

Tutorial on Ab Initio Redox Potential Calculations

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1 Introduction

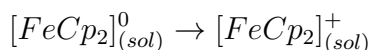
This tutorial introduces the reader to *ab initio* calculations of Redox Potentials allowing students of CHEM505 to solve Exercise 2 of Lecture 2 available on Classes v2 by using the software package Gaussian. For more information on the Gaussian code and its tools the reader can consult the [Gaussian reference manual](#) as well as the [Gaussian Tutorial](#) for Gibbs Free Energy calculations. Section 2, describes the problem and the calculations that are needed. The following sections explain an example of each of the calculations.

2 Redox Potential for $[\text{FeCp}_2]^{0/+}$

As an example, let us compute, the redox potential

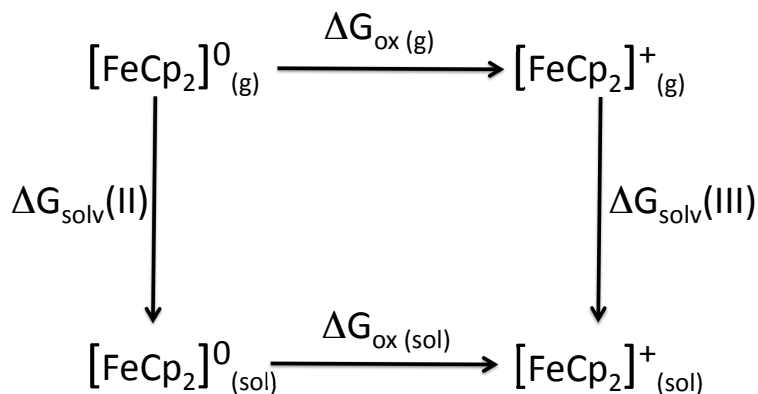
$$E_m^{0/+} = \frac{\Delta G_{\text{ox}(sol)}}{-nF}$$

of $[\text{FeCp}_2]^{0/+}$ from a calculation of the Gibbs free energy change $\Delta G_{\text{ox}(sol)}$ due to the reaction:



where $n = 1$ is the number of electrons involved and F is Faraday's constant 96,500 C.

To calculate the $\Delta G_{\text{ox}(sol)}$, we can use the Born-Haber Cycle:



which is an application of Hess's law, where $\Delta G_{solv}(\text{II})$ and $\Delta G_{solv}(\text{III})$ are the solvation free energies of $[\text{FeCp}_2]^0$ and $[\text{FeCp}_2]^+$, respectively, and $\Delta G_{ox(g)}$ is the free energy change due to oxidation reaction of $[\text{FeCp}_2]^+$ to $[\text{FeCp}_2]^+$ in the gas phase.

To do so, we optimize both species ($[\text{FeCp}_2]^{0/+}$) in the gas phase and perform a frequency calculation for the optimized structures. With that data, we calculate $\Delta G_{ox(g)}$. To calculate $\Delta G_{solv}(\text{II})$, $\Delta G_{solv}(\text{III})$, we use the same optimized structures and calculate solvent effects using the polarizable continuum model (PCM). For this example we use DMSO as the solvent. Also, notice that all the calculations will use the optimized structures of $[\text{FeCp}_2]^{0/+}$ in the gas phase, therefore, no optimizations nor frequency calculations are done in solution.

