Project 3: Quantum Chemical Calculation of the energies of atomic hydrogen and molecular hydrogen

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In the following lines are presented the scripts used for the optimization and computation of the thermodynamic quantities necessary to estimate the energy for the reaction $H_2 \rightarrow 2H$. As specified in the previous project's paper, all the code reported from hereon out is to be considered Gaussian code, unless explicitly indicated.

Firstly, the two input scripts to perform optimization and frequencies analysis on the two molecules appearing in the reaction are presented:

1. `H_opt.cmp`

```
#p B3LYP/6-31+g(d,p) opt freq pop=full gfinput
!for the single hydrogen atom, just performing thermochemical
    analysis, no optimization (since there is a single atom) is a
    viable option

hydrogen_atom

0 2   !single radical
H1

```

2. `H2_opt.cmp`

```
#p B3LYP/6-31+g(d,p) opt freq pop=full gfinput

molecular_hydrogen

0 1   !closed shell
H1
H2 1 d

d=0.7

```

1   Try to understand what has been done in the calculation and which thermodynamic properties have been determined

The structure of the output files is essentially the same as the one being analyzed in the *Project3* paper. Firstly, the keywords used in the input file are repeated together with other

general settings. Subsequently, keywords are transformed by Gaussian into a sequence of subroutine calls termed "links". The links are given together with the corresponding options set for each link in a proprietary format.

In **link L101**, the program reads in the structure of the system together with other parameters and prints the structure (in a slightly modified format) together with overall charge and spin multiplicity and the comments supplied in the input file.

Link L103 initializes the *Berny geometry optimization algorithm* named after its creator Bernhard Schlegel. This includes the generation of second derivative estimates for the optimization variables.

Link L202 determines the system's symmetry, selects symmetry properties for quantum calculations, and rotates the molecule so the center of mass is at the origin. It aligns the principal axis along the z-axis and places the principal plane of symmetry in the yz-plane. The final orientation, called "Standard orientation," is the reference for wavefunction and energy derivative data.

Calculation of the B3LYP/6-31+g(d,p) energy of the system is done in **link 502**. Some parameters such as the currently selected convergence criteria are listed first. The final SCF energy for the considered system is given in atomic units (Hartree).

For each geometry optimization step, the Berny geometry optimization algorithm requires the calculation of the first derivatives of the energy with respect to all structural coordinates together with an estimate for the respective second derivatives. All of this is done in the **L70x links**.

After optimization, if the `freq` keyword is chosen, additional frequency and thermochemistry analysis is performed. For convenience, a summary of the typical properties included is reported here:

- Force constants and resulting vibrational frequencies;

- Zero-Point correction, entalphy, Gibbs free energy;

- Thermal energy, heat capacity (C_v), entropy and molecular partition function, also highlighting the different contributes.

2   Find the energy in the output file and save it.

For **atomic hydrogen**:

```
1  E(UB3LYP) = -0.500272784191       A.U.
```

which gives:

$$E_H = -0.500272784191\,[Hartree] \cdot 627.5\,[(kcal/mol)/Hartree]$$
$$= -313.9211721\,[kcal/mol]$$

For **molecular hydrogen**, the energy found by Gaussian is:

```
1 E(RB3LYP) =   -1.17853933611      A.U.
```

which, in turn, gives:

$$E_{H_2} = -1.17853933611 \, [Hartree] \cdot 627.5 \, [(kcal/mol)/Hartree]$$
$$= -739.5334334 \, [kcal/mol]$$

If we also consider ZP energy contributes, the energy values become:

$$E_H = -0.500273 \, [Hartree] \cdot 627.5 \, [(kcal/mol)/Hartree]$$
$$= -313.9213075 \, [kcal/mol]$$
$$E_{H_2} = -1.168366 \, [Hartree] \cdot 627.5 \, [(kcal/mol)/Hartree]$$
$$= -733.149665 \, [kcal/mol]$$

3   Try to determine the energy of the reaction $H_2 \to 2H$

We can estimate the reaction energy as the difference between the energy sums of products and the energy sums of the reactants. In formulas:

$$\Delta E = 2 \cdot E_H - E_{H_2} = 105.30705 \, [kcal/mol]$$

Since ΔE is positive, we can say that the dissociation of molecular hydrogen into hydrogen atoms is and **endothermic** process, requiring energy.

