DFT Calculations & Energy/Force Decomposition Analysis

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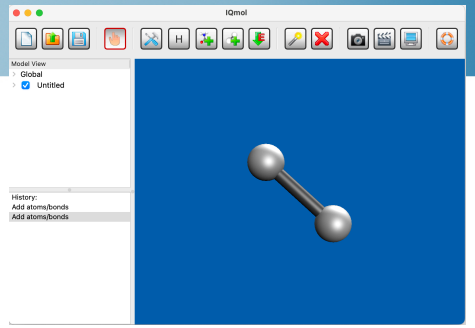
ISTCP Workshop — October 13, 2024

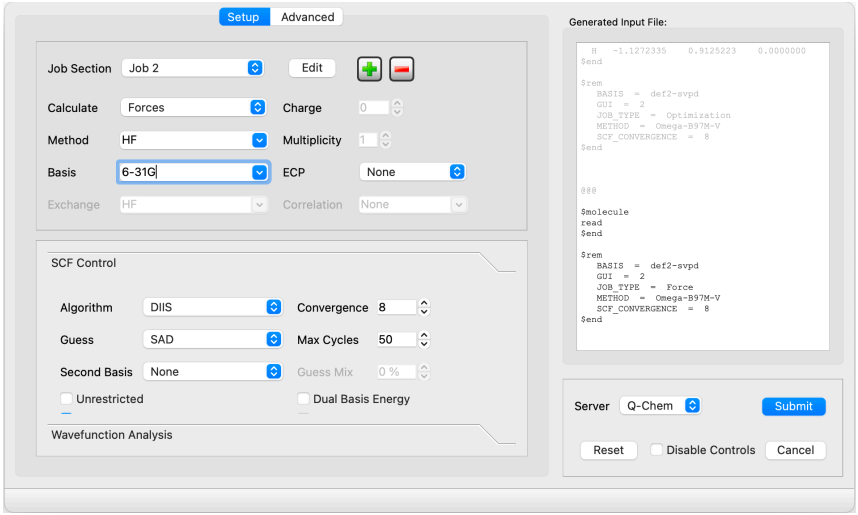
Goals

- Scientific Concepts:
  - Catalysis modeling
  - What effects does H_2 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