3 Geometry Optimization in Gas Phase

The Gaussian input file to optimize the geometry of $[\text{FeCp}_2]^0$ is:

```
#P ub3lyp/lanl2dz opt
```

```
FeCp2 Fe(II)
```

```
0 1
C      1.1976840000      -0.2527620000      -1.6915500000
C      0.6250050000       1.0559000000      -1.6864600000
C     -0.7966130000       0.9151750000      -1.6947570000
C     -1.1022240000      -0.4789880000      -1.7004300000
C      0.1308110000      -1.2004210000      -1.6990280000
Fe      0.0015150000      -0.0003450000      -0.0112620000
C      1.0430000000       0.5961410000       1.6772550000
C      0.8979560000      -0.8311860000       1.7047680000
C     -0.5167840000      -1.1251290000       1.6964690000
C     -1.2272490000       0.1161340000       1.6632850000
C     -0.2633640000       1.1728950000       1.6764190000
H     -0.7983370000      -2.0636740000       1.7126380000
H      1.5654340000      -1.5484640000       1.7243910000
H     -1.5148690000       1.7235990000      -1.6687820000
H     -2.0921210000      -0.9137470000      -1.6683510000
H      0.2343230000      -2.2764370000      -1.6622600000
H      2.2539700000      -0.4842260000      -1.6638720000
H      1.1716700000       1.9888870000      -1.6554330000
H     -0.4868670000       2.2308740000       1.6487970000
H      1.9787100000       1.1391230000       1.6626380000
H     -2.3016490000       0.2366480000       1.6355240000
```

To know more about the structure of the input file and how to run a Gaussian calculation you can consult the [Gaussian reference manual](#) and the [Gaussian Tutorial](#). Just to remind you, the first line indicates that it is an optimization using DFT with ub3lyp functional and lanl2dz as basis set. Be aware of the charge and spin multiplicity of the systems.

Once the calculation has finished, make sure the job was finished successfully and that you have obtained convergence in the optimization cycles. Then, you can extract the energy using the “grep” command in the terminal:

```
$ grep "SCF Done" "gaussian output"
```

You will see the Energies of all the cycles of the optimization, the last value is the final energy of the optimized system (SCFE_(g)(II)). This is the value I obtained:

```
$ SCF Done:  E(UB3LYP) =  -510.439067372      A.U. after  15 cycles
```

4 Frequency Calculation in Gas Phase

Now, we need to use the optimized structure and perform a frequency calculation. Here is the input file which contains the optimized structure of [FeCp₂]⁰. Notice that in the command line I used the “freq” keyword to perform this calculation.

```
#P ub3lyp/lanl2dz freq
```

```
FeCp2 Fe(II)
```

```
0 1
C    1.099253    -0.564333    -1.723869
C    0.877505     0.861856    -1.726343
C   -0.547242     1.091630    -1.732051
C   -1.206079    -0.192456    -1.732468
C   -0.188526    -1.216041    -1.727576
Fe   0.000847    -0.000951    -0.000007
C    0.863064     0.869912     1.729769
C    1.085387    -0.556089     1.735435
C   -0.202226    -1.208191     1.731319
C   -1.220207    -0.184928     1.723110
C   -0.561726     1.099319     1.722532
H   -0.373919    -2.275657     1.729005
H    2.047529    -1.049190     1.736238
H   -1.035224     2.056281    -1.729364
H   -2.274353    -0.358800    -1.730141
H   -0.360376    -2.283431    -1.721960
H    2.061083    -1.057841    -1.714723
```

H	1.644042	1.624162	-1.719142
H	-1.049851	2.063830	1.711752
H	1.629432	1.632432	1.725585
H	-2.288412	-0.351515	1.712897

Once the job has been completed make sure the job use finished successfully and that there are no negative values of frequencies since that would indicate you are not in the optimized structure and you would need to run another optimization with more strict convergence parameters. Once more I would invite you to consult the document [Thermochemistry in Gaussian](#) and the [Gaussian Tutorial](#) to know how to extract important thermochemical data from the output file.

The value we need to obtain from the output file is the thermal Correction to the Gibbs Free Energy (GibbsCorr(II)), I would use the “grep” command in the terminal to search for “Gibbs Free Energy”, the output is:

```
$ Thermal correction to Gibbs Free Energy=          0.134232
```

At this point, if we add the $SCFE_{(g)}(II) + GibbsCorr(II)$ we obtain an absolute value of the Gibbs Free Energy for $[FeCp_2]^0$ (G(II)), thus performing the same calculations for $[FeCp_2]^+$ we can obtain G(III) and calculate $\Delta G_{ox(g)}$.

