Manual of quickCBS

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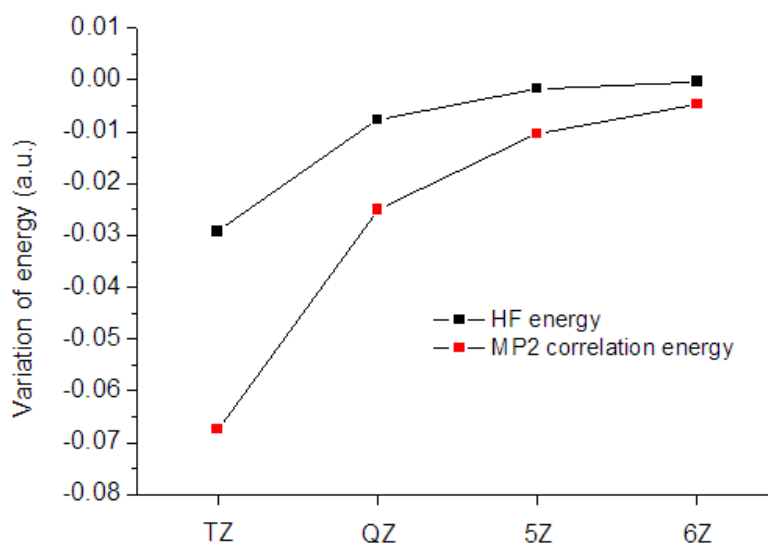
1. Introduction

Extrapolation is a technique to approximately obtain result at higher level of basis set based on the result calculated at two or more lower basis sets. If the aim of extrapolation is to estimate the result at complete basis set (CBS) limit, then it is known as CBS extrapolation. The quickCBS is a simple tool used for easily realizing extrapolation of energy by creating input files and analyzing output files of quantum chemistry program. Currently Gaussian program is supported.

If this tool is employed in your published work, please kindly cite as:

Tian Lu, quickCBS program, http://sobereva.com/soft/quickCBS (accessed month day, year)

2. Theoretical background

For post-HF methods, total electronic energy is sum of self-consistent field (SCF) energy and correlation energy. Because SCF energy and correlation energy have very different convergence behaviors with respect to increase of cardinal number of basis set, the CBS extrapolation formulae for these two kinds of energies are different, as described below. Below map is an illustration of typical convergence of the two energies.

SCF energy extrapolation

L will refer to the highest angular moment in present basis set. For example, cc-pVDZ, TZ, QZ, 5Z ... correspond to L=2, 3, 4, 5 ..., respectively, while def2-SVP, def2-TZVP, def2-QZVP correspond to L=2, 3, 4, respectively

When two basis sets corresponding to $L=M$ and $L=N$ (where $M>N$) are used for extrapolation, the working formula for obtaining SCF energy at CBS limit is

$$E_{\mathrm{SCF}}(\infty) = \frac{E_{\mathrm{SCF}}(M) \times \exp^{-\alpha\sqrt{N}} - E_{\mathrm{SCF}}(N) \times \exp^{-\alpha\sqrt{M}}}{\exp^{-\alpha\sqrt{N}} - \exp^{-\alpha\sqrt{M}}}$$

For example, when cc-pVTZ and cc-pVQZ are used, the M=4 and N=3, the $E_{\mathrm{SCF}}(M)$ and $E_{\mathrm{SCF}}(N)$ corresponds to cc-pVQZ and cc-pVTZ single point energies, respectively.

The parameter α has been fitted by various researchers. For (aug)-cc-pVnZ series, α=4.42 for DZ→TZ extrapolation, α=5.46 for TZ→QZ extrapolation. For def2- series, α=10.39 for def2-SVP→def2-TZVP extrapolation, α=7.88 for def2-TZVP→def2-QZVP extrapolation.

Correlation energy extrapolation

The formula for extrapolating correlation energy to CBS limit is

$$E_{\mathrm{corr}}(\infty) = \frac{E_{\mathrm{corr}}(N) \times N^{\beta} - E_{\mathrm{corr}}(M) \times M^{\beta}}{N^{\beta} - M^{\beta}}$$

For example, when cc-pVTZ and cc-pVQZ are used, the M=4, N=3, the $E_{\mathrm{corr}}(N)$ corresponds to correlation energy at CCSD(T)/cc-pVTZ level, which can be evaluated as $E_{\mathrm{CCSD(T)}}$/cc-pVTZ – E_{HF}/cc-pVTZ.

For (aug)-cc-pVnZ series, β=2.46 for DZ→TZ extrapolation, β=3.05 for TZ→QZ extrapolation. For def2- series, β=2.40 for def2-SVP→def2-TZVP extrapolation, β=2.97 for def2-TZVP→def2-QZVP extrapolation.

All aforementioned parameters can be found in ORCA manual.

