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 $1.889\,725$ to convert to a.u., the final bond lenght of H_2 is 0.7414 Å.

1.2 Energy

H_2 **DFT Energy** The total DFT energy of H_2 is $-1.176\,631$ Ha, $-32.017\,78$ 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 $1.889\,725$ to convert to a.u., the final bond lenght of H_2 is 1.1 Å.

2.2 Energy

N_2 **DFT Energy** The total DFT energy of N_2 is $-109.502\,491$ Ha, $-2979.715\,97$ 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 enethalpy 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/, -45.95 kJ/mol.

5 Effect of Functional Choice and Basis Set

In this section, we enumerated all 36 differenct conditions with different functional choice and basis set. Only basis set with polarization function are used.We use HF, PBE and B3LYP(B3) funtionals 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 $-45.95 \pm 0.35 kJ/mol$ from NIST website.NIST (2015). The bond length of N-H is $1.017\AA$ 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 ±2%. The best functional set combination is using PBE function for both stages calcuation, using 6-31+G* as basis set for geometry stage optimization and using 6-311+G* for DFT energy calculation with calculated formation energy -46.18 kJ/mol, with only 0.5% deviation from experimental value.

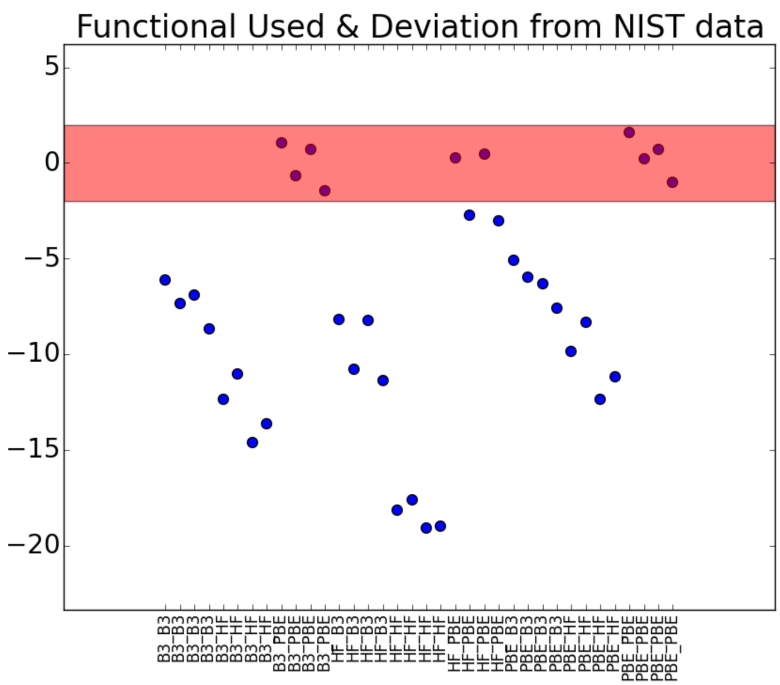

Figure 1: Overview of Formation Energy Deviation

5.2 B3LYP Function and Effect

If we use B3LYP functional as first stage function, to minimize the deviation from experimental data, we should keep using B3LYP as second stage function from Figure 2.