3.1   Determine the energy of H2 at fixed H-H distances (frozen coordinate) and construct a table of H2 energies as a function of the distance.

This can be achieved with the `scan` keyword (https://gaussian.com/scan/):

```
1 #p scan pop=full gfinput
2
3 molecular_hydrogen
4
5 0 1  !closed shell
6 H1
7 H2 1 d
8
9 d=0.5 100 0.01
```

The required table can be found at the end of the produced `log` file:

```
Summary of the potential surface scan:
   N        d           SCF
  ----   ---------   -----------
    1      0.5000      -1.04300
    2      0.5100      -1.05156
    3      0.5200      -1.05940
    4      0.5300      -1.06656
    5      0.5400      -1.07310
    6      0.5500      -1.07905
    7      0.5600      -1.08444
    8      0.5700      -1.08932
    9      0.5800      -1.09370
   10      0.5900      -1.09763
   11      0.6000      -1.10113
   12      0.6100      -1.10422
   13      0.6200      -1.10693
   14      0.6300      -1.10928
   15      0.6400      -1.11130
   16      0.6500      -1.11300
   17      0.6600      -1.11440
   18      0.6700      -1.11552
   19      0.6800      -1.11637
   20      0.6900      -1.11698
   21      0.7000      -1.11735
   22      0.7100      -1.11750
   23      0.7200      -1.11745
   24      0.7300      -1.11719
   25      0.7400      -1.11676
   26      0.7500      -1.11615
   27      0.7600      -1.11538
   28      0.7700      -1.11446
   29      0.7800      -1.11339
   30      0.7900      -1.11218
   31      0.8000      -1.11085
   32      0.8100      -1.10940
   33      0.8200      -1.10783
   34      0.8300      -1.10616
   35      0.8400      -1.10438
   36      0.8500      -1.10251
   37      0.8600      -1.10055
   38      0.8700      -1.09851
   39      0.8800      -1.09638
   40      0.8900      -1.09418
   41      0.9000      -1.09191
   42      0.9100      -1.08958
   43      0.9200      -1.08718
   44      0.9300      -1.08472
   45      0.9400      -1.08220
   46      0.9500      -1.07964
   47      0.9600      -1.07702
   48      0.9700      -1.07436
```

```
49      0.9800      -1.07165
50      0.9900      -1.06890
51      1.0000      -1.06611
52      1.0100      -1.06328
53      1.0200      -1.06042
54      1.0300      -1.05753
55      1.0400      -1.05461
56      1.0500      -1.05166
57      1.0600      -1.04868
58      1.0700      -1.04568
59      1.0800      -1.04265
60      1.0900      -1.03961
61      1.1000      -1.03654
62      1.1100      -1.03345
63      1.1200      -1.03035
64      1.1300      -1.02724
65      1.1400      -1.02411
66      1.1500      -1.02096
67      1.1600      -1.01781
68      1.1700      -1.01465
69      1.1800      -1.01147
70      1.1900      -1.00829
71      1.2000      -1.00511
72      1.2100      -1.00191
73      1.2200      -0.99872
74      1.2300      -0.99552
75      1.2400      -0.99232
76      1.2500      -0.98911
77      1.2600      -0.98591
78      1.2700      -0.98271
79      1.2800      -0.97951
80      1.2900      -0.97631
81      1.3000      -0.97311
82      1.3100      -0.96992
83      1.3200      -0.96673
84      1.3300      -0.96355
85      1.3400      -0.96037
86      1.3500      -0.95720
87      1.3600      -0.95404
88      1.3700      -0.95089
89      1.3800      -0.94774
90      1.3900      -0.94461
91      1.4000      -0.94148
92      1.4100      -0.93837
93      1.4200      -0.93526
94      1.4300      -0.93217
95      1.4400      -0.92909
96      1.4500      -0.92602
97      1.4600      -0.92296
98      1.4700      -0.91992
99      1.4800      -0.91689
```
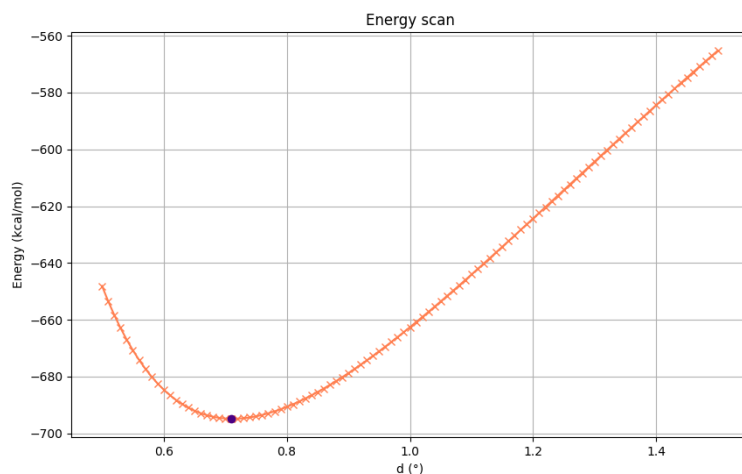
Figure 1: Energy values at different values of the inter-atomic distance. The black dot represents the energetic minimum

```
103    100        1.4900        -0.91387
104    101        1.5000        -0.91087
105    ----    ---------    -----------
```

