

Assignment A04: Molecular Orbitals & Configuration Interaction (CI) Methods

The central and most critical choice in any computational study concerns the choice of the theoretical method employed for the computations. In general, the better the electron correlation treatment of the theoretical method the better! Yet, the choice of basis set and the choice of theoretical method are the two major variables that determine overall computational demand. There are practical limits to the choice of the theoretical level (method/basis set) that constrain both the choice of the method and the choice of the basis set and one tends to work at a theoretical level that balances desired accuracy and computational demand. It is the primary purpose of Assignment A04 to learn about **Configuration Interaction (CI) theory**, **Møller-Plesset Perturbation theory (MPx)**, and about one popular **Density Functional Theory (DFT)**, method **B3LYP**, and to explore theoretical level effects on structures and energies for a simple reaction. In addition, it is another important purpose of A04 to expand your inventory of tools for electronic structure analysis by learning about molecular orbitals (core, valence, virtual).

The same set of specific tasks will be executed with several theoretical levels for one simple reaction. The reaction can be an isomerization (i.e., HNC/HCN, H₂C=C/HCCH, H-CO-NH₂/HO-CH=NH,...), a nucleophilic substitution (i.e., F⁻ + H₃C-Cl, H₃N + H₃CCl,...), a polar addition reaction (i.e., H₂O + CO₂, H₃N + CO₂, H₂O + H₂CO,...), or another reaction so long as the system is not too large or too complicated. The CI methods used here all start with the RHF reference wave function. **Assignment A04 builds on your work in Assignment A03.** The tasks are **(a)** to optimize the structures and perform vibrational analyses for substrates, products, and the transition state structures at commonly used entry-level correlated levels, **(b)** to perform “single-point energy” computations at higher correlated levels, and **(c)** to compute and plot selected molecular orbitals of formaldehyde.

The notations **M1**, **M2**, **TS**, **N**, **L** and **A-B** are used as in A03. As with A03, for the remainder of the description of tasks, we will consider an isomerization and simply refer to substrates and

products as **M1** and **M2**, respectively. You might also have to consider reagent **N** and leaving group **L** or reagent **A-B** in your work on A4.

(a) Reaction at RHF, MP2(full), MP2(fc), CISD(fc), and B3LYP With 6-311++G Basis**

Set. You already located the stationary structures **M1**, **M2** and **TS** for your reaction at the RHF/6-311++G** level in A03. Now optimize the stationary structures again and compute their vibrational frequencies with the same basis set but with the correlated methods. Use the highest possible symmetry. Request tight structure convergence criteria (“opt=tight”). Add the command “GFP” to the command line. No need to perform PES scans to explore the transition state region; start these TS searches with one of the TS structures you already determined in A03. (You may perform IRC computation at the new levels if you like, but that is not required.)

Note that “full” and “fc” request computations in the full active space and using the frozen core approximation, respectively. In the “Gaussian Calculation Setup” menu, note the “Include all electrons” option under “Methods” once you select “MP2”. Generate the GJF file for the CISD(fc) jobs by editing the respective files for the MP2(fc) jobs.

(b) Reaction Energies Based on Higher-Level Single-Point Energies. Perform single-point energy (SPE) computations at the Method2/Basis-Set2//Method1/Basis-Set1 level, where “Method2/Basis-Set2” describes the method and the basis set employed in an energy computation which is performed with the “Method1/Basis-Set1” optimized structure.

Using the MP2(full)/6-311++G** optimized structures, compute single-point energies at MP3(full), MP4(SDTQ,full), and CCSD(full) with the 6-311++G** basis set for **M1**, **M2** and **TS** (and **N**, **L**, **A-B** as needed).

Using the MP2(full)/6-311++G** optimized structures, compute CCSD(full) single-point energies for **M1**, **M2** and **TS** (and **N**, **L**, **A-B** as needed) with a basis set of your choice which is larger than the 6-311++G** basis set.

