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 $0.7414\,\text{Å}$.

1.2 Energy

H_2 **DFT Energy** The total DFT energy of H_2 is $-1.176\,631\,\text{Ha}$, $-32.017\,78\,\text{eV}$.

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 $1.1\,\text{Å}$.

2.2 Energy

N_2 **DFT Energy** The total DFT energy of N_2 is $-109.502\,491\,\text{Ha}$, $-2979.715\,97\,\text{eV}$.

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 $1.017 \mathring{A}$ 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.

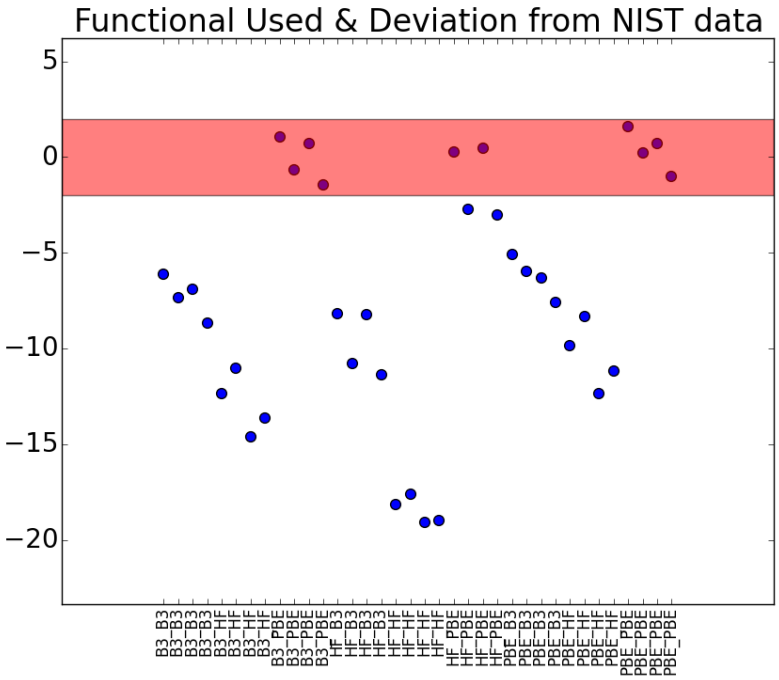

Figure 1: Overview of Formation Energy Deviation

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.

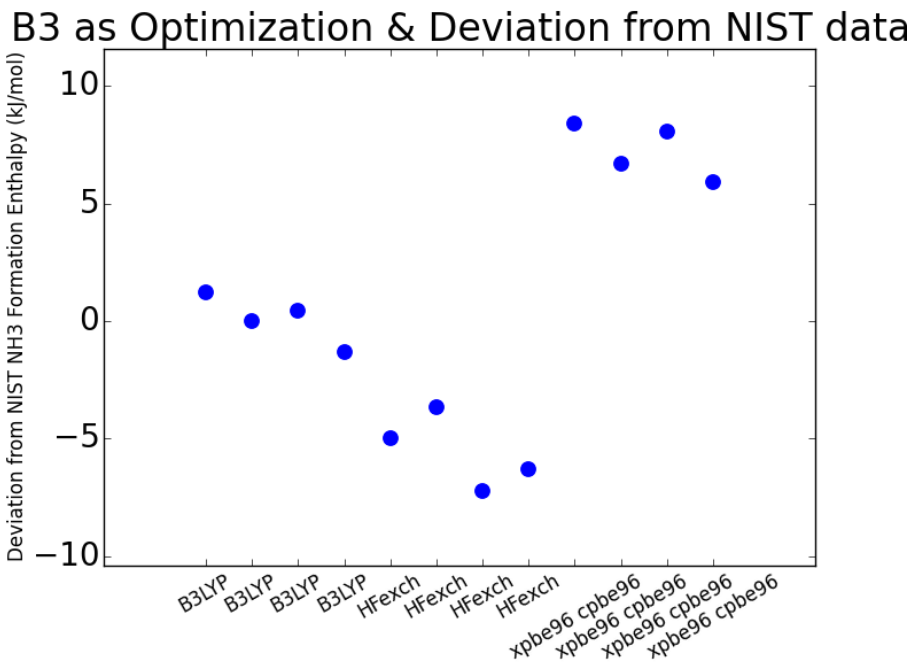

Figure 2: B3 as geometry optimization stage functional

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.

