

Nano 266
Quantum Mechanical Modeling of Materials
Lab 1

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1 Question 1

Geometry optimization and energy of H_2

1.1 Geometry

H_2 **Bond Length** From the geometry data, the x, y coordinates of both hydrogen atoms are zero, the Z coordinates are -0.3707 and 0.3707 . Scaling the coordinates by 1.889725 to convert to a.u., the final bond length of H_2 is 0.7414 \AA .

1.2 Energy

H_2 **DFT Energy** The total DFT energy of H_2 is -1.176631 Ha , -32.01778 eV .

2 Question 2

Geometry optimization and energy of N_2

2.1 Geometry

H_2 **Bond Length** From the geometry data, the x, y coordinates of both hydrogen atoms are zero, the Z coordinates are -0.55 and 0.55 . Scaling the coordinates by 1.889725 to convert to a.u., the final bond length of H_2 is 1.1 \AA .

2.2 Energy

N_2 **DFT Energy** The total DFT energy of N_2 is -109.502491 Ha , -2979.71597 eV .

3 Question 3

Geometry optimization and energy of NH_3

3.1 Non Polarized

NH_3 Bond Length and Bond Angle From the geometry data, the x, y, z coordinates of both hydrogen atoms and N atoms, the bond length between N and H is 1.005 91. Scaling the coordinates by 1.889 725 to convert to a.u., the final N-H bond length of is 1.9009 Å. The bond angle is 116.18°.

NH_3 Total DFT Energy Total DFT energy of NH_3 is -56.551 68 Ha, -1538.850 329 eV.

3.2 Polarized

NH_3 Bond Length and Bond Angle From the geometry data, the x, y, z coordinates of both hydrogen atoms and N atoms, the bond length between N and H is 1.018 01. Scaling the coordinates by 1.889 725 to convert to a.u., the final N-H bond length of is 1.018 Å. The bond angle is 107.68°.

NH_3 Total DFT Energy Total DFT energy of NH_3 is -56.551 68 Ha, -1538.850 329 eV.

4 Formation enthalpy of NH_3

To get the right formation enthalpy of NH_3 , we first reset the basis set of H_2 and N_2 in Q1 and Q2 with polarization functions. After rerun H_2 and N_2 calculations, we get the thermal correction and DFT energy of each parts as table show below.

Compound	Energy (Ha)	Correction (kcal/mol)	Enthalpy H (kcal/mol)
H_2	-1.176 63	8.436	-729.903782
N_2	-109.560 56	5.580	-68744.00271
NH_3	-56.573 63	24.042	-35476.07972

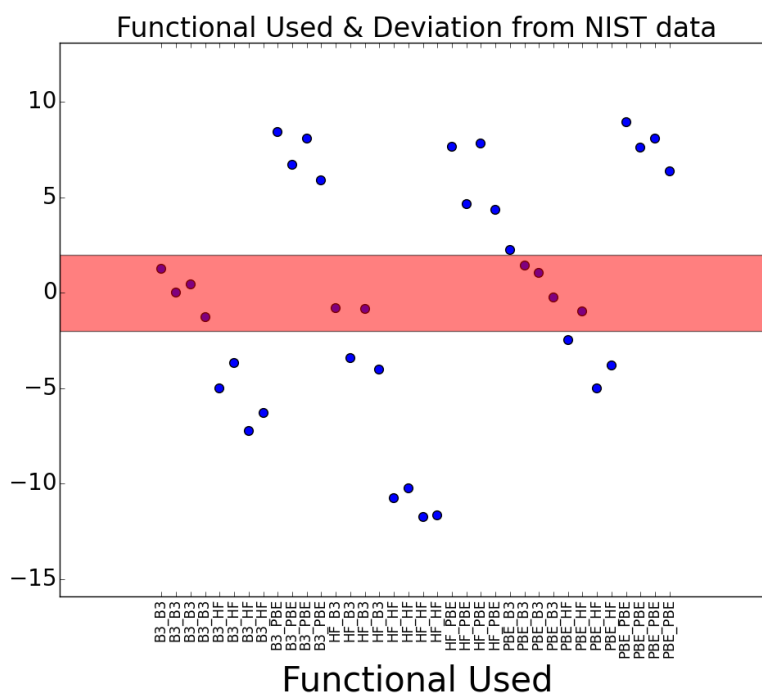
Given by the formula: $0.5N_2 + 1.5H_2 > NH_3$, the calculated formation enthalpy is -38.59 kJ/mol. NIST (2015), which is not far from the experimental data of NIST source: <http://cccbdb.nist.gov/>, -38.95 kJ/mol.