Where `N` is the step number for the scan, `d` is the distance between hydrogen atoms considered for the specific scan step, `SCF` is the actual energy for the current configuration considered in the scan step.

4   MOLPRO code

In the following section, the analogous script used on MOLPRO software is presented:

- `h.inp`

```
1     ***,hydrogen
2     memory,50,m
3
4
5     basis=6-31+G(d,p)
6     geometry={
7     H
8     }
9
10    {ks,b3lyp,
11    wf,charge=0,spin=1}
12    put,molden,molpro.molden.h
13    ---
14
```

returns:

```
1          ...
2          !RKS STATE 1.1 Energy                          -0.496862054342
3          ...
4
```

- h2.inp

```
1     ***,hydrogen_mol
2
3     basis=6-31+G(d,p)
4     geometry={angstrom,nosym
5     H1
6     H2, H1, d
7     }
8
9     d=0.74
10
11    {ks,b3lyp
12    wf,charge=0,spin=0}
13    optg !perform optimization
14    {frequencies;thermo}
15    put,molden,molpro.molden.h2
16    ---
17
```

returns:

```
1       ...
2       Electronic Energy at 0 [K]:                          -1.171773 [H]
3       Electronic Energy + Zero-Point correction:           -1.161603 [H]
4       Electronic Energy at    298.150 [K]:                 -1.159243 [H]
5       Enthalpy H at           298.150 [K]:                 -1.158299 [H]
6       Free Enthalpy G at      298.150 [K]:                 -1.173092 [H]
7       ...
8
```

- h2_scan.inp

```
1     ***,hydrogen_mol_scan
2
3     basis=6-31+G(d,p)
4     geometry={angstrom,nosym
5     H1
6     H2, H1, d
7     }
8
9     d=0.5
10
11
12    do i=1,100 ! loop over 100 points
```

```
13
14      {ks,b3lyp}
15      step(i)=i
16      eb3lyp(i)=energy !store energy for dft calculation
17      rhh(i)=d
18      d=d+0.01   !increment d by 0.01
19
20      end do
21
22      {table,step,rhh,eb3lyp}
23
24      ---
25
```