The sum of SCF energy and correlation energy at CBS limit corresponds to full single point energy at CBS limit, which is needed in practical studies.

$$E_{\mathrm{full}}(\infty) = E_{\mathrm{SCF}}(\infty) + E_{\mathrm{corr}}(\infty)$$

More knowledge about extrapolation can be found in Section 5.9 of Introduction to Computational Chemistry (3ed, 2017) and my blog article "On the basis set extrapolation of energy" (http://sobereva.com/172).

3. Usage of quickCBS

quickCBS makes the calculation of CBS extrapolated energy based on Gaussian as easy as possible. In the program package, the "quickCBS" without suffix is Linux version, the "quickCBS.exe" is Windows version.

Please first open the *settings.ini* in quickCBS folder and check the comments, which describe meaning of each option. Under the default setting, the quickCBS performs CBS extrapolation using

aug-cc-pVTZ and aug-cc-pVQZ at CCSD(T) level.

Example 1: aug-cc-pV(TZ→QZ) extrapolation at CCSD(T) level

Below I use water molecule as example to briefly show how to use quickCBS.

Write a Gaussian input file of water molecule with name *H2O.gjf*, put it into the folder of quickCBS. The content of the file should like below, note that no keyword should be given

```
%mem=1500MB
%nproc=4
#

test

0 1
O      0.000000    0.118836    0.000000
H      0.756750   -0.475377    0.000000
H     -0.756750   -0.475307    0.000000
```

Boot up quickCBS, input *H2O* and then choose option 1, then press ENTER button to exit the program. You should find *H2O_aug-cc-pVTZ.gjf* and *H2O_aug-cc-pVQZ.gjf* have been generated in current folder. Run them by Gaussian, then put the output files *H2O_aug-cc-pVTZ.out* and *H2O_aug-cc-pVQZ.out* to the quickCBS folder.

Boot up quickCBS and input *H2O* again, then choose option 2, you will find below information on screen

```
Loading H2O_aug-cc-pVTZ.out in current folder
SCF energy =      -76.06018530 a.u.
Full energy =     -76.34232050 a.u.
Correlation energy =       -0.28213520 a.u.

Loading H2O_aug-cc-pVQZ.out in current folder
SCF energy =      -76.06554850 a.u.
Full energy =     -76.36356180 a.u.
Correlation energy =       -0.29801330 a.u.

Alpha value used:     5.46000
Beta value used:      3.05000

SCF energy at CBS limit =           -76.06716445 a.u.
Correlation energy at CBS limit =    -0.30931675 a.u.
Full energy at CBS limit =          -76.37648121 a.u.
```

The meaning of each term is very easy to comprehend. The SCF and CCSD(T) energies are firstly loaded from the Gaussian output files, and then all needed data are automatically derived based on them. The finally outputted -76.37648121 a.u. is just the CCSD(T)/CBS energy.

Example 2: jul-cc-pV(DZ→TZ) extrapolation at MP2 level

Open the *settings.ini* and make below modification (other terms should keep unchanged)

```
CBStype= 1
diffuse= jul-
theory= MP2
fullenelab= MP2=
```

Then redo all steps as the last example, the final output will be

```
Loading H2O_jul-cc-pVDZ.out in current folder
SCF energy =        -76.04056600 a.u.
Full energy =       -76.25896080 a.u.
Correlation energy =      -0.21839480 a.u.


Loading H2O_jul-cc-pVTZ.out in current folder
SCF energy =        -76.06006010 a.u.
Full energy =       -76.32805000 a.u.
Correlation energy =      -0.26798990 a.u.


Alpha value used:      4.42000
Beta value used:       2.46000


SCF energy at CBS limit =              -76.06639990 a.u.
Correlation energy at CBS limit =       -0.29697012 a.u.
Full energy at CBS limit =             -76.36337002 a.u.
```

4. On the calculation of binding energy at CBS limit with consideration of counterpoise correction

At a given basis set, the counterpoise corrected binding energy between A and B in dimer AB can be expressed as

$$E_{\text{bind}} = E_{AB} - E_A - E_B + E_{\text{BSSE}}$$
$$\because E_{\text{BSSE}} = \left(E_A - E_A^{(AB)} \right) + \left(E_B - E_B^{(AB)} \right)$$
$$\therefore E_{\text{bind}} = E_{AB} - E_A^{(AB)} - E_B^{(AB)}$$

where $E_A^{(AB)}$ is energy of monomer A under dimer basis functions at optimized geometry of dimer.

The E_{AB} at CBS limit can be evaluated using quickCBS in the exact way described above. The $E_A^{(AB)}$ at CBS limit can also be easily obtained with help of quickCBS, you only need to write the .gjf file like below (water dimer is taken as example)

```
#

test

0 1
```

```
O          -1.55100712    -0.11452001     0.00000000
H          -1.93425915     0.76250306     0.00000000
H          -0.59967705     0.04071200     0.00000000
O-bq        1.35062510     0.11146901     0.00000000
H-bq        1.68039813    -0.37374103    -0.75856106
H-bq        1.68039813    -0.37374103     0.75856106
```