

Package Manual for gCP

Version 2.01

November 8, 2016

1 Theory

The central idea is to add in a semi-empirical fashion an energy correction ΔE_{gCP} to the energies of molecular (or periodic) systems in order to remove artificial overbinding effects from BSSE.^{1,2} As the focus lies on the contribution of individual atoms a natural outcome is its ability to yield also intramolecular BSSE corrections. The parametrization is constructed such that it approximates the Boys and Bernadi³ counterpoise (CP) correction ΔE_{CP} in the intermolecular case

$$\Delta E_{CP} \approx \Delta E_{gCP} , \quad (1)$$

where e.g. for a complexation reaction $A + B \rightarrow C$ our correction is given by

$$\Delta E_{gCP} = E_{gCP}(C) - E_{gCP}(A) - E_{gCP}(B) . \quad (2)$$

In practice, E_{gCP} can simply be added to the HF/DFT energy

$$E_{total} = E_{HF/DFT} + E_{gCP} . \quad (3)$$

The central equation over all atoms N reads:

$$E_{gCP} = \sigma \cdot \sum_a^N \sum_{\mathbf{T}}' \sum_b^N e_a^{miss} \cdot f_{dec}(r_{ab} + \mathbf{T}) , \quad (4)$$

where the energy e_a^{miss} is a measure for the incompleteness for the chosen target basis set (that is typically small), and $f_{dec}(r_{ab})$ is a decay function that depends on the inter-atomic distance R_{ab} . In molecular systems, the sum over the translation invariant vectors \mathbf{T} is omitted. For periodic systems, a sum over all atompairs inside a supercell is utilized with default distance-cutoff of 60 Bohr analogue to the non-periodic version. The prime (') indicates that for $\mathbf{T} = 0$, $a \neq b$. The scaling factor σ is one out of 4 parameters needed for every <method>/<basis set> combination. Since version 2.01, corrections for three compound methods can be performed, namely HF-3c,^{4,5} PBEh-3c,⁶ and HSE-3c.⁷ In HF-3c, Hartree-Fock is evaluated in a (near) minimal MINIX basis set. The London dispersion is covered by the D3 dispersion correction and the BSSE is corrected by a special gCP parametrization. Additionally, a short-range basis set correction (SRB) is applied

$$E_{SRB} = -\frac{1}{2}s \sum_{a,b}^{pairs} (Z_a Z_b)^{3/2} \exp \left[-\gamma (R_0^{ab})^{3/4} r_{ab} \right] , \quad (5)$$

which corrects some overestimated bond length of electronegative elements. The third correction is automatically added to the gCP energy if the method **hf3c** is invoked. Note that the total gCP-SRB energy can become negative. PBEh-3c is constructed similarly: a modified PBE hybrid functional is evaluated in a double-zeta def2-mSVP basis set. No third pairwise additive correction is needed. However, the gCP is slightly modified by an additional short-range damping to improve the thermochemistry of the compound method.

$$E_{gCP}^{damped} = \sum_a^N \sum_{\mathbf{T}}' \sum_b^N e_a^{miss} \cdot f_{dec}(r_{ab} + \mathbf{T}) \times \frac{1}{1 + 4(r_{ab}/(R_0^{ab}))^{-6}} . \quad (6)$$

The gCP is automatically switched to its damped variant for the method **pbeh3c**. HSE-3c is very similar to PBEh-3c, but the exchange functional from PBE is replaced by a screened exchange variant of the HSE type.⁷ This substantially improves the numerical stability of solid state systems. HSE-3c can be converged with small to vanishing band gaps. As the gCP for PBEh-3c and HSE-3c has been adjusted together with the D3 dispersion correction, the scaling parameter σ could be set to unity.

Small basis sets show not only a large BSSE, but general shortcomings. These effects are not always clearly distinguishable. If computationally affordable, large basis sets (triple- ζ and higher) are always preferable for a given system.

2 Quick Start

Download the tarball from the homepage.⁸ After unpacking the tarball, simply call **make**. The Intel compiler *ifort* and the GNU compiler *gfortran* are semi-automatically detected. If you prefer a different compiler edit the Makefile according to your liking. The code should (and must!) compile without any errors.