(c) Core-MOs, Valence-MOs, LUMO and LUMO+1 of Formaldehyde at RHF/6-311++G**

Level. Use the wave function of the RHF/6-311++G** optimized structure. Load the CHK file into *GaussView* and compute the MOs using the “Surfaces and Contours” menu and using “medium” grid size. Save the “CUBE” files. Plot each MOs with an isodensity value of 0.004 electrons/au⁻³. Save the MO image to file.

(d) Write-Up. Submit one Word file “A04_‘your_last_name(s)’.docx”. The file must contain a discussion followed by two Tables and two Figures (see below). Each Table and each Figure with its legend on a separate page. Use page breaks and section breaks as needed. Compute relative energies in an XL file “A04_‘your_last_name(s)’.xlsx” (this file will be an updated version of “A03_‘your_last_name(s)’.xlsx”) and submit this file only to the instructor.

In **Table 1**, list the theoretical level in column 1 and list total energies of **M1**, **M2** and **TS** in columns 2 – 4 in Hartree to 6 digits; one row for each theoretical level. Write a table title and appropriate column headers. In column 1, use “Method2/Basis-Set2//Method1/Basis-Set1” as needed. Build Table 1 by adding the new data to Table 1 of A03. For a nucleophilic substitution reaction, you need to add two columns for **N** and **L**. For a polar addition reaction, you need to add one column for **A-B**.

In **Table 2**, list the theoretical level in column 1 and list reaction energies (isom.: **M2** vs. **M1**; SN-rxn.: **L** + **M2** vs. **M1** + **N**; Add-rxn.: **M2** vs. **M1** + **A-B**) and activation energies (isom.: **TS** vs. **M1**; SN-rxn.: **TS** vs. **M1** + **N**; Add-rxn.: **TS** vs. **M1** + **A-B**) in columns 2 and 3 in kcal/mol and to 2 digits; one row for each theoretical level. In column 1, use “Method2/Basis-Set2//Method1/Basis-Set1” as needed. Build Table 2 by adding the new data to Table 2 of A03. Write a table title and appropriate column headers.

In **Figure 1**, show images of your “best structures” of **M1**, **TS**, and **M2**. Decide what you consider to be the highest level structures among the structures you determined with the methods MP2(full), MP2(fc), CISD(fc), and B3LYP and with the 6-311++G** basis set. Use the Table feature of Word (a three cell table). Write a figure legend.

As with A03: Display molecule with “Ball & Stick”, scale radii to 65%, save TIF files (enlarge 2x, “White Background”) and insert cropped TIF files into Word file as “enhanced metafile”.

In **Figure 2**, show images of the occupied MOs and of LUMO and LUMO+1 computed for H_2CO at RHF/6-311++G**. Use the Table feature of Word (table with 2 columns and 5 rows, most stable MOs in bottom row). Figure 2 *must fit* on one page. Write a figure legend.

Computation Times. In your XL file (but not in Table 1), include the computation times (in hours to at least 1 digit; 1.5 h equals 1 hour and 30 minutes) for **M1**, **M2** and **TS**. Add those three numbers and use them as “total time” for computation of your reaction at that level. (Computation of **N**, **L** and **A-B** are relatively fast and we need not keep track of those times.)

In your **Discussion**, very briefly describe what you did and what theoretical dependencies you found for the stationary structures, the reaction energies, and the activation energies. Refer to Tables 1 and 2 and to Figure 1 in the discussion at the most appropriate location. Comment on the computation times needed for the various levels. Cite the correct references for the methods and for the basis sets used as endnotes at the end of the Discussion section. Explain Figure 2 using the terms core MO, valence MO, virtual MO, HOMO and LUMO, and explain the terms “full active space” and “frozen core approximation” for this specific example.

Submission & Deadlines: Submit both the “A04_‘your_last_name(s)’ .docx” file and the “A04_‘your_last_name(s)’ .xlsx” file as attachments to email on Tuesday, 10/04/16 by midnight. Bring one (stapled) hardcopy of the “A04_‘your_last_name(s)’ .docx” file only to class on Wednesday, 10/05/16, for evaluation by peer review.