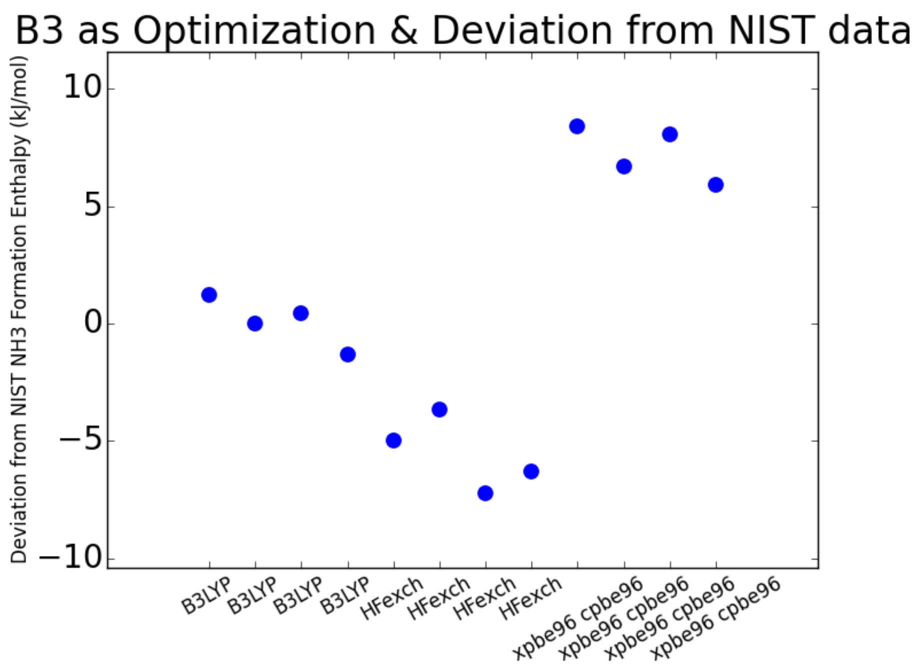

Figure 2: B3 as geometry optimization stage functional

5.3 HF Function and Effect

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

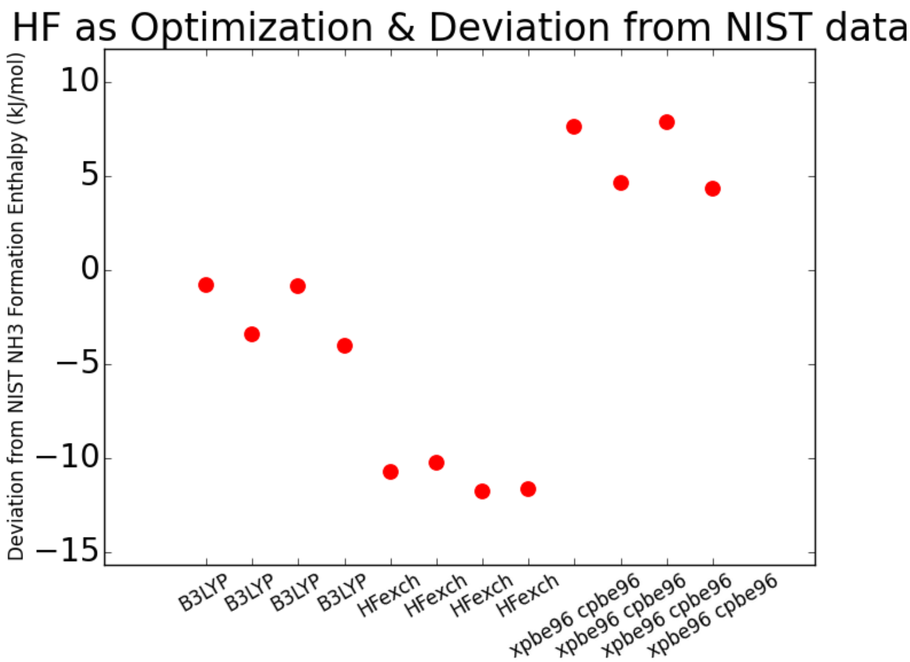

Figure 3: HF as geometry optimization stage functional

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. The B3LYP functional use 6-31+G* (optimization stage) and 6-311+G* (energy stage) gives the best geometry prediction with highest accuracy.

5.7 CPU wall time and effectiveness

If we could accept 2% as deviation, from Figure 7, using HF functional for geometry optimization and PBE for DFT energy calculation might be the most efficient calculation strategy with relatively good accuracy within 2%.