$$\Delta G_{ox(g)} = G(III) - G(II)$$

5 PCM Calculation (Solvent Effects)

To calculate the solvent effects we need to use the keyword “SCRF” and indicate that PCM will be used with DMSO as the solvent. Here I include the input file for $[FeCp_2]^0$. Notice that is the same structure than the one in the frequency calculation input since it is the optimized geometry.

```
#P ub3lyp/lanl2dz SCRF=(PCM,Solvent=DiMethylSulfoxide)
```

```
FeCp2 Fe(II)
```

```
0 1
C 1.099253 -0.564333 -1.723869
C 0.877505 0.861856 -1.726343
C -0.547242 1.091630 -1.732051
C -1.206079 -0.192456 -1.732468
C -0.188526 -1.216041 -1.727576
Fe 0.000847 -0.000951 -0.000007
C 0.863064 0.869912 1.729769
C 1.085387 -0.556089 1.735435
C -0.202226 -1.208191 1.731319
C -1.220207 -0.184928 1.723110
C -0.561726 1.099319 1.722532
H -0.373919 -2.275657 1.729005
H 2.047529 -1.049190 1.736238
H -1.035224 2.056281 -1.729364
H -2.274353 -0.358800 -1.730141
H -0.360376 -2.283431 -1.721960
H 2.061083 -1.057841 -1.714723
H 1.644042 1.624162 -1.719142
H -1.049851 2.063830 1.711752
H 1.629432 1.632432 1.725585
H -2.288412 -0.351515 1.712897
```

You can include more options in the input file to perform more specific calculations, I would recommend you to consult the section of “SCRF” in the [Gaussian reference manual](#). Once the job is done, make sure that the job has finished successfully. The Energy is extracted the same way than for the calculation in gas phase. In this calculation only one line will be the outcome after using the command “grep”. This is because even though is self-consistent it is not an optimization. The Energy with solvent effects ($SCFE_{(solv)}(II)$) that I obtained is:

```
SCF Done: E(UB3LYP) = -510.444248948 A.U. after 13 cycles
```

At this point we can calculate the $\Delta G_{solv}(II)$ for $[FeCp_2]^0$,

$$\Delta G_{solv}(II) = SCFE_{(solv)}(II) - SCFE_{(g)}(II)$$

with homologous calculations for $[FeCp_2]^+$ we can obtain $\Delta G_{solv}(III)$

6 Redox Potential

Once we have done all these calculations we are ready to calculate $\Delta G_{ox(sol)}$ and obtain $E_m^{(0/+)}$ for $[\text{FeCp}_2]^{0/+}$, make sure all the units are consistent. The values obtained in Gaussian for this exercise are in Hartree.

These are the values I obtained for $[\text{FeCp}_2]^0$:

```
SCF(g) (II) :      SCF Done:  E(UB3LYP) = -510.439067386
SCF(solv) (II):   SCF Done:  E(UB3LYP) = -510.444248948
GibbsCorr (II):  Thermal correction to Gibbs Free Energy= 0.134232
```

These are the values I obtained for $[\text{FeCp}_2]^+$:

```
SCF(g) (III) :      SCF Done:  E(UB3LYP) = -510.170289413
SCF(solv) (III):   SCF Done:  E(UB3LYP) = -510.239713457
GibbsCorr (III):  Thermal correction to Gibbs Free Energy= 0.132483
```

which led me to a value of $E_m^{(0/+)} = 5.52$. When comparing this result to the experimental value ($E_m^{(0/+)} = 5.3$ V), reported by Connelly and Geiger *Chem. Rev.***1996**, *96*, 877-910, you will realize that these kind of calculations might be very dependent on the level of theory and basis set. In fact, the following table includes results of calculations with larger basis sets, for different solvents.

Basis(Fe/C and H)	Acetonitrile	DMSO	DCM
LACVP/6-31G	5.172	5.160	5.340
LACVP/6-311G*	5.135	5.124	5.304
LACVP/cc-pVTZ(-f)	5.086	5.078	5.256

Notice that the values for DMSO obtained with these larger basis sets are in better agreement with the experimental value than the value obtained with the LAN2DZ basis set for Iron and D95V basis set for Carbon and Hydrogen; D95V which is a considerable smaller basis. Therefore, it is important to run benchmark calculations to ensure that the level of theory and basis sets are judiciously chosen before exploring unknown complexes.