# DFT Calculations & Energy/Force Decomposition Analysis

Martin Head-Gordon ISTCP Workshop — October 13, 2024



#### Goals

- Scientific Concepts:
  - Catalysis modeling
  - What effects does H<sub>2</sub> 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<sub>2</sub>

- Create H<sub>2</sub> molecule in IQmol
  - Use 運 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

			IQmol			nol			
			Model View	<b>I</b>	) H 🍒 🧃		0 🖺 📃		
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						Reset	Disable Contro	ls Cancel	



# Part 2: Frequency of H<sub>2</sub> Bound to Cu<sup>+</sup>

- Create H<sub>2</sub>...Cu<sup>+</sup> 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

	Setup	Advanced	Generated Input File:			
lob Section	Job 1 📀	Edit 📑 드	Smolecule 1 1 Cu 0.4117537 -0.0402635 0.0000000 H -1.1855664 0.4793123 0.0000000			
Calculate	Geometry 📀	Charge 1	H -1.2434158 -0.3245173 0.0000000 \$end			
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SCF Control			888			
SCF COntrol			Smolecule read			
Algorithm	DIIS	Convergence 8	Şend Srem			
Guess	SAD	Max Cycles 50 🗘	BASIS = def2-svpd GUI = 2 JOB TYPE = Frequency			
Second Basi	s None	Guess Mix 0 %	METHOD = wB97M-V SCF_CONVERGENCE = 8 SYMMETRY = FALSE			
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...

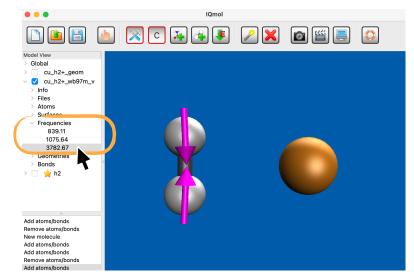
Model View > Global > \_\_\_\_\_ou\_h2+\_geom > \_\_\_\_\_ou\_h2+\_wb97m\_v

History: New molecule New molecule Add atoms/bonds Remove atoms/bo 🔀 H 🗛 承 🖡 🦻 🗙 🙆 🞬



## **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<sub>2</sub> alone
  - 1. What does the **difference in frequency** imply about the effect of the Cu<sup>+</sup> ion ("adsorption") on the H<sub>2</sub> 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?

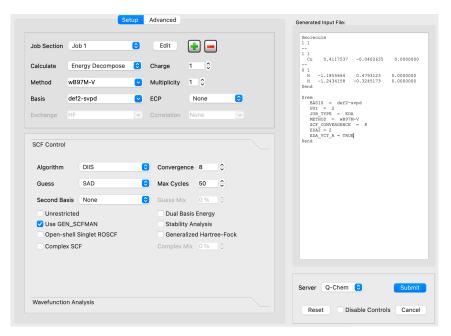


Frequencies: Free: 3783 cm<sup>-1</sup> Adsorbed: 4384 cm<sup>-1</sup> Bond Lengths: Free: 0.76 cm<sup>-1</sup> Adsorbed: 0.80 cm<sup>-1</sup>



### Part 3: Energy Decomposition Analysis

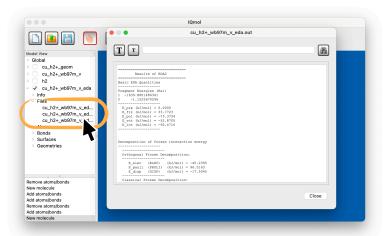
- Use optimized geometry from Part 1
- Setup
  - Calculate: Energy Decompose
  - Manually enter method/basis:
    - Method: wB97M-V
    - Basis: def2-svpd
  - Charge = +1, Mult = 1
  - Manual Modifications:
    - "EDA2 = 2"
    - "EDA\_VCT\_A = TRUE"
    - Separate fragments with "--"
    - Set charge/multiplicity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





## Energy Decomposition Analysis

- Open text-based output file
- Scroll to "Results of EDA2"
- Compare EDA for the "adsorbed" H<sub>2</sub>...Cu<sup>+</sup> 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	Generated Input File:
Job Section	Job 1	📀 Edit 📑 💻	Smolecule 1 1  0 1
Calculate	Forces	🗘 Charge 0 🗘	H -1.1855664 0.4793123 0.000000 H -1.2434158 -0.3245173 0.000000 
Method	HF	Multiplicity 2 🗘	1 1 Cu 0.4117537 -0.0402635 0.000000 Send
Basis	6-31G	ECP None	Srem BASIS - def2-svpd FDA = TRUE
Exchange	HF	Correlation None	GUI = 2 JOB_TYPE = Force METHOD = wB97M-V SCF_CONVERGENCE = 8
SCF Control			\$end
Algorithm	DIIS	Convergence 8	
	SAD	ᅌ Max Cycles 50 🗘	
Guess	SAD		
Guess Second Ba		Imax by side         Imax by side           Imax by side         Imax by side	
	sis None		Server Q-Chem 😒 Subm



#### **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?

			cu_	_h2+_wb97m	_v_fda_2.o	ut			
	The FORCE DECONDUCTION:           THE FORCE DECONDUCTION:           Parses convertiend from 4.x.           Printing forces in intermal decision           Printing forces in intermal decision           Data of the force and the force           Data of the force           Data	Coordinates CO 142,247 0.000 -0.001 on Analysis: a: 3 22 -0.0000 00 -0.0000 23 -0.0000 27 -0.0000 27 -0.0000 27 -0.0000 28 -0.0000 28 -0.0000 28 -0.0000 29 -0.0000 29 -0.0000 20 -0.0000 20 -0.0000 21 -0.0000 22 -0.0000 23 -0.0000 24 -0.0000 25 -0.0000 26 -0.0000 27 -0.0000 28 -	E1ec 132.543 -444.765 -184.641	709 -70.286 661.654 274.770	FRG 51.247 216.889 90.129	908. 377.992 -224.298 -51.633	07 53,842 -33,877 -22,359	T09 -0.3253 34:135 16:136	æ
lew molecule iemove molecule iew molecule									Close

Printing forces in in	cernar coordinat	.es					
Coord.	GD	Elec	VDW	FRZ	POL	СТ	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