


DFT Calculations & Energy/Force Decomposition Analysis

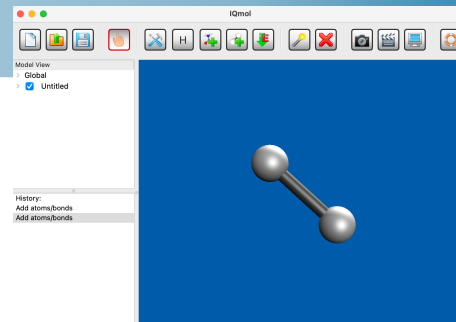
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ISTCP Workshop — October 13, 2024

Goals

- Scientific Concepts:
 - Catalysis modeling
 - What effects does H₂ adsorption have on a copper surface?
 - What forces contribute to this process?
- Learning Objectives:
 - Geometry optimization using DFT
 - Visualize and interpret IR spectra in IQmol
 - Run and interpret force decomposition analysis calculations

Part 1: Frequency of H₂

- Create H₂ molecule in IQmol
 - Use  to minimize energy
- Job 1: Geometry Optimization
 - Calculate: Geometry
 - Manually enter method/basis:
 - Method: wB97M-V
 - Basis: def2-svpd
 - Charge = 0, Mult = 1
- Job 2: Frequency
 - Click green “+” button
 - Calculate: Frequency



Setup **Advanced**

Job Section: Job 2 Edit + -

Calculate: Forces + Charge: 0

Method: HF + Multiplicity: 1

Basis: 6-31G + ECP: None

Exchange: HF + Correlation: None +

SCF Control

Algorithm: DIIS + Convergence: 8

Guess: SAD + Max Cycles: 50

Second Basis: None + Guess Mix: 0%

☐ Unrestricted ☐ Dual Basis Energy

Wavefunction Analysis

Generated Input File:

```

H      -1.1272335    0.9125223    0.0000000
Send

$rem
BASIS = def2-svpd
GUI = 2
JOB_TYPE = Optimization
METHOD = Omega-B97M-V
SCF_CONVERGENCE = 8
Send

###
$molecule
read
Send

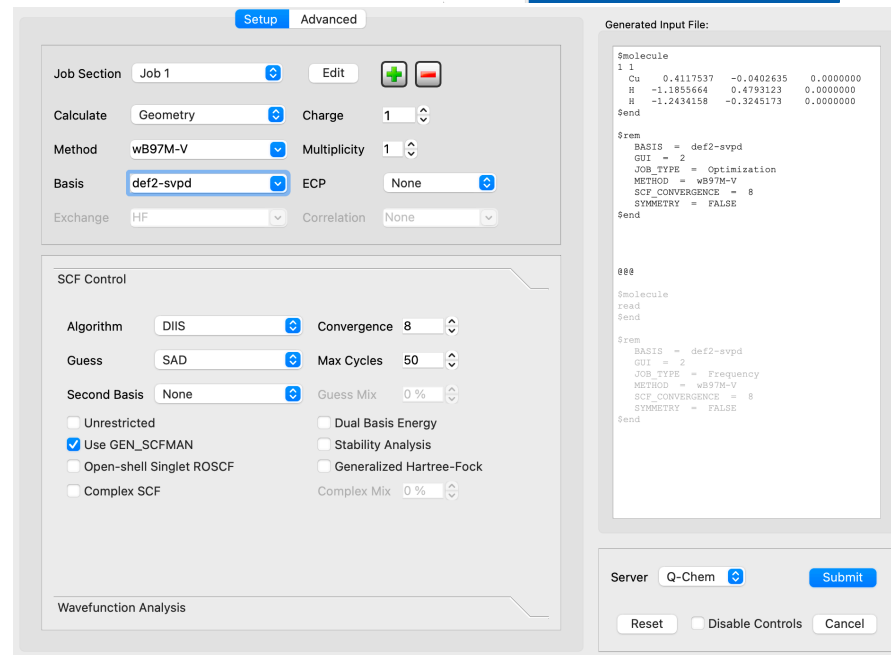
$rem
BASIS = def2-svpd
GUI = 2
JOB_TYPE = Force
METHOD = Omega-B97M-V
SCF_CONVERGENCE = 8
Send
    
```

Server: Q-Chem Submit

Reset ☐ Disable Controls Cancel

Part 2: Frequency of H₂ Bound to Cu⁺

- Create H₂...Cu⁺ in IQmol
 - H-H bond: 0.8Å
 - Cu-H-H angle: 76°
 - Create Cu fragment:
Opt (⌘) in Mac, Alt in Linux/Windows
- Job 1: Geometry Optimization
 - Calculate: Geometry
 - Manually enter method/basis:
 - Method: wB97M-V
 - Basis: def2-svpd
 - Charge = +1, Mult = 1
- Job 2: Frequency
 - Click green “+” button
 - Calculate: Frequency