5 Effect of Functional Choice and Basis Set

In this section, we enumerated all 36 different conditions with different functional choice and basis set. Only basis set with polarization function are used. We use HF, PBE and B3LYP(B3) functionals with 6-31G* and 6-311G* basis set, for each compound calculation, there are two stages, i.e. Geometry optimization stage and DFT energy stage. The experimental formation enthalpy for NH_3 is $-45.95 \pm 0.35 \text{ kJ/mol}$ from NIST website. NIST (2015). The bond length of N-H is 1.017 Å based on Wiki (2015) data. The bond angle is 107.8° based on wiki Wiki (2015) data also.

5.1 Overview

From the Figure 1, we could find that with difference functional set, the deviation of formation enthalpy various a lot. But the combination of different functional set provides us with enough data point that fall in the accepted deviation band, the band width is $\pm 2.5 kJ/mol$. The best functional set combination is using B3LYP function for both stages calculation, using 6-311+G* as basis set for geometry stage optimization and using 6-31+G* for DFT energy calculation with formation energy -39.04 kJ/mol.



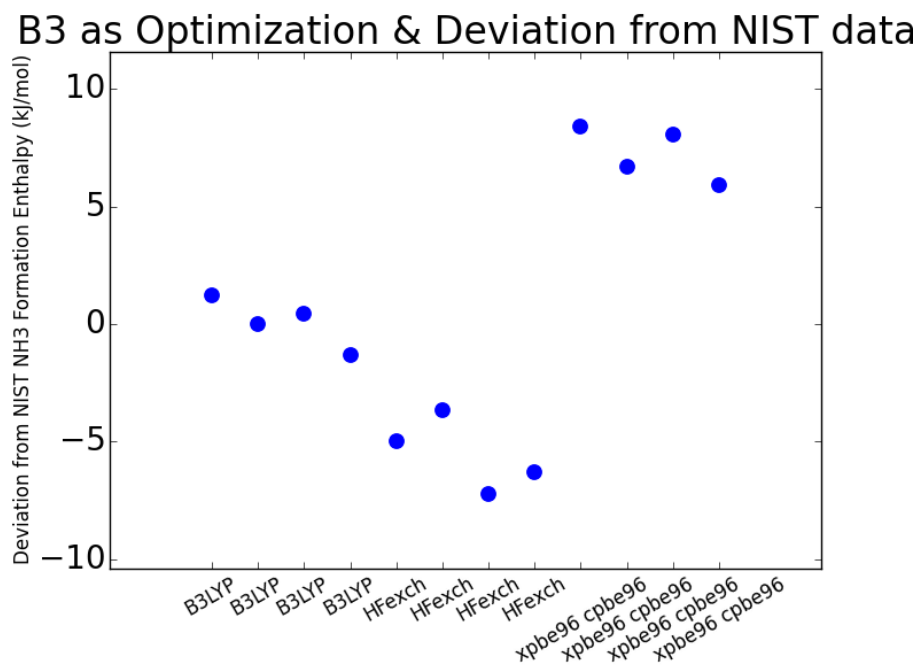


Figure 2: B3 as geometry optimization stage functional

tion Figure 3.

5.4 PBE Function and Effect

If we use PBE functional as first stage function, to minimize the deviation from experimental data, B3LYP should still be considered as second stage function Figure 4.

5.5 Function and Geometry Angle Prediction

Using different functional, the N-H bond predicted are not much different and all pretty close to the data we found from online source wiki Wiki (2015), as show in Figure 5. The blue horizontal line is the experimental angle data we found from wiki.

5.6 Function and Bond Length Prediction

Using different functional, the N-H bond length predicted are not much different and all pretty close to the data we found from online source wiki Wiki (2015), as show in Figure 6. The blue horizontal line is the experimental angle data we found from wiki.

