

State transition and rate constant

Pérez Alvarado Luis Raymundo, School of Chemistry, UNAM

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Abstract

Introduction

Hartree-Fock(HF) is one of the most famous methods of approximation to the determination of the wave function and energy for a quantum many-body system.[1]

HF approximation is used to solve the Schrödinger equation, this is the general form.

$$\hat{H}\Psi = E\Psi \quad (1)$$

The Hamiltonian operator in Schrödinger equation independent of time.

$$\hat{H} = \frac{n^2}{2} \sum_{\alpha} \frac{1}{m\alpha} \nabla_{\alpha}^2 - \frac{n^2}{2m} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\alpha > \beta} \frac{z_{\alpha} z_{\beta} e^2}{r_{\alpha\beta}} \quad (2)$$
$$\sum_{\alpha} \sum_i \frac{z_{\alpha} e^2}{r_{\alpha i}} + \sum_i \sum_{i > j} \frac{e^2}{r_{ij}}$$

Where the last term of the equation (2) represents the repulsion of electrons and does not have an exact solution, in the approximation made in HF it is proposed that each electron be considered an average density of all the others electrons.[2][3]

The difference between the exact nonrelativistic energy (E_{nonrel}) and the energy using HF (E_{HF}) is called correlation energy (E_{corr}), this term is a consequence of the repulsion of n electrons.[4]

$$E_{corr} = E_{nonrel} - E_{HF} \quad (3)$$

The enthalpy of formation (ΔH_f) calculation is an example of the things that can be done using computational chemistry, solving equation (1) the thermodynamic properties can be calculated and use in Hess's law to obtain ΔH_f . [5]

$$\Delta H_{formation} = \Delta H_{fproducts} - \Delta H_{freactives} \quad (4)$$

Methods

The modeling of the systems CH_4 , $\cdot OH$, TS , $CH_3\cdot$ and H_2O was performed with gaussView separately.

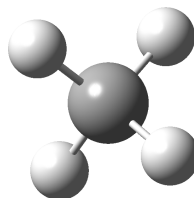


Figure 1: Methane.

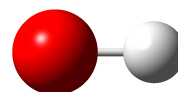


Figure 2: Hydroxyl radical.

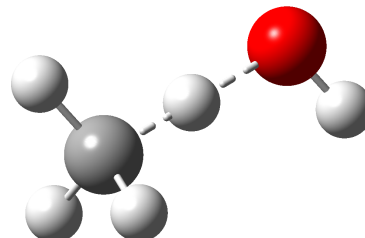


Figure 3: Transition state.

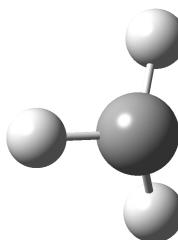


Figure 4: Methyl radical.

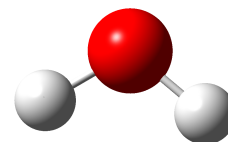
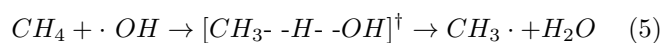


Figure 5: Water.

In the input file with extension .gjf /.com, the following settings was used for F and F_2 to perform a calculation with the HF method.



The global reaction is describe in 5

```
//hardware configuration
% nprocshared=4
% mem=1500MB
//parameters for Hartree-Fock method
# opt freq HF/6-31+g(d)
```

The calculations of the F and F_2 systems were performed with HF.

After finish calculations with HF, the procedure was repeated with B3LYP and MP2 methods, and use the same hardware configuration and the same base set and just change the method.

```
//parameters for B3LYP method
# opt freq B3LYP/6-31+g(d)
//parameters for MP2 method
# opt freq MP2/6-31+g(d)
```

NOTE: In the case of F is not necessary to use opt configuration because does not need geometry optimization.

Results

Through the data calculated in table 2, the reaction profile was plotted (Fig 2)

Graph 1 Free energy VS Reaction coordinate

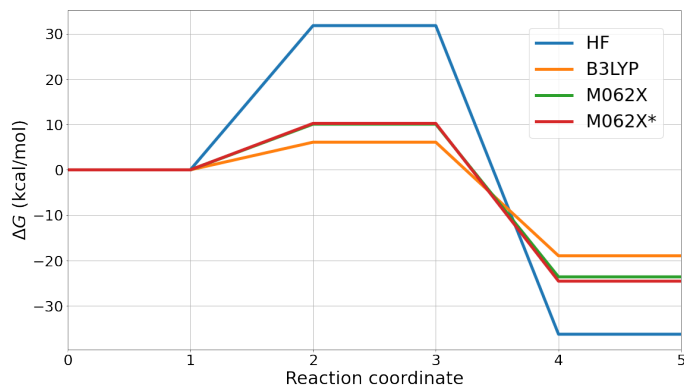


Figure 6: Profile reaction.