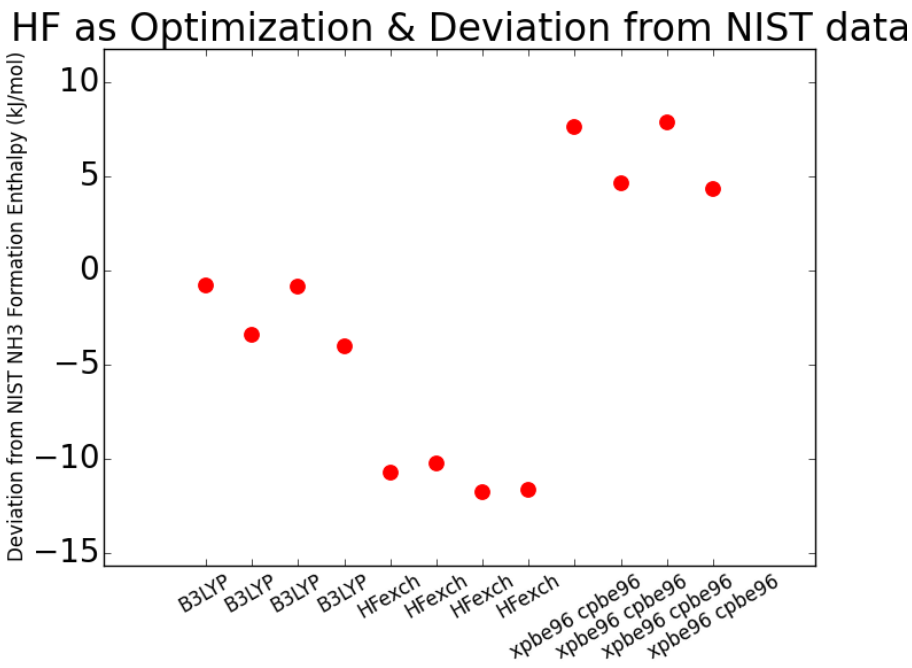

Figure 3: HF as geometry optimization stage functional

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

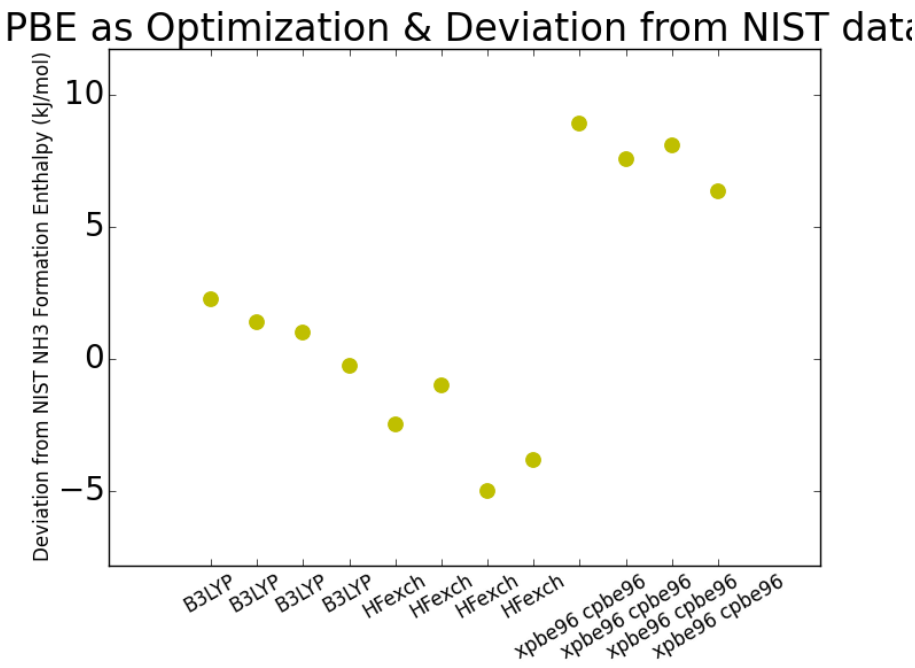

Figure 4: PBE as geometry optimization stage functional

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.