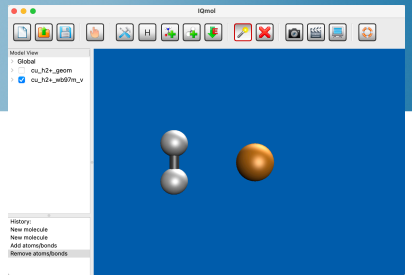
Part 1: Frequency of H_2

- Create H_2 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



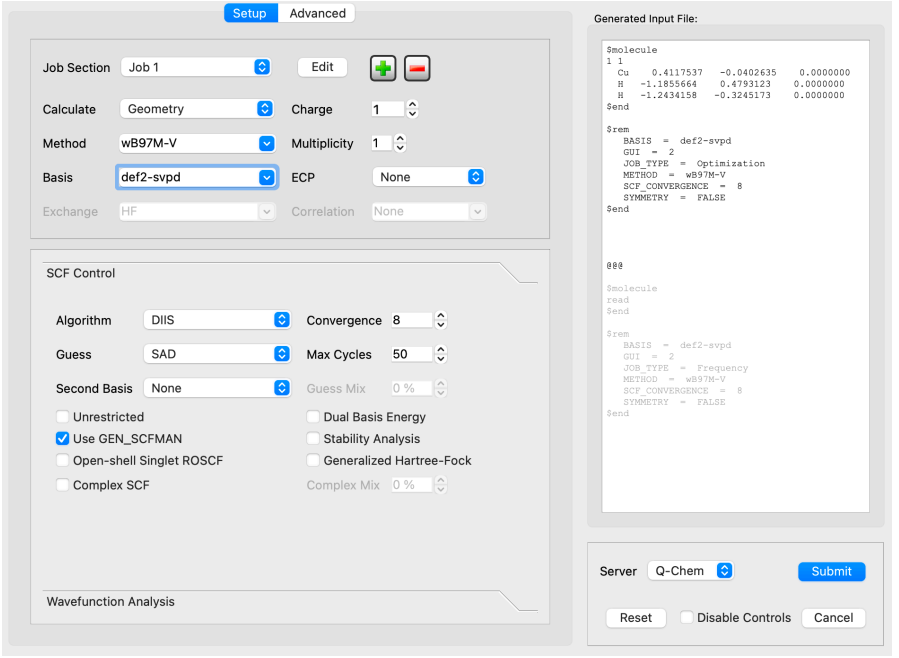


Part 2: Frequency of H_2 Bound to Cu^+



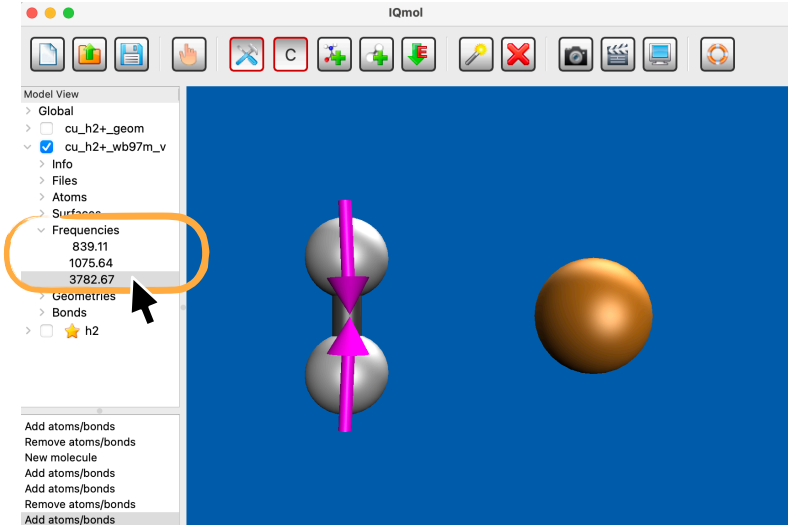
- Create H_2…Cu^+ in IQmol
  - H-H bond: 0.8Å
  - Cu-H-H angle: 76°
  - Create Cu fragment:

    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



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 H_2 alone
  1. What does the **difference in frequency** imply about the effect of the Cu^+ ion (“adsorption”) on the H_2 bond strength?
  2. **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?