Through the data calculated in table 2, the reaction profile was plotted (Fig 1)

Graph 2 Enthalpy VS Reaction coordinate
asdasd

Table 1 ETE values for HF, B3LYP, and MP2 methods using the 6-31G basis set and time(t) of each calculation.

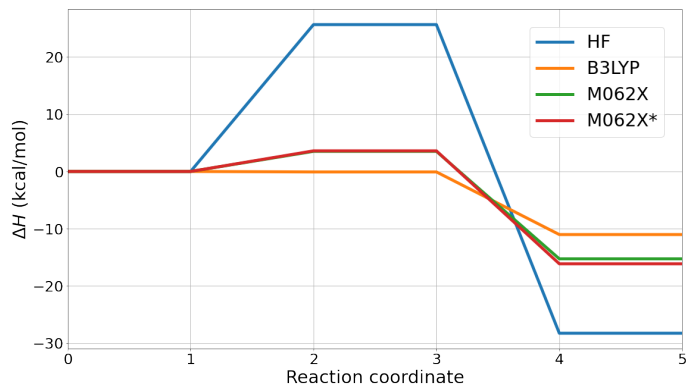


Figure 7: Profile reaction.

Using equation (4) the enthalpy of formation of the F_2 is calculated.

$$\Delta H_{f(F_2)} = \Delta H_{F_2} - 2\Delta H_F$$

Using the factor of conversion $627.509 \frac{kcal}{mol}$ [6] H_E units of ΔH_f are converted into $\frac{kcal}{mol}$.

Knowing a reference value that is $-158.739 \frac{kJ}{mol}$ [7] the error percentage is calculated for each method.

Table 2 Enthalpy of formation of F_2 calculated with HF, MP2, and B3LYP methods and his percentage error.

Method	$\Delta H_{f(F_2)}(H_E)$	$\Delta H_{f(F_2)}(\frac{kcal}{mol})$	%Error
HF	0.060	37.705	47.653
MP2	-0.054	-34.262	2.316
B3LYP	-0.055	-34.577	2.117

NOTE: The reference value was used in $\frac{kcal}{mol}$ in the determination of $\%Error = \frac{|valCalc - valRef|}{valRef} \cdot 100\%$, and all decimals were used during the calculations, but was rounded to 3 significant decimal places.

Discussion

Comparing the percentage of error of each method can see those post-HF methods, in this case, B3LYP is based in *density Functional Theory*(DFT) and MP2 based in *Perturbation Theory* have an acceptable error, but the error of the HF method is not acceptable at all!, this is because HF does not consider the E_{corr} , and this is the reason why **HF** it is **useless** for the calculation of systems with more than one electron.

In this particular case to calculate the thermodynamic properties of F_2 and F the best method using the set of bases 6-31G is **B3LYP** considering that the percentage error is the lowest compared to the others two and has a low computational cost.

References

- [1] Wikipedia, “Hartree–fock method.” https://en.wikipedia.org/wiki/Hartree%E2%80%93Fock_method.
- [2] L. van Dommelen, “The hartree-fock approximation.” http://eng-web1.eng.famu.fsu.edu/~dommelen/quantum/style_a/hf.html.
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- [4] I. N. Levine, *Quantum Chemistry 7th*, p. 298. PEARSON, 2013.
- [5] S. Cohen, “Hess’s law.” [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Thermodynamics/Thermodynamic_Cycles/Hesss_Law](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Thermodynamic_Cycles/Hesss_Law).
- [6] Wikipedia, “Hartree.” <https://en.wikipedia.org/wiki/Hartree>.
- [7] A. T. Tables, “Enthalpy of formation of f_2 .” [https://atct.anl.gov/Thermochemical%20Data/version%201.122/reaction/?&species_number\[\]=6&species_number\[\]=20&c1=-1&c2=2](https://atct.anl.gov/Thermochemical%20Data/version%201.122/reaction/?&species_number[]=6&species_number[]=20&c1=-1&c2=2).