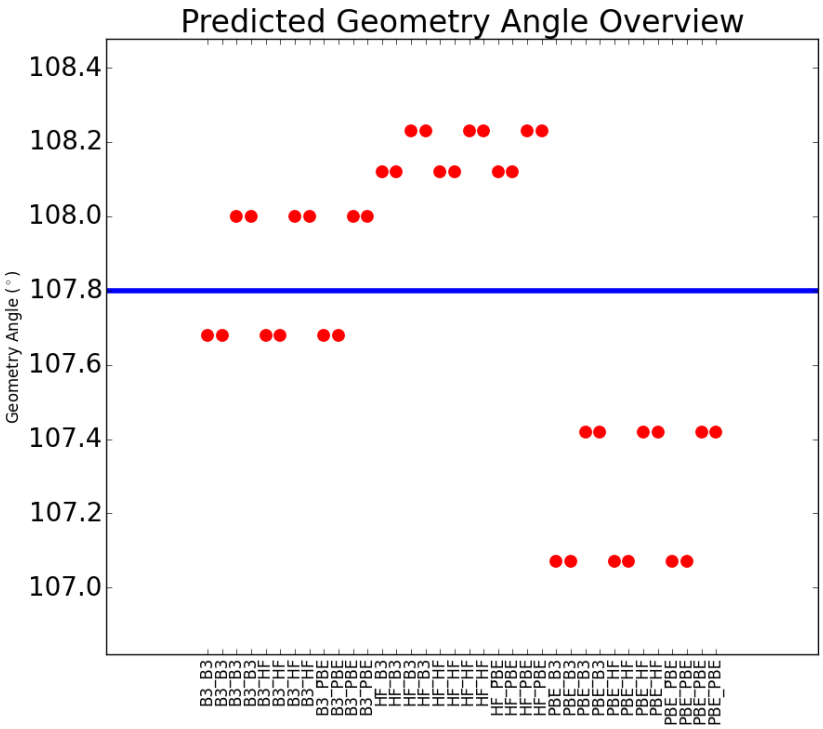

Figure 5: N-H angle predicted by various functional set

References

NIST (2015). Ammonia thermochemistry data.

Wiki (2015). Wiki ammonia thermochemistry data.