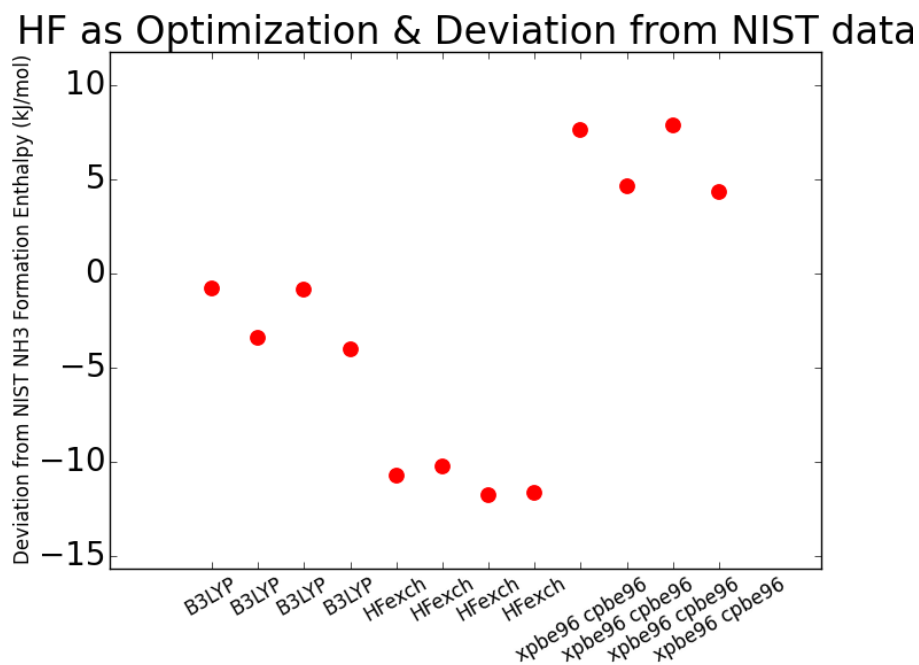


Figure 3: HF as geometry optimization stage functional

5.7 CPU wall time and effectiveness

If we could accept $\pm 2.5 \text{ kJ/mol}$ as deviation, from Figure 7, using HF functional for geometry optimization and B3LYP for DFT energy calculation might be the most efficient calculation strategy with relatively good accuracy.

5.8 Basis set effect

In this section, we will investigate the effect of 6-31+G* and 6-311+G* basis set in second stage (DFT energy calculation) calculation, from the below bar chart 8, using 6-311+G* as second stage function, the predicted formation energy is more close to experimental value with decreased standard deviation also.

Row content	Formation Enthalpy(kJ/mol)
6-31+G* mean value	-39.640336
6-31+G* standard deviation	6.651545
6-311+G* mean value	-38.815557
6-311+G* standard deviation	5.669244

PBE as Optimization & Deviation from NIST data

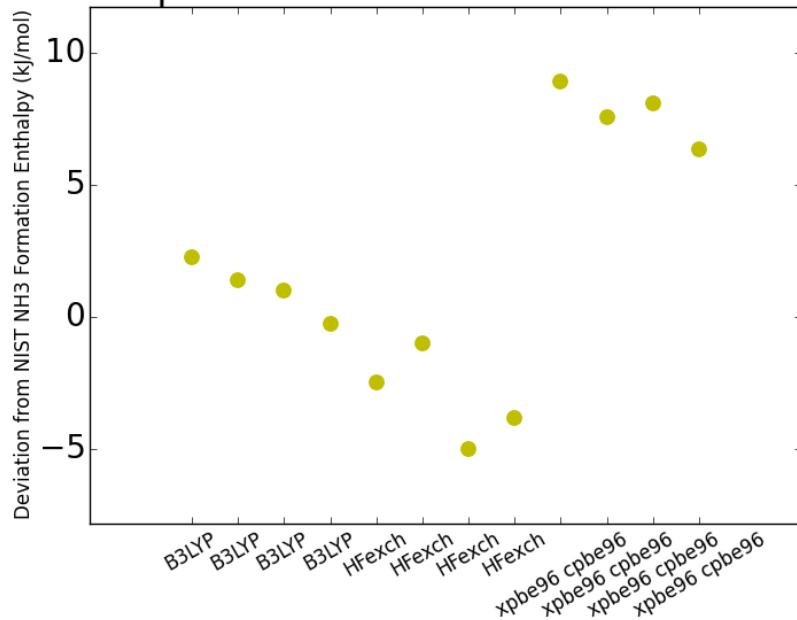


Figure 4: PBE as geometry optimization stage functional

Row content	Wall Time (s)	N-H Angle	N-H Length
6-31+G* mean value	26.588889	107.623333	1.015263
6-31+G* standard deviation	13.591214	0.456645	0.010470
6-311+G* mean value	26.588889	107.623333	1.015263
6-311+G* standard deviation	13.282392	0.456645	0.010470

6 Question 6

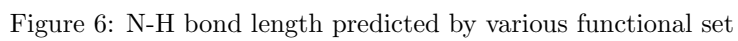
For the reaction to happen, we need to break $N - N$ triple bond, the atomic energy of each N is -54.6 Ha. Compared with energy of N_2 , -109.53 Ha, the dissociation energy of N_2 is 0.33 Ha = 8.98 ev, 207.08 kcal/mol. This is also the reaction barrier of reaction.