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

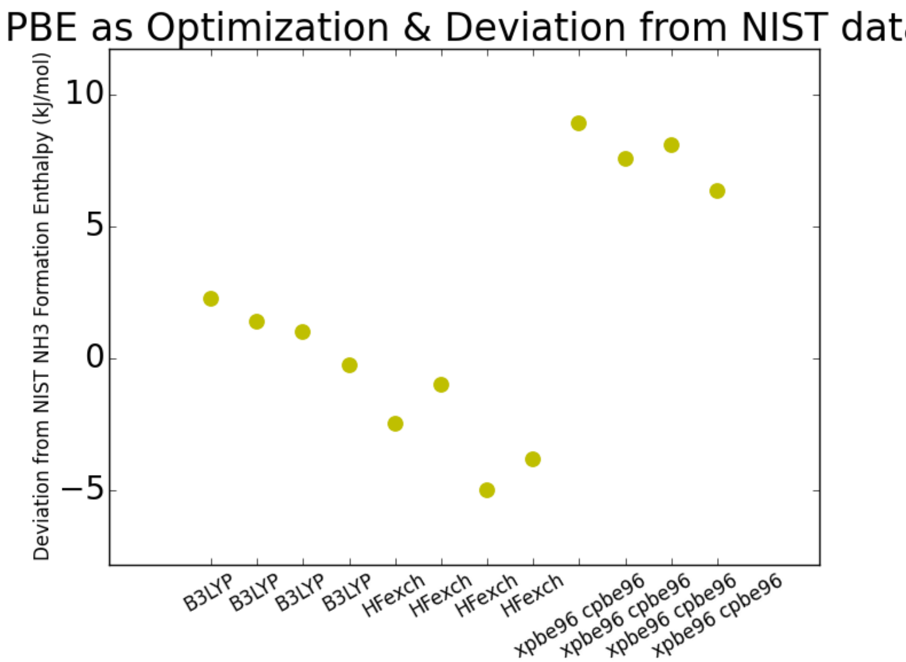

Figure 4: PBE as geometry optimization stage functional

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

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 N2, -109.53 Ha, the dissociation energy of N2 is 0.33 Ha = 8.98 ev, 207.08 kcal/mol. This is also the reaction barrier of reaction.

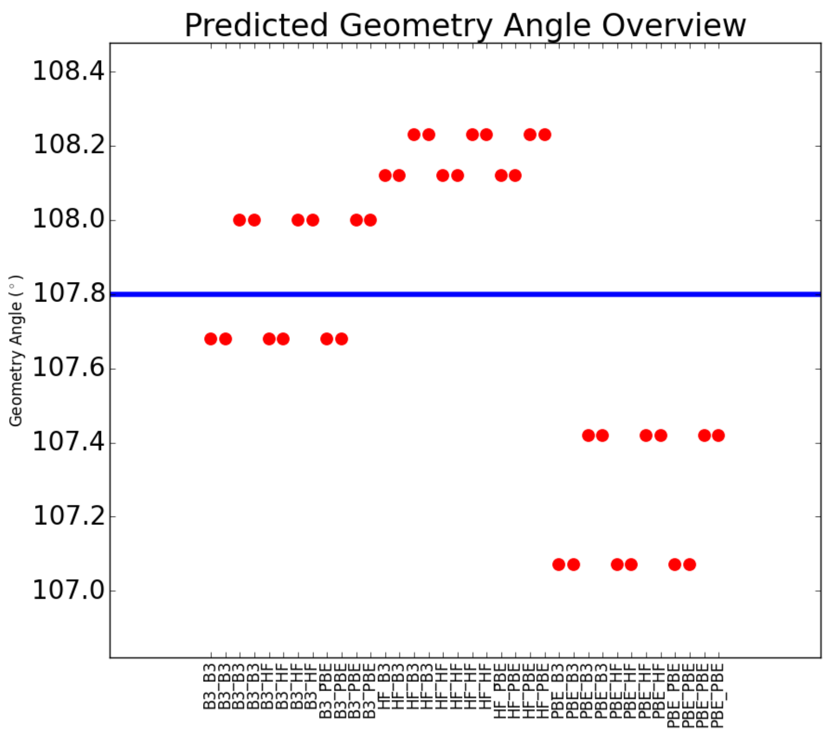

Figure 5: N-H angle predicted by various functional set

References

NIST (2015). Ammonia thermochemistry data.

Wiki (2015). Wiki ammonia thermochemistry data.