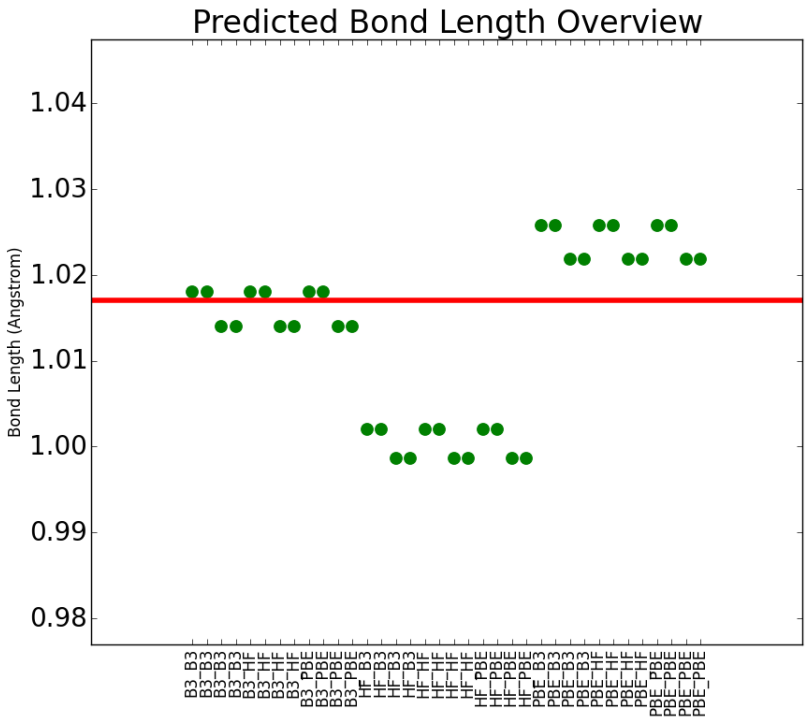

Figure 6: N-H bond length predicted by various functional set

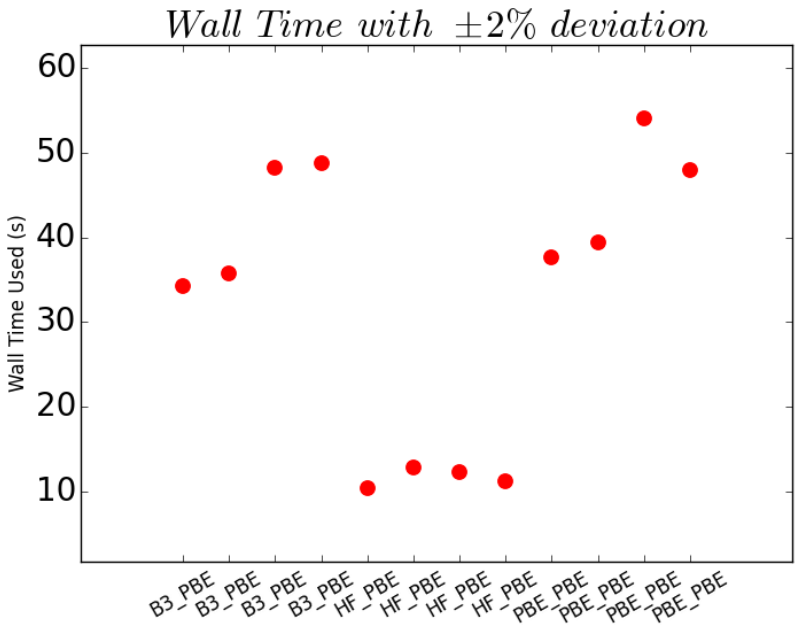

Figure 7: CPU walltime summary within acceptable deviation

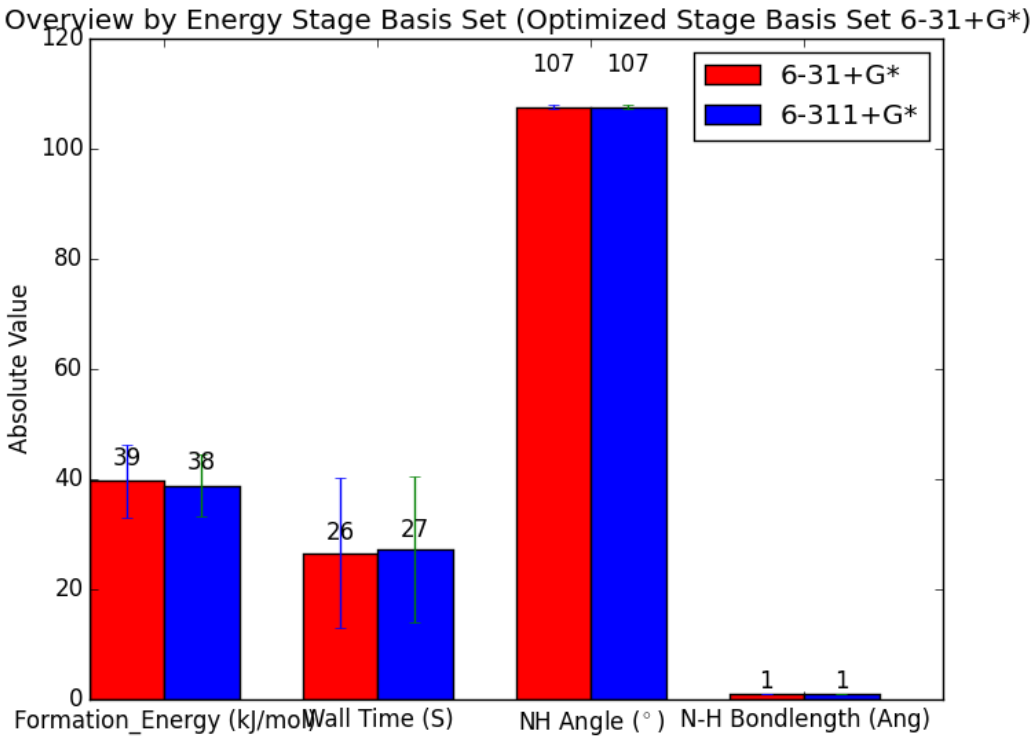

Figure 8: CPU walltime summary within acceptable deviation

Compounds	Functional_Used	Basis_Set	Formation_Energy (kJ/mol)	Deviation Formation Energy	CPU_Time_Sum	Geometry_A	Bond_Length (Ang)
NH3	B3LYP_B3LYP	6-31+G*_6-31+G*	-39.83094374	0.88094374	33.6	107.68	1.018
NH3	B3LYP_B3LYP	6-31+G*_6-311+G*	-38.58772362	-0.36227638	33.8	107.68	1.018
NH3	B3LYP_B3LYP	6-311+G*_6-31+G*	-39.04273413	0.09273413	46.7	108	1.01399
NH3	B3LYP_B3LYP	6-311+G*_6-311+G*	-37.29418063	-1.65581937	46.1	108	1.01399
NH3	B3LYP_HFexch	6-31+G*_6-31+G*	-33.58840718	-5.36159282	32.6	107.68	1.018
NH3	B3LYP_HFexch	6-31+G*_6-311+G*	-34.92813201	-4.02186799	34.4	107.68	1.018
NH3	B3LYP_HFexch	6-311+G*_6-31+G*	-31.34384303	-7.60615697	48.8	108	1.01399
NH3	B3LYP_HFexch	6-311+G*_6-311+G*	-32.31036487	-6.63963513	48.7	108	1.01399
NH3	B3LYP_xpbe96 cpbe96	6-31+G*_6-31+G*	-47.01229846	8.06229846	34.3	107.68	1.018
NH3	B3LYP_xpbe96 cpbe96	6-31+G*_6-311+G*	-45.30234227	6.35234227	35.7	107.68	1.018
NH3	B3LYP_xpbe96 cpbe96	6-311+G*_6-31+G*	-46.66231896	7.71231896	48.2	108	1.01399
NH3	B3LYP_xpbe96 cpbe96	6-311+G*_6-311+G*	-44.4756626	5.5256626	48.7	108	1.01399
NH3	HFexch_B3LYP	6-31+G*_6-31+G*	-37.78575303	-1.16424697	8.5	108.12	1.00204
NH3	HFexch_B3LYP	6-31+G*_6-311+G*	-35.15130964	-3.79869036	9.4	108.12	1.00204
NH3	HFexch_B3LYP	6-311+G*_6-31+G*	-37.72231646	-1.22768354	10.7	108.23	0.99864
NH3	HFexch_B3LYP	6-311+G*_6-311+G*	-34.57870883	-4.37129117	12.2	108.23	0.99864