The program can be invoked by typing

```
gcp <coordinate-filename> [-options]
```

The coordinates can be given in Turbomole (unit = a.u.) or XMOL (unit = Å) format for molecular calculations and in CRYSTAL (unit = a.u.) and VASP (unit = Å) format for periodic calculations.

3 Changelog

V 2.02

added : parametrization for HSE-3c

V 2.01

added : new compound correction gCP-SRB for HF-3c

added : new damped correction for PBEh-3c

V 1.06

added : new basis sets MINIX, DZP, def-TZVP, cc-pVDZ, aug-cc-pVDZ

added : special method combinations TPSS/def2-SVP, PW6B95/def2-SVP

V 1.05

added : Periodic boundary conditions with energies, atom gradients, and cell gradients.

added : basis set: pob-TZVP

V 1.04

BUG : def2-SVP had wrong parameters for Li,Na,Mg,K. They have been updated. The old parameters set is available as `svp_old`, eg. `gcp coord -l hf/svp_old`

added basis sets: `sv(p)` (=def2-SV(P)) and `sv.x` (def2-SV(P/h,c) which means no polarization fcts on H and C) eg: `gcp coord -l "dft/sv(p)"` (the " " are important)

added ecp-basis set: LANL2DZ for Sc-Zn to be combined with 6-31G(d)

V 1.03 [added] HF/MINIX parametrization. (internal use only)

V 1.02 [added] support for frozen cart. coordinates using Turbomole coordinates files.

V 1.01 [BUG] fixed output in kcal/mol (showed kJ/mol)

4 Program Options

`-level <string>`

Choose one of the implemented `<method>/<basis set>` combinations. If not given, the program expects a parameter file in the home directory (`$HOME/.gcppar.$HOSTNAME`, see below for further information) The following combinations for `<string>` are available:

HF/MINIS	DFT/MINIS
HF/MINIX	DFT/MINIX
HF/SV	DFT/SV
HF/def2-SV(P)	DFT/def2-SV(P)
HF/def2-SVP	DFT/def2-SVP
HF/DZP	DFT/DZP
HF/def-TZVP	DFT/def-TZVP
HF/def2-TZVP	DFT/def2-TZVP
HF/631Gd	DFT/631Gd
HF/def2-TZVP	DFT/def2-TZVP
HF/cc-pVDZ	DFT/cc-pVDZ
HF/aug-cc-pVDZ	DFT/aug-cc-pVDZ
-	DFT/SV(P/h,c)
-	DFT/LANL
-	DFT/pobTZVP
-	TPSS/def2-SVP
-	PW6B95/def2-SVP

The basis sets are:

minis: Huzinaga's minimal basis set in the valence scaled version (EMSL: MINI(S)).

minix: A modified Huzinaga's minimal basis set as defined in.⁹

sv: Ahlrichs' split-valence double- ζ basis set SV.

svx: Ahlrichs' def2-SV(P/h,c) basis set; without polarization functions on H and C.

def2-sv(p): Ahlrichs' def2-SV(P) basis set

def2-svp: Ahlrichs' polarized split-valence double- ζ basis set def2-SVP.

svp_old: Ahlrichs' polarized split-valence double- ζ basis set def2-SVP. Slightly wrong parameters for Li, Na, Mg, K.

dzp: Ahlrichs' polarized full double- ζ basis set DZP **def-tzvp**: Ahlrichs' polarized triple- ζ basis set def-TZVP (first version).

def2-tzvp: Ahlrichs' polarized triple- ζ basis set def2-TZVP (second version).

cc-pvdz: Dunning's correlation consistent double- ζ basis set cc-pVDZ

aug-cc-pvdz: Dunning's augmented correlation consistent double- ζ basis set aug-cc-pVDZ

631gd: Pople's double- ζ basis set 6-31G* (or: 6-31G(d)) without polarization functions on H.

lanl: 6-31G(d) on all main group elements and LANL2DZ on Sc-Zn.

pobTZVP: Solid-state optimized triple- ζ basis set introduced in.¹⁰

Old input like **tz** for the def2-TZVP basis set are still working. For the parametrization of **dft** the hybrid-functional B3-LYP was used, but the corrections will work with essentially any density functional, as the BSSE is rather insensible to the choice of the functional.

