Assignment A03: Basis Sets: Exponents and Contraction Coefficients

One very important choice in any computational study concerns the choice of the basis set employed for the computations. In general, the larger the basis set the better! Yet, there are practical limits that constrain the choice of basis set and one tends to work with a basis set that balances accuracy and computational demand. So far, we have been using the entry-level 6-31G* basis set, a widely used polarized split-valence basis set. It is the primary purpose of Assignment A03 to learn about basis sets (collections of exponents and contraction coefficients) and to explore the effects of the basis set choice on a simple reaction (basis set effects on structures and energies). In addition, it is another important purpose of A03 to expand your inventory of tools for potential energy surface analysis by learning about transition state structure searches and the determination of intrinsic reaction paths (IRC).

The same set of specific tasks will be executed with five basis sets for one simple reaction. The reaction can be an isomerization (i.e., HNC/HCN, H_2C=C/HCCH, H-CO-NH_2/HO-CH=NH,…), a nucleophilic substitution (i.e., F^- + H_3C-Cl, H_3N + H_3CCl,…), a polar addition reaction (i.e., H_2O + CO_2, H_3N + CO_2, H_2O + H_2CO,…), or another reaction so long as the system is not too large or too complicated. The tasks are **(a)** to locate the substrates and products and to compute their vibrational frequencies, **(b)** to find the transition state region with a suitable PES scan, to locate the transition state structure **TS** and to compute its vibrational frequencies, and **(c)** to determine the intrinsic reaction paths (IRC) connecting **TS** with substrates and products. For isomerization reactions, the minima **M1** and **M2** are the two isomers. In the case of a nucleophilic substitution, the minima **M1** and **M2** are the substrate and the product, respectively, and you also need to study the nucleophile reagent **N** and the leaving group **L**. In the case of a polar addition, the minima **M1** and **M2** are the substrate and the product, respectively, and you also need to study the molecule **A-B** that is being added to the substrate. Perform all of the tasks at the RHF level in conjunction with different basis sets. The purpose of A03 is to learn about basis sets and basis set effects. (Method effects will be explored in Assignment A04.)

For the reminder 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**.

(a) Reaction at RHF/6-31G* Level. Optimize the structures of **M1** and **M2** and compute their vibrational frequencies. Use the highest possible symmetry. Here and in all other optimizations in A03 (minima and transition state structures), request tight structure convergence criteria by adding the command "opt=tight". Mark "Use tight convergence criteria" in the "Job Type" menu of *GaussView*, or edit the GJF file and add "opt=tight" directly to the command line. Here and in all other optimizations in A03, add the command "GFP" (Gaussian function print) so that the basis set information will be printed to the LOG file. Write "GFP" in the "Additional Keywords" field of *GaussView* and type update, or edit the GJF file and add "GFP" directly to the command line.

A good initial guess structure is needed for the determination of the transition state structure **TS**. Identify an internal coordinate that will change significantly as the reaction proceeds from **M1** to **M2**, (i.e., HNC angle or HCN angle, H-N bond length or H-C bond length) and perform a PES scan along this coordinate (cf. A02). Select the structure in the transition region of the scan that is highest in energy (closest to the top of the scan profile) as your initial guess structure for the optimization of the transition state structure. Locate the transition state structure **TS** and compute its vibrational frequencies using "Opt+Freq" as "Job Type", optimizing to "TS (Berny)", and with the calculation of force constants at the initial structure ("Once").

The IRC computation requires the optimized structure of the transition state and the force constants of the transition state structure. One can read these data from the CHK file of the TS optimization (and you will learn how to do this later). For now, use the optimized TS structure in the GJF file of the IRC job, select "IRC" in "Job Type", request to follow the IRC in both directions (to **M1** and to **M2**), and re-compute the forces in the IRC job ("Calculate Once").

You will quickly accumulate a large number of files and it is important that you use systematic names that inform about level and system. For example, use "L1_optf_M1.gjf" for the **M1** search at your first level (i.e., RHF/6-31G* here). Use "L1_TS-scan.gjf", "L1_optf_TS.gjf", and "L1_TS-IRC.gjf", respectively, to scan the transition stage region, to locate **TS**, and to perform that IRC computation, respectively.

(b) Reaction at Levels RHF/6-311G*, RHF/6-311G, and RHF/6-311++G**.** Perform all of the tasks of part (a) again with the polarized triply-split valence basis sets without and with diffuse function augmentation.

(c) Reaction at RHF/DZP Level Using Basis Set Exchange Data and General Basis Set Input. Perform all of the tasks of (a) one more time with the "DZP + Diffuse (Dunning)" basis set available at the Basis Set Exchange. Add the basis set information for every element in your system to the GJF input file. Refer to the Gaussian online manual for input format.

(d) Write-Up. Submit one Word file "A03_'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 and generate IRC plots in an XL file "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 of five theoretical levels. Write a table title and appropriate column headers. 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. Write a table title and appropriate column headers.

In **Figure 1**, show images of your highest-level structures of **M1**, **TS**, and **M2**. Use the Table feature of Word (a three cell table). Write a figure legend. No need to show **N**, **L**, or **A-B**.

Generation of images of molecular models: Display molecule with "Ball & Stick", scale radii to 65%, generate image as TIF files with "Save Image File…" in the "Edit" menu (enlarge 2x, "White Background"). Crop TIF files. Insert image into Word file as "enhanced metafile".

In **Figure 2**, show unmarked plots of internal coordinate scan, indicate the position of the **TS** with marks (kcal/mol, relative to **M1**, **M1** + **N**, or **M1** + **A-B**), and indicate the position of the substrate **M1** (isomerization) and product **M2** (isomerization and addition). Show all levels in the same Figure. Use different color and different marks for each level. Use minor and major tick intervals, label axes. Do this in Excel and then insert XL graphs into Word file as "enhanced metafile" or as "PDF". Write a figure legend.

In your **Discussion**, very briefly describe what you did and what basis set dependencies you found for the stationary structures, the reaction energies, and the activation energies. Refer to Tables 1 and 2 and to Figures 1 and 2 in the discussion at the most appropriate location. Cite the correct references for the basis sets used as endnotes at the end of the Discussion section. No need to explain the methods; assume you write for computational chemists (and no need to cite references about the methods in this assignment).

The rubric for A03 differs very slightly depending on the type of the reaction (Table 1 & Fig. 2).

Submission & Deadlines: Submit both the "A03_'your_last_name(s)'.docx" file and the "A03_'your_last_name(s)'.xlsx" file as attachments to email on Tuesday, 09/27/16 by midnight. Bring one (stapled) hardcopy of the "A03_'your_last_name(s)'.docx" file only to class on Wednesday, 09/28/16, for evaluation by peer review.