NH3	HFexch_HFexch	6-31+G*_6-31+G*	-27.81721836	-11.13278164	7.1	108.12	1.00204
NH3	HFexch_HFexch	6-31+G*_6-311+G*	-28.33731461	-10.61268539	6.9	108.12	1.00204
NH3	HFexch_HFexch	6-311+G*_6-31+G*	-26.83908624	-12.11091376	10.1	108.23	0.99864
NH3	HFexch_HFexch	6-311+G*_6-311+G*	-26.9409624	-12.0090376	9.7	108.23	0.99864
NH3	HFexch_xpbe96 cpbe96	6-31+G*_6-31+G*	-46.23419862	7.28419862	10.4	108.12	1.00204
NH3	HFexch_xpbe96 cpbe96	6-31+G*_6-311+G*	-43.23656332	4.28656332	12.8	108.12	1.00204
NH3	HFexch_xpbe96 cpbe96	6-311+G*_6-31+G*	-46.42701365	7.47701365	12.2	108.23	0.99864
NH3	HFexch_xpbe96 cpbe96	6-311+G*_6-311+G*	-42.94157538	3.99157538	11.1	108.23	0.99864
NH3	xpbe96 cpbe96_B3LYP	6-31+G*_6-31+G*	-40.84405565	1.89405565	37.3	107.07	1.02575
NH3	xpbe96 cpbe96_B3LYP	6-31+G*_6-311+G*	-39.99836519	1.04836519	36.4	107.07	1.02575
NH3	xpbe96 cpbe96_B3LYP	6-311+G*_6-31+G*	-39.61290936	0.66290936	45.4	107.42	1.02187
NH3	xpbe96 cpbe96_B3LYP	6-311+G*_6-311+G*	-38.35598502	-0.59401498	50.7	107.42	1.02187
NH3	xpbe96 cpbe96_HFexch	6-31+G*_6-31+G*	-36.11382954	-2.83617046	37.9	107.07	1.02575
NH3	xpbe96 cpbe96_HFexch	6-31+G*_6-311+G*	-37.61551004	-1.33448996	35.8	107.07	1.02575
NH3	xpbe96 cpbe96_HFexch	6-311+G*_6-31+G*	-33.57705251	-5.37294749	45.9	107.42	1.02187
NH3	xpbe96 cpbe96_HFexch	6-311+G*_6-311+G*	-34.77483042	-4.17516958	46.5	107.42	1.02187
NH3	xpbe96 cpbe96_xpbe96 cpb	6-31+G*_6-31+G*	-47.53632027	8.58632027	37.6	107.07	1.02575
NH3	xpbe96 cpbe96_xpbe96 cpb	6-31+G*_6-311+G*	-46.1827511	7.2327511	39.4	107.07	1.02575
NH3	xpbe96 cpbe96_xpbe96 cpb	6-311+G*_6-31+G*	-46.67443679	7.72443679	54	107.42	1.02187
NH3	xpbe96 cpbe96_xpbe96 cpb	6-311+G*_6-311+G*	-44.93126697	5.98126697	48	107.42	1.02187