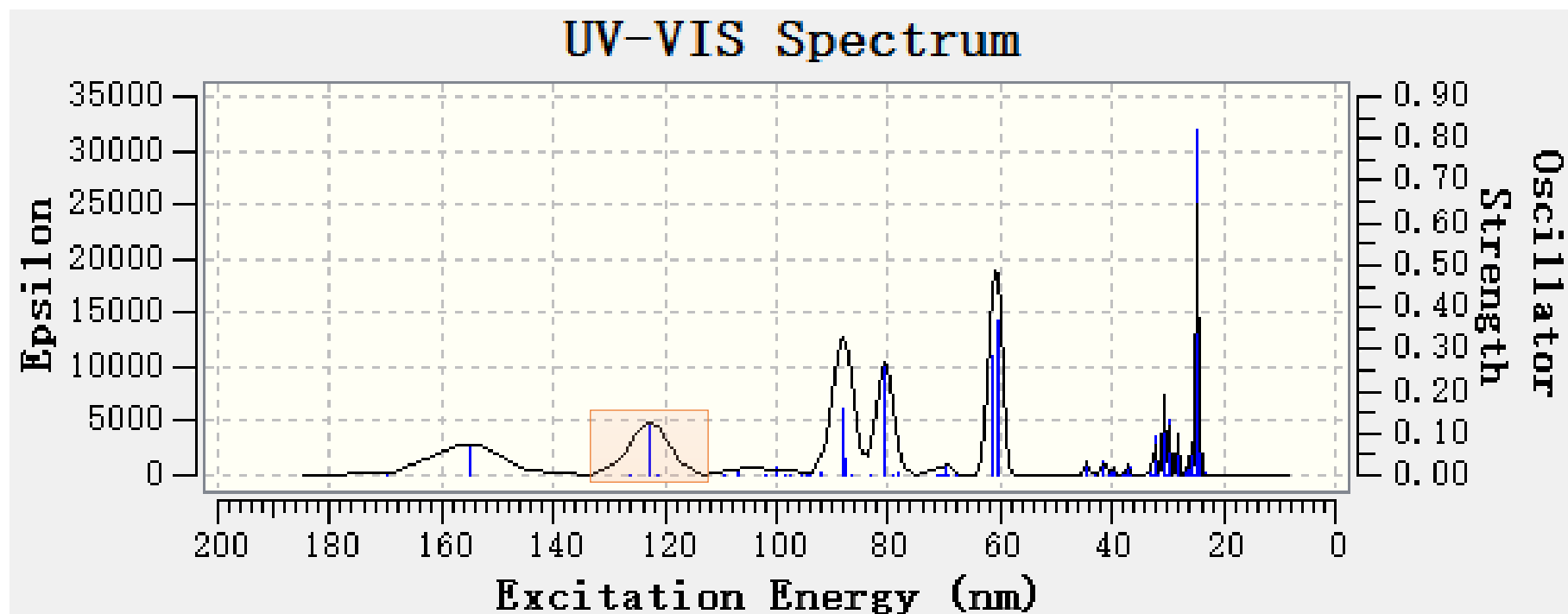
## 4.6 UV-vis Spectrum



➤ Keyword: **TD=(50-50,nstates=50)**

✓ Result presentation by using GaussView

- Open “log” file
- UV-vis spectrum (GaussSum)



