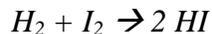


## Solution to 10.675 Homework #2

due 10/7/04

1) For the following gas-phase reaction:



(a) First optimize each structure using Hartree-Fock, 3-21G, (RHF/3-21G) and calculate thermodynamic data by performing a frequency analysis, including the change in standard-state enthalpy and Gibbs free energy of reaction.

(b) Using the checkpoint file that results from (a), perform a single point calculation using the basis sets assigned to your number (see next page). How does this change the standard-state enthalpy of reaction determined in (a)? (You need not perform another geometry optimization or frequency calculation. Note, in particular, to perform a frequency calculation, you **must** first perform a geometry optimization using the **same method and basis set** as in your frequency calculation. Why?) Also, perform optimizations using your method and report the differences in standard state enthalpies and Gibbs free energy of reaction.

(c) Compare your thermodynamic and structural results with experimental data, for example from the CRC handbook or another source.

Solution:

All the results are summarized in the table below:

For thermal data:

	(a)			
	RHF/3-21G			
	a1	a2	a3	a4
	Correction to Enthalpy	Correction to Free Energy	Enthalpy	Gibbs free energy
H <sub>2</sub> /a.u.	0.013914	-0.000857	-1.109046	-1.123817
I <sub>2</sub> /a.u.	0.004322	-0.025441	-13775.68091	-13775.71068
HI/a.u.	0.008478	-0.014988	-6888.398071	-6888.421537
Rxn/a.u.			-0.006183	-0.008581
Rxn/kcal/mol			-3.88	-5.38
Exp./kcal/mol			-2.27	-3.81

	(b)				
	B3LYP/3-21G				
	single point calc		reoptimize		
	b1	b2=a1+b1	b3=a2+b1	b4	b5
	Electronic E	Enthalpy	Free Energy	Enthalpy	Gibbs free energy
H <sub>2</sub> /a.u.	-1.1705204	-1.1566064	-1.1713774	-1.15712	-1.171921
I <sub>2</sub> /a.u.	-13781.13065	-13781.12633	-13781.1561	-13781.12656	-13781.15642
HI/a.u.	-6891.150658	-6891.14218	-6891.16565	-6891.142717	-6891.166209
Rxn/a.u.		-0.0014252	-0.0038232	-0.001752	-0.004075
Rxn/kcal/mol		-0.89	-2.40	-1.10	-2.56
Exp./kcal/mol				-2.27	-3.81

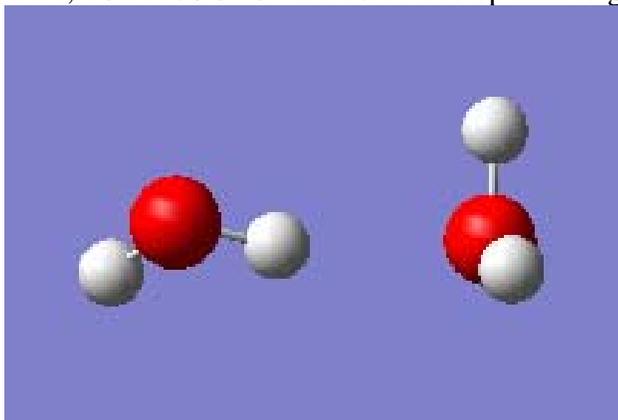
For structural data:

unit: Angstrom	H-H	O-O	H-O
RHF/3-21G	0.7348	2.8648	1.6384
B3LYP/3-21G	0.7462	2.9022	1.6615
Exp.	0.74611	2.662	1.609

2) Compute the hydrogen bond energy of the gas-phase water dimer ( $2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}-\text{H}_2\text{O}$ ) using a method and basis set of your choice. Document the approach that you took and report the energy.

Solution:

Here, B3LYP/6-31G\* are used. The optimized geometry is plotted as below.



(Courtesy of Gaussian, Inc. Used with permission.)

We calculate the hydrogen bond energy as following (the energies used here are: Sum of electronic and zero-point Energies):

$$\begin{aligned} E(\text{H-bond}) &= E(\text{dimer}) - 2 * E(\text{H}_2\text{O}) \\ &= (-152.784289) - 2 * (-76.387785) \\ &= -0.00872 \text{ a.u.} \\ &= -22.87 \text{ kJ/mol} \end{aligned}$$

Experimental value is about 23.3 kJ/mol. (<http://www.lsbu.ac.uk/water/hbond.html>)

This table summarizes all the results obtain by the whole class. Therefore, you can compare the accuracy of different methods and basis sets. Those marked in yellow mean they are problematic.

Name	ID	Method/Basis Set	1b-DH/kcal/mol	1b-DG/kcal/mol
<b>Experiment</b>			-2.27	-3.81
<b>Part 1a</b>		RHF/3-21G	-3.884	-5.384
Student 1		MP2/3-21G	-0.132	-1.575
Student 2		BLYP/3-21G*	-4.892	-3.322
Student 3		BLYP/3-21G**	0.715	-0.064
Student 4		BLYP/LANL2DZ	-5.730	-7.120
Student 5		MP2/LANL2DZ	-5.839	-7.260
Student 6		BLYP/LANL2DZ	-5.734	-7.127
Student 7		BLYP/LANL2DZ	-5.734	-7.127
Student 8		BLYP/LANL2DZ	-2.867	-3.564
Student 9		B3LYP/LANL2DZ	-6.500	-8.000
Student 10		B3LYP/3-21G**	0.162	-0.638
Student 11		BPW91/LANL2DZ	-6.191	-7.627
Student 12		B3LYP/LANL2DZ	-6.709	-8.143
Student 13		BLYP/LANL2DZ	-5.734	-7.126
Student 14		BLYP/LANL2DZ	-16.158	-4.816
Student 15		BLYP/LANL2DZ	-5.730	-7.130
Student 16		MP2/3-21G+	miss	miss
Student 17		B3PW91/LANL2DZ	-7.000	-8.459
Student 18		RHF/LANL2DZ	-4.740	-5.462
Student 19		B3LYP/LANL2DZ	-6.700	-8.131

(Image by MIT OCW.)