Generated Input File:

```

$molecule
1 1
Cu 0.4117537 -0.0402635 0.0000000
H -1.1855664 0.4793123 0.0000000
H -1.2436158 -0.3245173 0.0000000
$end

$rem
BASIS = def2-svpd
GUI = 2
JOB_TYPE = Optimization
METHOD = wB97M-V
SCF_CONVERGENCE = 8
SYMMETRY = FALSE
$end

====

$molecule
read
$end

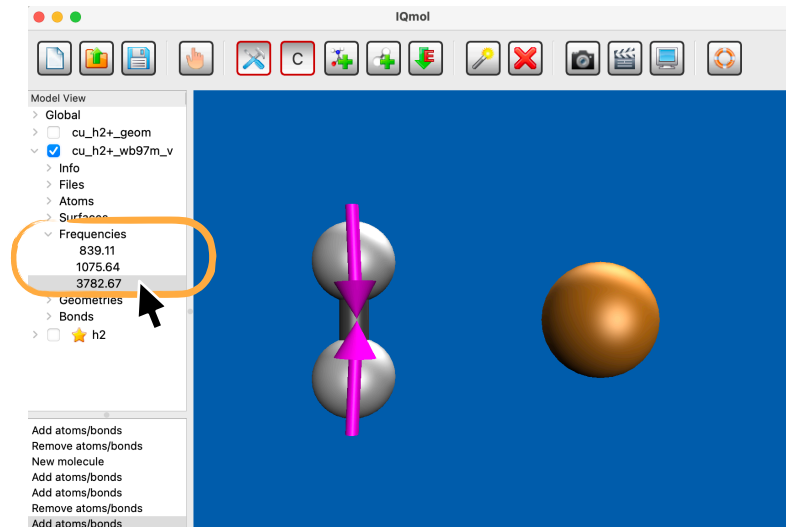
$rem
BASIS = def2-svpd
GUI = 2
JOB_TYPE = Frequency
METHOD = wB97M-V
SCF_CONVERGENCE = 8
SYMMETRY = FALSE
$end
  
```

Server: Q-Chem Submit

Reset Disable Controls Cancel

Frequency Shift Results

- Which mode corresponds to the H-H stretch?
 - Select modes under “Frequencies”
 - Can view coordinates in output file
- Compare to H-H stretch in H₂ alone
 - What does the **difference in frequency** imply about the effect of the Cu⁺ ion (“adsorption”) on the H₂ bond strength?
 - Compare the H-H bond lengths** using the magic wand tool. Does this agree with the results from Q1?
- Bonus:** Compare to B3LYP/6-31G. Which shift prediction is closest to experiment?



Frequencies:

Free: 3783 cm⁻¹

Adsorbed: 4384 cm⁻¹

Bond Lengths:

Free: 0.76 cm⁻¹

Adsorbed: 0.80 cm⁻¹

Part 3: Energy Decomposition Analysis

- Use optimized geometry from Part 1
- Setup
 - Calculate: Energy Decompose
 - Manually enter method/basis:
 - Method: wB97M-V
 - Basis: def2-svpd
 - Charge = +1, Mult = 1
 - Manual Modifications:
 - “EDA2 = 2”
 - “EDA_VCT_A = TRUE”
 - Separate fragments with “--”
 - Set charge/multiplicity for fragments
- Calculate again with a distant Cu⁺ ion (~4Å)

Setup Advanced

Job Section Job 1 Edit

Calculate Energy Decompose Charge 1

Method wB97M-V Multiplicity 1

Basis def2-svpd ECP None

Exchange HF Correlation None

SCF Control

Algorithm DIIS Convergence 8

Guess SAD Max Cycles 50

Second Basis None Guess Mix 0 %

☐ Unrestricted ☐ Dual Basis Energy

☒ Use GEN_SCFMAN ☐ Stability Analysis

☐ Open-shell Singlet ROSCF ☐ Generalized Hartree-Fock

☐ Complex SCF ☐ Complex Mix 0 %

Wavefunction Analysis

Generated Input File:

```

Molecule
1 1
--
1 1
Cu 0.4117537 -0.0402635 0.0000000
0 1
H -1.1855664 0.4793123 0.0000000
H -1.2434158 -0.3245173 0.0000000
$end

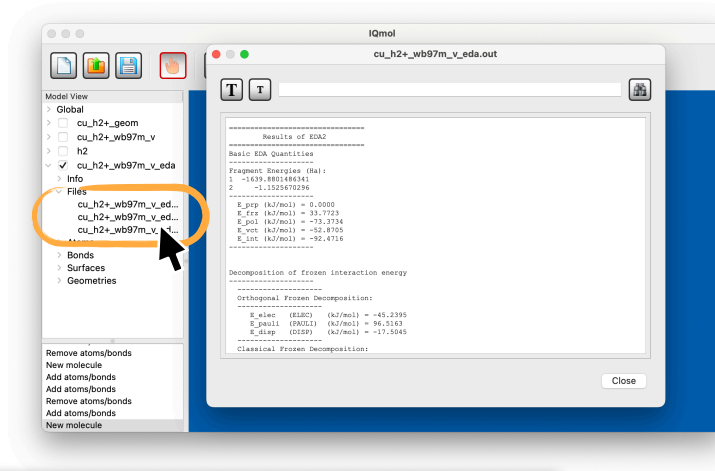
$rem
BASIS = def2-svpd
GUI = 2
JOB_TYPE = EDA
METHOD = wB97M-V
SCF_CONVERGENCE = 8
EDA2 = 2
EDA_VCT_A = TRUE
$end
  