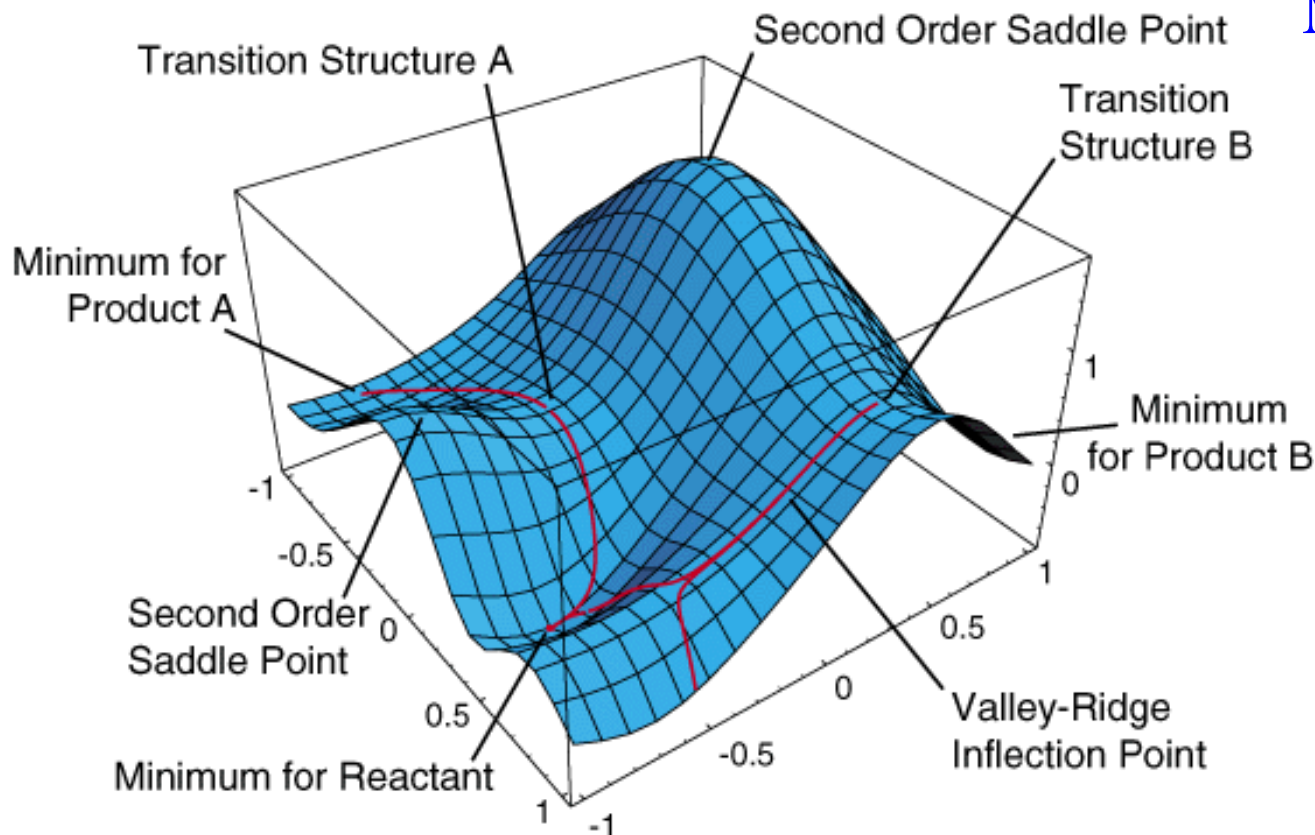


## 4.7 Transition State Search

➤ 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)

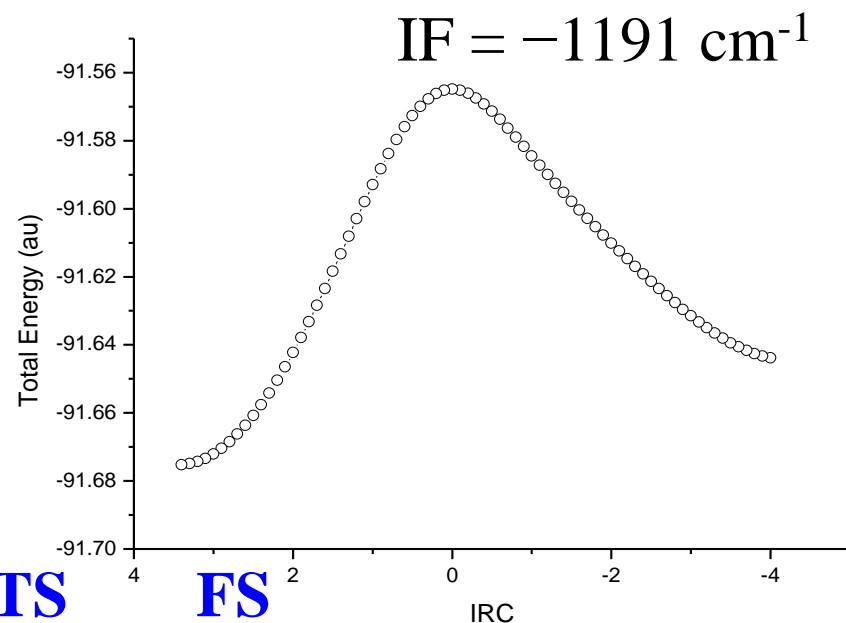
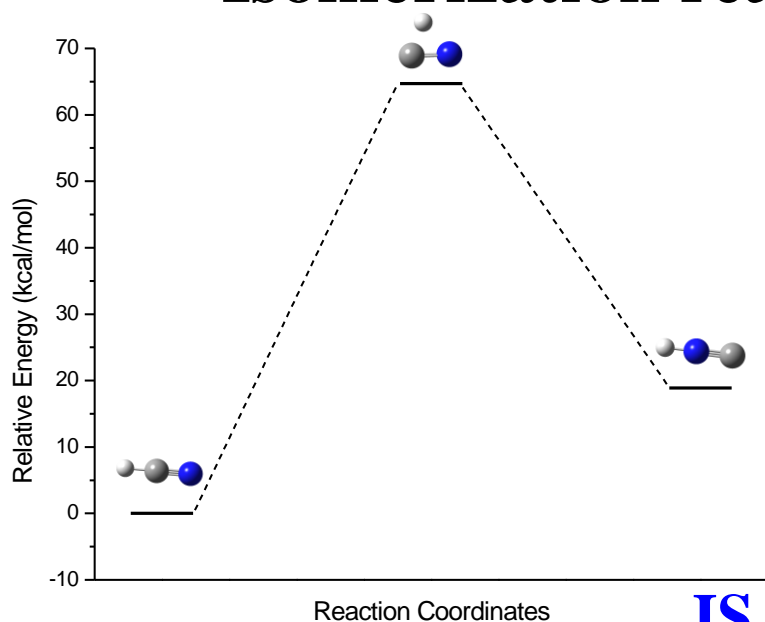
- ✓ a **maximum** with respect to **one coordinate**, and minima with respect to the rest of coordinates.
- ✓ The unique character of a transition state: **an imaginary vibrational mode**.
- ✓ To identify whether a stationary point is a minimum or a transition state, one has to do vibrational frequency 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)**

**Isomerization reaction: HCN  $\leftrightarrow$  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 and A. Frisch, *Exploring Chemistry with Electronic Structure Methods* (3rd Edition), Gaussian Inc., **2015**.
2. [www.gaussian.com](http://www.gaussian.com)

# 10月14日Presentation

1. 极化图像的建立，以 $\text{H}_2\text{O}$ 上电荷分布的变化为例：
  - (1) 周围放置2个真实的 $\text{H}_2\text{O}$ 分子；
  - (2) 周围放置2个 $\text{H}_2\text{O}$ 的背景点电荷；
  - (3) 溶剂化模型cyclohexane中。
2. 噻吩分子第一激发态(singlet)的TDDFT优化。

