

Course on Density Functional Theory (69609) - Final Projects

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I. COMPUTATIONAL PROJECT

This first part of the project has to be handed in separately by each student.

A. Basic Notions

1. Basis sets

Write a *short* essay on the logic behind the construction of basis sets. You can use one of these books: [1–3]. You may also find the following reference useful: <http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/basis-sets.pdf>. You can use iQMOL/QCHEM [4] calculations for experimenting with these basis functions to demonstrate the points. Please explain concepts like: primitive Gaussian functions (GFs), contractions (CGFs), explain how contractions are built in the various approaches and the logic behind the ideas. Your short review should touch on the following points:

1. Minimal basis sets (for example STO-3G).
2. Pople basis sets: Split valence double and triple zeta functions (for example 4-31G etc), including polarized and diffuse basis sets (example: 6-31G**,6-311+G**).
3. Correlation consistent polarized (ccp) basis sets.

2. Functionals

You can get a brief sense of functionals and their properties in the review of ref. [5]. Please write a short paragraph on LDA, GGA (e.g. BLYP and PBE) and hybrid (e.g. B3LYP) functionals. You can use other sources existing on the internet.

B. Computations on fluoroethylene and substituents

1. Basis set “convergence”

Determine the geometry of fluoroethylene ($\text{H}_2\text{C} = \text{CHF}$) in the basis 6-31G* using B3LYP calculations

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Table I. The systems to be studied.

R	Molecule	Name
H	$\text{H}_2\text{C} = \text{CH}_2$	Ethylene
F	$\text{H}_2\text{C} = \text{CHF}$	Fluoroethylene
OH	$\text{H}_2\text{C} = \text{CHOH}$	Vinyl alcohol
CH_3	$\text{H}_2\text{C} = \text{CHCH}_3$	Propene
NH_2	$\text{H}_2\text{C} = \text{CHNH}_2$	Vinylamine

and then, at this frozen geometry and using the basis sets: STO-3G, 3-21G, 6-31G*, 6-311+G**, cc-pVDZ, cc-pVTZ, and cc-pVQZ each of these has a set of M functions for the molecule. Then study the following topics:

1. **CPU time vs M:** Plot the CPU time (computation time) as a function of M on a log-log plot. Explain qualitatively the behavior. Assuming the CPU time as a function of basis size is of the functional form $T(M) = A \times (M - M_0)^n + T_0$ (what is meaning of each constant?) determine n and A and T_0 ?
2. **Energy vs M:** Plot the energy $E(M)$ as a function of basis-set size M and the relative error $r(M) = 100 \times \frac{E(M) - E(\infty)}{|E(\infty)|}$ vs M . You will need to estimate what $E(\infty)$ is. Usually this is done by assuming a functional form and fitting. You can experiment with some forms, for example, $E(M) = E(\infty) + e^{-\beta(M - M_0)}(E_0 - E_\infty)$ or $E(M) = E_\infty + (E_0 - E_\infty) \left(\frac{2M_0}{M + M_0}\right)^n$ (for this analysis to me useful, take $M_0 < M_{max}/10$ where M_{max} is the largest value of M you are using. If one wants the fastest possible calculation with basis-set error $< 0.05\%$, which basis should one work with? For the rest of the calculations use this basis set.
3. **Dipole moment:** Using B3LYP at the geometry in the basis of the previous subsection, calculate the dipole moment μ vector as a function of M . Compare the convergence of the dipole moments with M to that of the energy. Can you explain the difference? Compare to the experimental dipole (1.4 D).

2. Substituents

Consider the following substituents of the type $\text{H}_2\text{C} = \text{CHR}$ where R is given in Table I.

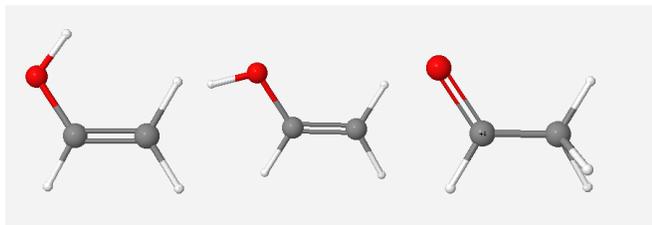


Figure 1. The conformers for R=OH.

For these systems, determine the stable structures, bond lengths and angles [QCHEM creates the z-matrix for you] (using B3LYP and the 6-31G* basis set). Please determine and discuss the effect of substituent R on:

1. The CC bond length; is there a correlation between the charge on R (use QCHEM's population analysis to determine this) and this bond length? Try to explain, especially note the case of $R=F$.
2. The ionization energy

3. Conformers

Note that substituents may have several low-energy conformers. Please try to explore them (one or two examples are enough); for example, for the $R = OH$ system there are 3 conceivable conformers shown in Fig. 1. Estimate the conformer relative abundance at 300K and 1000K (i.e. their ratio of concentration or partial pressure).

II. READING AND PRESENTING A PAPER ON DFT BASICS

For this second part of the project, you need to study a DFT topic and prepare a 20 min talk presenting the background, the questions, and the main conclusions. I can help if you need to consult. Please choose one of the below-listed topics, let me know your choice, and wait for me to approve. I strive for each talk to cover a different matter, and I tend to assign issues using a first-come, first-serve approach.

List of topics:

1. Exchange-correlation holes: how they explain the success of functionals. Jones [6], Burke [7], Pribram-Jones *et al.* [8]. You can read about the adiabatic connection in my notes (chapter 5.4).
2. The basics of density functional theory for electronic systems in thermal equilibrium. Argaman and Makov [9], Mermin [10].
3. Beyond LDA: the generalized gradients approximation Perdew *et al.* [11].
4. Density functional theory with correct long-range behavior. Baer and Neuhauser [12] You can read about the adiabatic connection in my notes (chapter 5.4).
5. The basic idea behind Becke's hybrid functional (B3LYP) Becke [13]. You can read about the adiabatic connection in my notes (chapter 5.4)
6. Density functional calculations using a stochastic approach Baer *et al.* [14], Cytter *et al.* [15], Fabian *et al.* [16]

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- [3] F. Jensen, *Introduction to computational chemistry* (Wiley, Chichester ; New York, 1999).
- [4] Please download the app iQMOL (<http://iqmol.org/>) and this can be used for all calculations.
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- [14] R. Baer, D. Neuhauser, and E. Rabani, *Physical Review Letters* **111**, 106402 (2013).
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