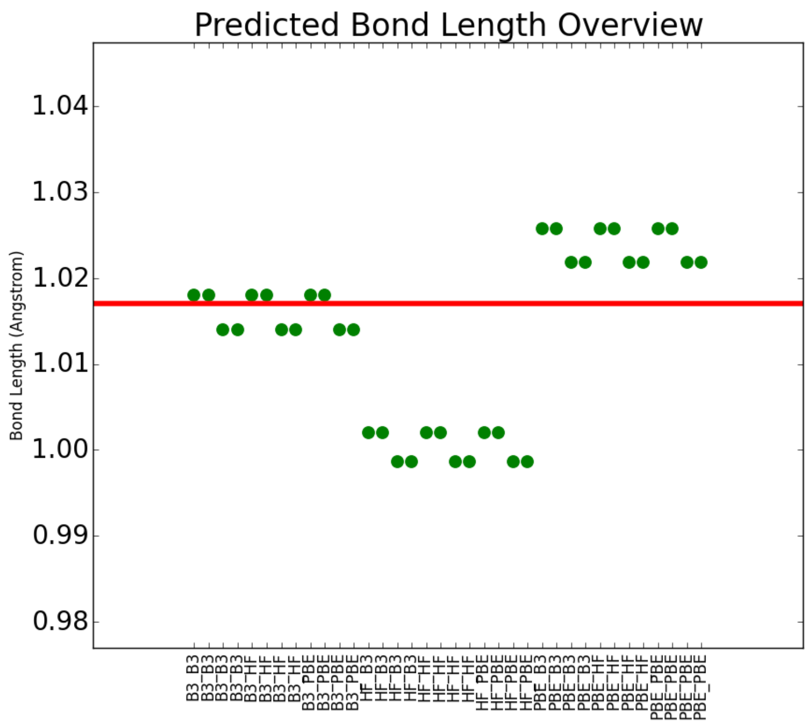

Figure 6: N-H bond length predicted by various functional set

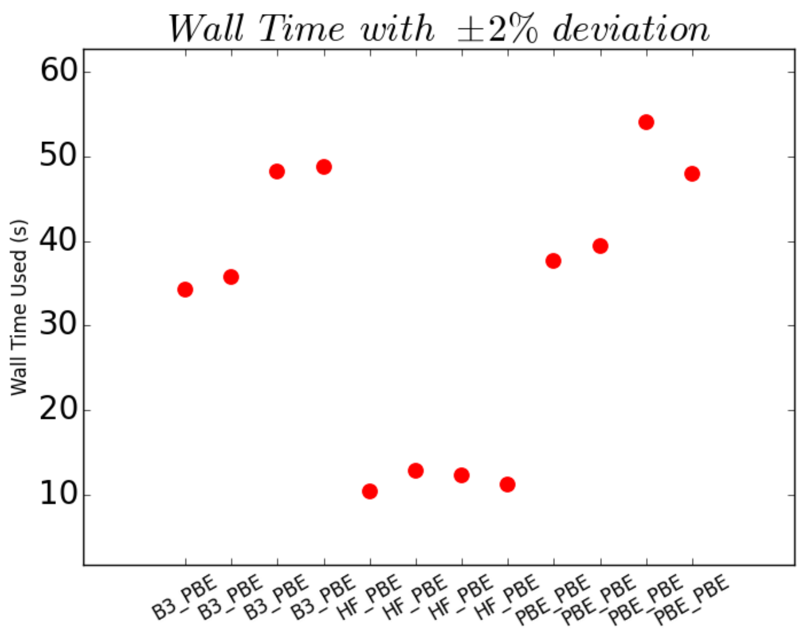

Figure 7: CPU walltime summary within acceptable deviation

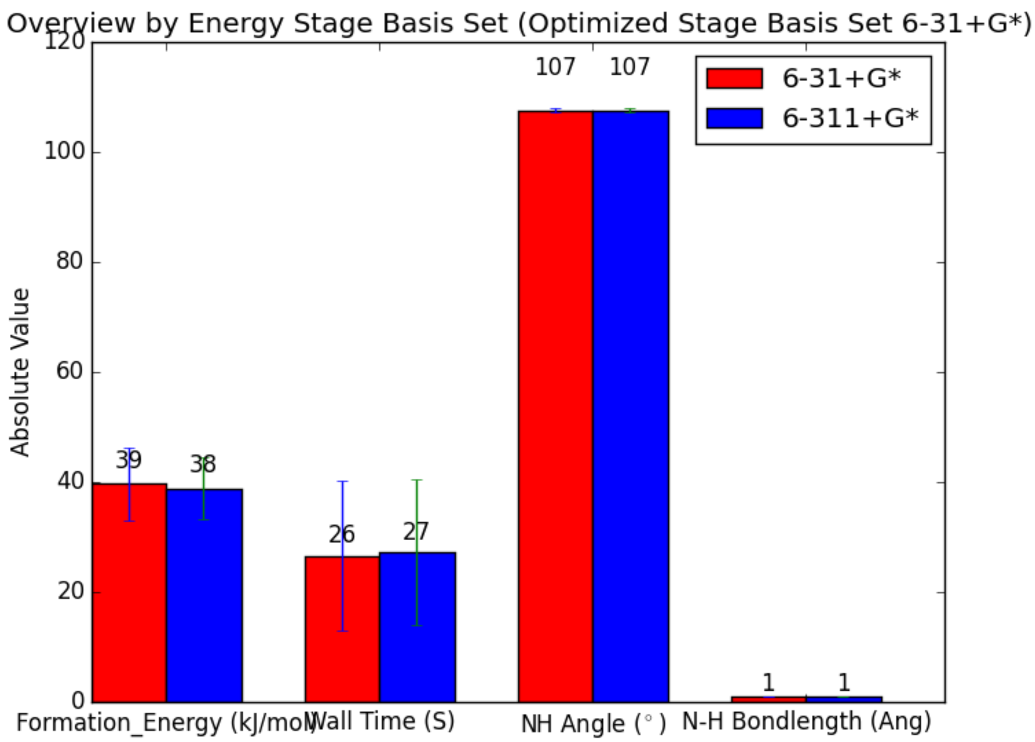

Figure 8: CPU walltime summary within acceptable deviation