For **dft/sv(p)** it is necessary to care about the brackets on the unix command line: Either as **"dft/sv(p)"** or **dft/sv\ (p\)**.

`-pbc`

Use the periodic boundaries, molecular version is the default.

`-grad`

Calculates the gCP gradient. Will be automatically added to the Turbomole-file **gradient** if existent, otherwise the gradient will be written to **gcp_gradient**.

-h

Prints an overview over all program options and other helpful information.

-noprint

Suppress printout.

-parfile

Produce an extended parameter file (see below).

-local

Read a parameter file from the local working directory.

-hess

Perform a numerical hessian calculation using analytical first derivatives. Prints out the resulting hessian matrix in Turbomole format in **gcp_hessian**.

-test

This will stop the program before calculating the energy/gradient, but after the parameter setup. This is useful if you want to check parameters, etc. before the actual run. Additionally, a check is performed if 'steric clashes', i.e. distances below 0.7 Å are existent.

-v

Verbose output. Currently, this prints the gradient into the standard output (stdout, console). The file **gcp_gradient** is not written.

-vasp

Define input as VASP POSCAR file.

-hf3c

Compute combined gCP-SRB correction for HF-3c.

-pbeh3

Compute damped gCP correction for PBEh-3c.

4.1 Using parameter files

Two kinds of parameter files can be read in: A short and an extended version. Both are read from `$HOME/.gcppar.$HOSTNAME` by default. If the option **-local** is specified the file is read in from the current working directory: **.gcppar**

The short version reads in: **basis-keyword sigma eta alpha beta** e.g.:

```
sv 0.2 0.4 0.8 0.9
```

The extended version can be generated by calling **gcp <coord> -parfile -level <method>**. The file **gcp.param** is printed:

```
# comment line
sigma
eta
alpha
beta
nbas emiss (for all elements)
```

This can then be modified and read-in in the usual way. Note that **#** is a keyword used to identify the extended version of the parameter file. Therefore, one must not delete it.

5 Example calls

```
gcp coord -level hf/minis
```

This will do a gCP correction for a HF/MINIS calculation using the coordinates from the file `coord`.

```
gcp water.xyz -level dft/631gd -grad -noprint
```

This can be used to calculate the gCP correction for a B3-LYP/6-31G* calculation, using coordinates from the file `water`. It will also calculate the gradient, and add it to the file `gradient` (a Turbomole file), if existent. Otherwise, the gradient will be written to `gcp_gradient`.

```
gcp STRUC.INCOOR -pbc -level dft/svp -grad -stress
```

This will calculate the gCP correction for a B3-LYP/def2-SVP calculation, using coordinates and periodic boundaries from the CRYSTAL output file `STRUC.INCOOR`. It will also calculate the gradient and cell gradient and write it to the file `gcp_gradient` and `gcp_cellgradient`, respectively.

References

- [1] Kruse, H.; Grimme, S. *J. Chem. Phys.* **2012**, *136*, 154101.
- [2] Brandenburg, J. G.; Alessio, M.; Civalleri, B.; Peintinger, M. F.; Bredow, T.; Grimme, S. *J. Phys. Chem. A* **2013**, *117*, 9282–9292.
- [3] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.
- [4] Sure, R.; Grimme, S. *J. Comput. Chem.* **2013**, *34*, 1672–1685.
- [5] Brandenburg, J. G.; Grimme, S. *Top Curr Chem* **2014**, *345*, 1–23.
- [6] Grimme, S.; Brandenburg, J. G.; Bannwarth, C.; Hansen, A. *J. Chem. Phys.* **2015**, *143*, 054107.
- [7] Brandenburg, J. G.; Caldeweyher, E.; Grimme, S. *Phys. Chem. Chem. Phys.* **2016**, *18*, 15519–15523.
- [8] See website by the group of Prof. Stefan Grimme: <http://www.thch.uni-bonn.de/tc/>.
- [9] Sure, R.; Grimme, S. *J. Comp. Chem.* **2013**, *34*, 1672–1685.
- [10] Peintinger, M. F.; Oliveira, D. V.; Bredow, T. *J. Comput. Chem.* **2013**, *34*, 451–459.