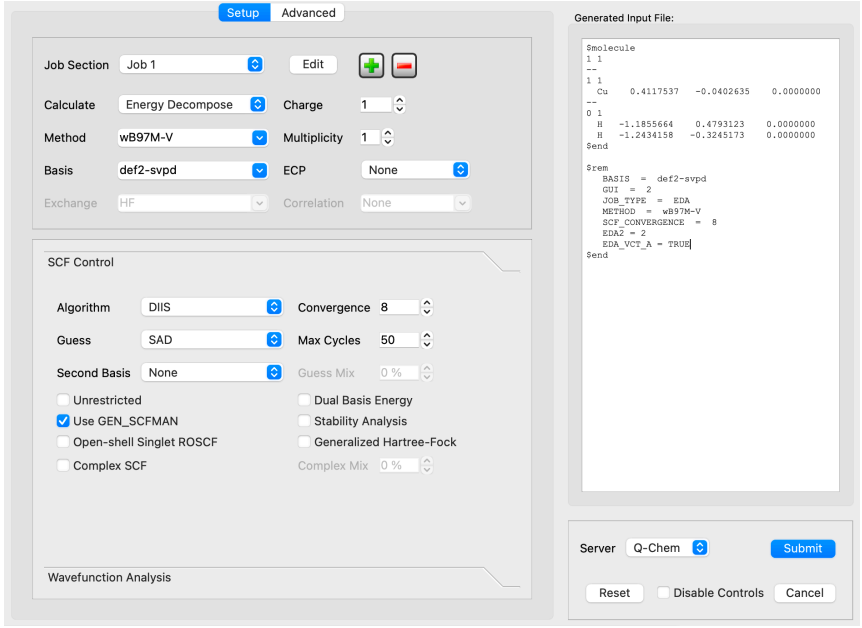


Frequencies:
Free: 3783 cm^{-1}
Adsorbed: 4384 cm^{-1}

Bond Lengths:
Free: 0.76 cm^{-1}
Adsorbed: 0.80 cm^{-1}

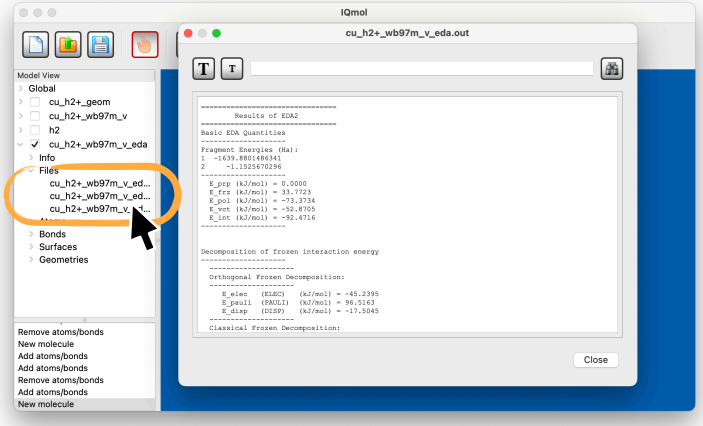
Part 3: Energy Decomposition Analysis

- 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)



Energy Decomposition Analysis

- Open text-based output file
- Scroll to “Results of EDA2”
- Compare EDA for the “adsorbed” H_2…Cu^+ complex to the “freed” one
  - Do the differences you observe make sense?
  - What are the largest contributors?



“Adsorbed” EDA Output

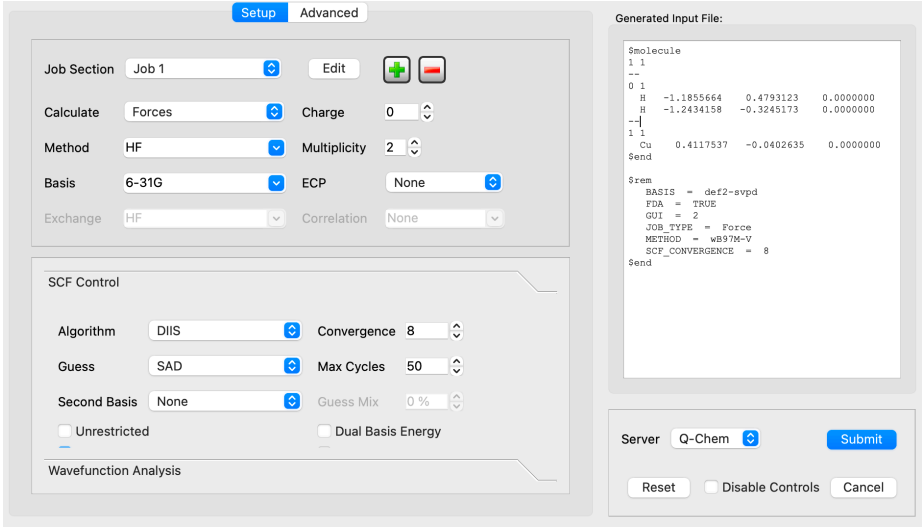
```
Simplified EDA Summary (kJ/mol)
--------------------
 PREPARATION       0.0000
 FROZEN            33.7723 (ELEC + PAULI + DISP)
[ELEC + PAULI = 51.2768, DISP = -17.5045]
 POLARIZATION     -73.3734
 CHARGE TRANSFER -52.8705
 TOTAL            -92.4716      (PRP + FRZ + POL + CT)
--------------------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

“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)
--------------------
```

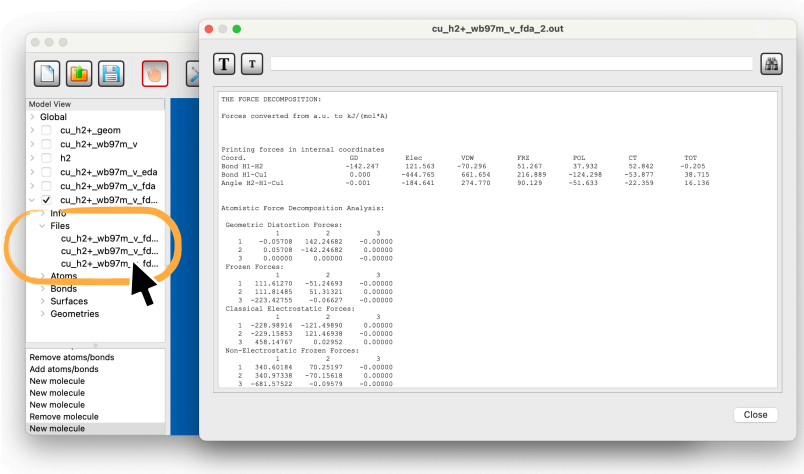
Part 4: Force Decomposition Analysis

- 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



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
```