returns:

```
1        STEP    RHH      EB3LYP
2        1.0    0.50    -1.09876873
3        2.0    0.51    -1.10655154
4        3.0    0.52    -1.11369428
5        4.0    0.53    -1.12023928
6        5.0    0.54    -1.12623061
7        6.0    0.55    -1.13170544
8        7.0    0.56    -1.13669684
9        8.0    0.57    -1.14123782
10       9.0    0.58    -1.14535815
11      10.0    0.59    -1.14908685
12      11.0    0.60    -1.15244839
13      12.0    0.61    -1.15546543
14      13.0    0.62    -1.15816378
15      14.0    0.63    -1.16056046
16      15.0    0.64    -1.16267711
17      16.0    0.65    -1.16453022
18      17.0    0.66    -1.16613736
19      18.0    0.67    -1.16751129
20      19.0    0.68    -1.16866893
21      20.0    0.69    -1.16962422
22      21.0    0.70    -1.17038887
23      22.0    0.71    -1.17097452
24      23.0    0.72    -1.17139190
25      24.0    0.73    -1.17165306
26      25.0    0.74    -1.17176658
27      26.0    0.75    -1.17174158
28      27.0    0.76    -1.17158619
29      28.0    0.77    -1.17130940
30      29.0    0.78    -1.17091822
31      30.0    0.79    -1.17042067
32      31.0    0.80    -1.16982275
33      32.0    0.81    -1.16913099
34      33.0    0.82    -1.16835007
35      34.0    0.83    -1.16748853
```

```
36    35.0    0.84    -1.16655047
37    36.0    0.85    -1.16553718
38    37.0    0.86    -1.16445683
39    38.0    0.87    -1.16331432
40    39.0    0.88    -1.16211278
41    40.0    0.89    -1.16085700
42    41.0    0.90    -1.15954907
43    42.0    0.91    -1.15819334
44    43.0    0.92    -1.15679301
45    44.0    0.93    -1.15535211
46    45.0    0.94    -1.15387178
47    46.0    0.95    -1.15235516
48    47.0    0.96    -1.15080586
49    48.0    0.97    -1.14922621
50    49.0    0.98    -1.14761838
51    50.0    0.99    -1.14598437
52    51.0    1.00    -1.14432680
53    52.0    1.01    -1.14264646
54    53.0    1.02    -1.14094539
55    54.0    1.03    -1.13922725
56    55.0    1.04    -1.13749112
57    56.0    1.05    -1.13574046
58    57.0    1.06    -1.13397545
59    58.0    1.07    -1.13219882
60    59.0    1.08    -1.13041128
61    60.0    1.09    -1.12861398
62    61.0    1.10    -1.12680855
63    62.0    1.11    -1.12499568
64    63.0    1.12    -1.12317615
65    64.0    1.13    -1.12135241
66    65.0    1.14    -1.11952426
67    66.0    1.15    -1.11769252
68    67.0    1.16    -1.11585836
69    68.0    1.17    -1.11402264
70    69.0    1.18    -1.11218533
71    70.0    1.19    -1.11034878
72    71.0    1.20    -1.10851288
73    72.0    1.21    -1.10667838
74    73.0    1.22    -1.10484579
75    74.0    1.23    -1.10301597
76    75.0    1.24    -1.10118828
77    76.0    1.25    -1.09936537
78    77.0    1.26    -1.09754675
79    78.0    1.27    -1.09573299
80    79.0    1.28    -1.09392435
81    80.0    1.29    -1.09212145
82    81.0    1.30    -1.09032461
83    82.0    1.31    -1.08853454
84    83.0    1.32    -1.08675106
85    84.0    1.33    -1.08497452
86    85.0    1.34    -1.08320576
```

```
86.0    1.35    -1.08144482
87.0    1.36    -1.07969194
88.0    1.37    -1.07794769
89.0    1.38    -1.07621167
90.0    1.39    -1.07448496
91.0    1.40    -1.07276753
92.0    1.41    -1.07105939
93.0    1.42    -1.06936096
94.0    1.43    -1.06767216
95.0    1.44    -1.06599297
96.0    1.45    -1.06432413
97.0    1.46    -1.06266568
98.0    1.47    -1.06101899
99.0    1.48    -1.05938136
100.0   1.49    -1.05775433
```