```

Server Q-Chem Submit

Reset Disable Controls Cancel

Energy Decomposition Analysis

- Open text-based output file
- Scroll to “Results of EDA2”
- Compare EDA for the “adsorbed” H₂...Cu⁺ complex to the “freed” one
 - Do the differences you observe make sense?
 - What are the largest contributors?



“Adsorbed” EDA Output

Simplified EDA Summary (kJ/mol)

```
-----
PREPARATION      0.0000
FROZEN           33.7723 (ELEC + PAULI + DISP)
[ELEC + PAULI = 51.2768, DISP = -17.5045]
POLARIZATION     -73.3734
CHARGE TRANSFER -52.8705
TOTAL            -92.4716      (PRP + FRZ + POL + CT)
-----
```

“Free” EDA Output

Simplified EDA Summary (kJ/mol)

```
-----
PREPARATION      -0.0000
FROZEN          -3.6415 (ELEC + PAULI + DISP)
[ELEC + PAULI = -3.5183, DISP = -0.1233]
POLARIZATION     -1.5317
CHARGE TRANSFER -1.3020
TOTAL            -6.4752      (PRP + FRZ + POL + CT)
-----
```

Part 4: Force Decomposition Analysis

- Use optimized geometry from Part 1
- Reorder atoms (H=1, H=2, Cu=3) using Edit > Reindex Atoms
- Setup
 - Calculate: Forces
 - Manually enter method/basis:
 - Method: wB97M-V
 - Basis: def2-svpd
 - Charge = +1, Mult = 1
 - Manual Modifications:
 - “FDA = 1”
 - Separate fragments with “--”
 - Set charge/multiplicity for fragments

Setup Advanced

Job Section: Job 1 Edit

Calculate: Forces Charge: 0

Method: HF Multiplicity: 2

Basis: 6-31G ECP: None

Exchange: HF Correlation: None

SCF Control

Algorithm: DIIS Convergence: 8

Guess: SAD Max Cycles: 50

Second Basis: None Guess Mix: 0%

☐ Unrestricted ☐ Dual Basis Energy

Wavefunction Analysis

Generated Input File:

```

$molecule
1 1
--
0 1
H -1.1855664 0.4793123 0.0000000
H -1.2434158 -0.3245173 0.0000000
-1
1 1
Cu 0.4117537 -0.0402635 0.0000000
Send

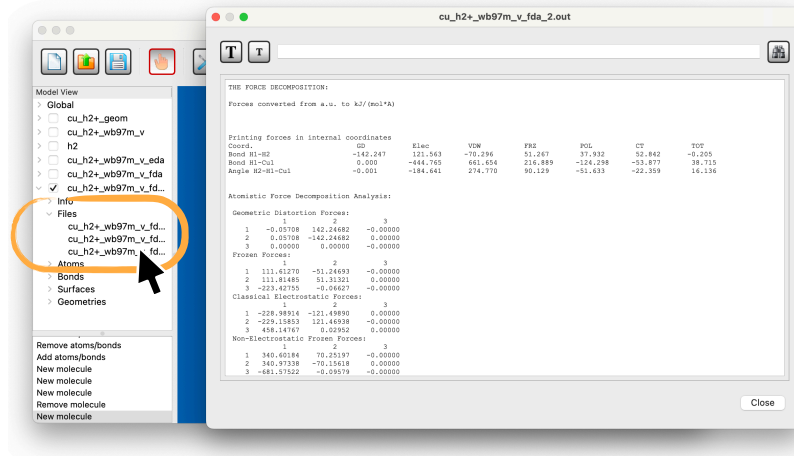
$rem
BASIS = def2-svpd
FDA = TRUE
GUI = 2
JOB_TYPE = Force
METHOD = wB97M-V
SCF_CONVERGENCE = 8
Send
  
```

Server: Q-Chem Submit

Reset Disable Controls Cancel

Force Decomposition Analysis

- Which forces contribute?
 - Open text-based output file
 - Find FDA output section
- Which forces contribute to lengthening the H-H bond? Which contribute to shortening it?



Printing forces in internal coordinates

Coord.	GD	Elec	VDW	FRZ	POL	CT	TOT
Bond H1-H2	-142.247	121.563	-70.296	51.267	37.932	52.842	-0.205
Bond H1-Cu1	0.000	-444.765	661.654	216.889	-124.298	-53.877	38.715
Angle H2-H1-Cu1	-0.001	-184.641	274.770	90.129	-51.633	-22.359	16.136