References

NIST (2015). Ammonia thermochemistry data.

Wiki (2015). Wiki ammonia thermochemistry data.





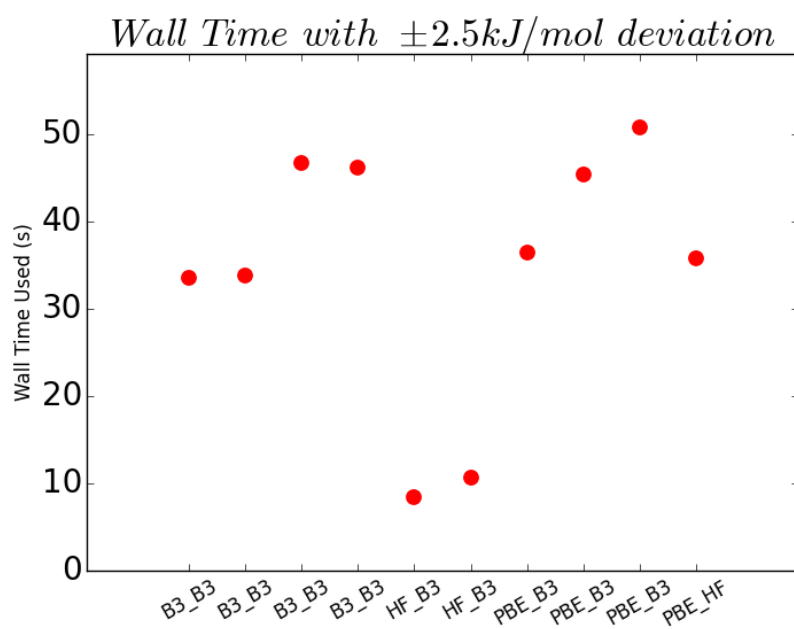


Figure 7: CPU walltime summary within acceptable deviation

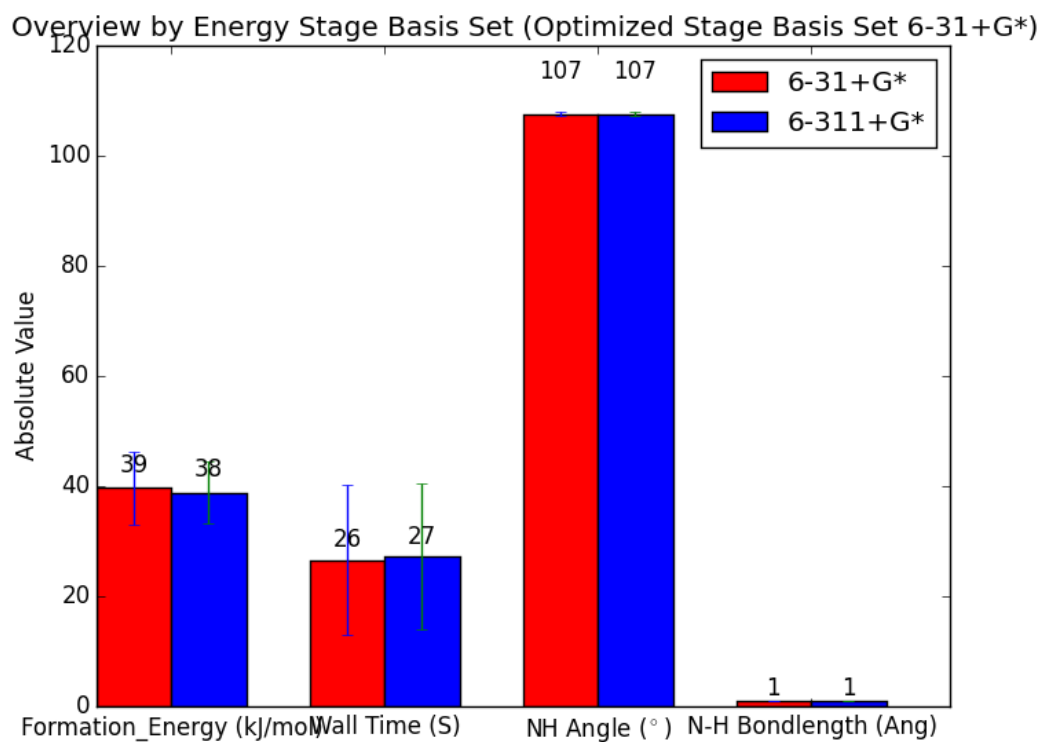


Figure 8: CPU walltime summary within acceptable deviation