Advanced Electronic Structure Theory

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These exercises are intended to help you digest some of the concepts presented in the lectures and to gain practical experience running calculations using the Turbomole program package.

Preparing input and running Turbomole

1. Log on to the place where the calculations are to be performed (details will be given during the session).
2. Prepare a fresh directory in which to set up the input files and to run the calculation. As a rule of thumb, each new calculation should be set up and run in a new directory to avoid contaminating a the new calculation with the restart files from a previous one.
3. The Turbomole package is a set of executables that each does a specific task. For example: the `dscf` executable runs self-consistent-field calculations including HF and DFT; the `grad` executable computes the gradient of the HF or DFT energy for geometry optimisation; the `ccsdf12` executable computes the correlation energy using the CCSD(T) or CCSD(T)(F12) methods; plus many more… For a full description, please refer to the manual pages http://www.turbomole-gmbh.com/turbomole-manuals.html
4. Each executable takes its input from the `control` file, which is rather complicated to set up by hand. Fortunately, there is an interactive program `define` that creates the `control` file for you. Alternatively, you can use the GUI TmoleX.
5. Run `define` by typing `define` in the command prompt and follow the on-screen instructions to set up the `control` file in the chosen directory. Alternatively, use TmoleX to create the `control` file.
6. In that directory, run the relevant executables, piping the output to file for future reference. E.g., to compute a DFT energy, type `dscf | tee dscf.out`

Exercise : IP and EA of the F atom

Goal: To compare the accuracy and basis set dependence of DFT and CCSD(T) for predicting the very simple example of the ionisation potential and electron affinity of the F atom, which are measured experimentally to be 17.423 eV and 3.401 eV, respectively.

1. Compute the energy of F^+ as predicted by B3LYP in a def2-TZVP basis.
   Hints:
   a. Trust the default options
   b. For this simple case, it is easiest to use the `ai` command in the geometry menu
   c. The syntax for specifying the basis is `b all def2-TZVPP`
   d. Use the `eht` option to determine the orbital occupation for the initial guess
   e. Enter 1 when molecular charge is requested (for the cation)
   f. Trust the default orbital occupation provided by `define`
   g. Enter the `dft` menu when it appears and type `dft on` followed by `func b3-lyp`.
   h. When define finishes properly, your directory should contain the files `basis coord control mos`.
   i. Compute the dft energy by typing `dscf | tee dscf.out`

2. Compute the B3LYP/def2-TZVPP energies of neutral F and F^- in a similar way. Thus evaluate the IP and EA of fluorine as predicted by this DFT approximation. Why is the EA so bad? Use the `eiger` command to extracts the MO energy levels from the output files (run in each directory individually). Describe how the DFT description of F^- is qualitatively wrong!
   For experts (*if the above took only you 10 mins to complete*) : try using larger basis sets with more diffuse functions to see if this solves the problem.

3. Compute the IP and EA at the CCSD(T) level using an aug-cc-pVDZ basis and compare them to the B3LYP values and to experiment
   Hints:
   a. Run through define just as for the dft example above.
   b. To save effort, you can load a pre-existing coord file using `a coord`
   c. The syntax for specifying the basis is `b all aug-cc-pVDZ`
   d. Instead of entering the `dft` menu, enter the `cc` menu. In this menu, you need to enter a few submenus to activate the options we want to use (please accept apologies for the inelegance of the input menus at present - work in progress!)
      i. `freeze` to only correlate the electrons in valence orbitals
      ii. `cbas` to pick up the correct density fitting basis
      iii. `method ccsd(t)` to active this method
   e. Compute the CCSD(T) energy by first typing `dscf | tee dscf.out` to perform the HF calculation, then `ccsdf12 | tee ccsdpt.out` to perform the correlation calculation

4. As a byproduct of 3. you have also computed the IP and EA at the HF and MP2 levels of theory. How do these compare?

5. Repeat 3. but using an aug-cc-pVTZ basis. How do the computed IP and EAs change when increasing the basis? Is this basis set dependence also present for the HF energies?

6. The basis set dependence of the correlation energy can be reduced using the extrapolation formula below. Compute a better estimate of the IP and EA using the HF energy from the aug-cc-pVTZ calculations and an extrapolated correlation energy. Here X = 3 and Y = 2 for your aug-cc-pVTZ and aug-cc-pVDZ calculations respectively.

$$E_\infty^{\mathrm{corr}} = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3}$$

7. An alternative and cheaper way to reduce basis set errors is to perform F12 calculations. Compute the IP and EA at the CCSD(T)(F12) level using an aug-cc-pVDZ basis and compare them to the CCSD(T) and B3LYP values and to experiment
   Hints:
   a. For the F12 calculation, specify the basis as `b all YP-aug-cc-pVDZ`. (This is the same orbital basis as aug-cc-pVDZ but is linked to the larger density fitting sets needed for F12).
   b. Enter the cc menu and activate
      i. `freeze` to only correlate the electrons in valence orbitals
      ii. `cbas` to pick up the correct density fitting basis
      iii. `cabs` to pick up the correct F12 auxiliary basis
      iv. `jkbas` to pick up the correct Fock fitting basis
      v. `method ccsd(t)` to active this method
      vi. `f12` to activate the F12 method (leave all options therein as default)
   c. Compute the CCSD(T)(F12) energy by first typing `dscf | tee dscf.out` to perform the HF calculation, then `ccsdf12 | tee ccsdpt-f12.out` to perform the correlation calculation

8. Repeat 7. but with the aug-cc-pVTZ basis.