Package Manual for DFT-D3 Ver. 3.2 Rev 0

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1 Treatment of Dispersion Interactions with DFT-D3

1.1 Introduction

DFT-D3 is an atom-pair wise (atom-triple wise) dispersion correction which can be added to the KS-DFT energies (and gradient):[1]

$$E_{DFT-D3} = E_{KS-DFT} + E_{disp} \tag{1}$$

with E_{disp} being the sum of the two- and three-body contributions to the dispersion energy:

$$E_{disp} = E^{(2)} + E^{(3)}. \tag{2}$$

The most important two-body term is given at long range by

$$E_{disp} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n}. \tag{3}$$

In order to match the long- and midrange correlation of D3 with the semilocal correlation computed by the functional, an adequate damping function $f_{n,d}$ must be included. C_n^{AB} denotes the averaged (isotropic) nth-order dispersion coefficient for atom pair AB, and r_{AB} is their internuclear distance. s_n is a functional-dependent scaling factor (see below). D3 has also been successfully coupled to semiempirical electronic structure methods. The program can be invoked by typing

```
dftd3 <coordinate-filename> [-options]
```

The coordinates can be given in Turbomole, XMOL, or VASP format.

1.2 Damping Functions

In order to avoid near singularities for small distances (r_{AB}), the dispersion contribution needs to be damped at short distances. One possible way is to use rational damping as proposed by Becke and Johnson:[2–4]

$$E^{(2)} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n + f(R_0^{AB})^n} \tag{4}$$

with[4]

$$R_0^{AB} = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}} \tag{5}$$

and

$$f(R_0^{AB}) = a_1 R_0^{AB} + a_2. \tag{6}$$

Damping the dispersion contribution to zero for short ranges (as in Ref.[1]) is also possible:

$$E^{(2)} = -\frac{1}{2}\sum_{A\neq B}\sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n} f_{d,n}(r_{AB}) \tag{7}$$

with

$$f_{d,n} = \frac{1}{1+6(r_{AB}/(s_{r,n}R_0^{AB}))^{-\alpha_n}}. \tag{8}$$

Note that the R_0^{AB} used with this damping are from Ref.[1] For more information on the supported damping functions, see Ref.[5] We recommend the Becke-Johnson (BJ)-damping, because it does not lead to artificial repulsive forces.

In 2016, Sherrill and coworkers revised the zero- and BJ-damped D3 methods, improving in particular the short-range behavior of the method.[6] These are termed D3M and D3M(BJ) in the following (where "M" stand for "modified"). In D3M(BJ), the rational damping form of D3(BJ) (see Eqs. 4 and 6) is retained and solely the parameters s_8, a_1, and a_2 are refitted. In D3M, the zero-damping function (see Eq. 8) is modified to:

$$f_{d,n} = \frac{1}{1+6(r_{AB}/(s_{r,n}R_0^{AB}) + R_0^{AB}\beta)^{-\alpha_n}}. \tag{9}$$

While $s_{r,8} = 1$, $\alpha_6 = 14$, $\alpha_8 = \alpha_6 + 2$, and $s_6 = 1$ ($s_6 < 1$ for double-hybrid functionals) are kept fixed, s_8, $s_{r,6}$, and the newly introduced parameter β were refitted.

1.3 Three-body term

It is possible to calculate three-body dispersion contributions with DFT-D3, according to the Axildor-Teller-Muto model:

$$E^{(3)} = -\frac{1}{6}\sum_{A\neq B\neq C} \frac{C_9^{ABC}(3\cos\theta_a\cos\theta_b\cos\theta_c + 1)}{(r_{AB}r_{BC}r_{CA})^3} f_{dmp}(\overline{r}_{ABC}), \tag{10}$$

where θ_a, θ_b and θ_c are the internal angles of the triangle formed by r_{AB}, r_{BC} and r_{CA}. The C_9 coefficient is approximated by:

$$C_9^{ABC} \approx -\sqrt{C_6^{AB}C_6^{AC}C_6^{BC}}. \tag{11}$$

The three-body contribution has a small effect on medium-sized molecules. The damping function $f_{dmp}(\overline{r}_{ABC})$ is similar to equation 8. Here, $\overline{r}_{ABC}$ is the geometric mean of r_{AB}, r_{BC} and r_{AB}.

Three-body contributions can be used with both variants of the two-body term. However, the three-body term itself will always be calculated in the zero damping scheme. For the impact of the three-body contribution on the thermochemistry of supramolecular systems and binding energies of molecular crystals see Refs. 7,8. Usually including the term leads to an improvement of the interaction energy, but has a neglegible impact on

the geometries. The analytical gradient is available from version 3.1. To reduce the cost of the three-body calculation, a consistent cutoff was introduced. All triples, with one distance larger than 40 a.u. are discarded. This reduces the three-body energy by approximately 1%, but speeds up the calculation by two orders of magnitude. Small differences to previous versions may occure due to the reduced cutoff.

1.4 Periodic Systems

For periodic systems the dispersion energy is calculated according to the real-space summation

$$E_{disp} = -\frac{1}{2}\sum_{A}\sum_{B}\sum_{\mathbf{T}}{}'\sum_{n=6,8} s_n \frac{C_n^{AB}}{|r_{AB}+\mathbf{T}|^n}, \tag{12}$$

where r_{AB} is a vector between atoms A and B, and $\mathbf{T}$ is a translation vector of the unit cell. The prime ($'$) indicates that for $\mathbf{T} = 0$, the term with $A = B$ is excluded. Since a periodic system has an infinite number of pairs, a cutoff has to be introduced. Only interactions with $|r_{AB} + \mathbf{T}| < r_{max}$ are considered. As default this cutoff is set to $r_{max} = 95$ a.u. A second cutoff for the calculation of the coordination number (CN) has to be chosen. Since the coordination number is a local property, this cutoff is set to a smaller value of 40 a.u.

1.5 Implemented Functionals

A frequently extended list of parameterized functionals can be found on our web-site.[9] Note that correcting Hartree-Fock (HF) is only recommended with BJ-damping. You can also use your own parameters by creating the file *.dftd3par.$hostname* in your home directory, where hostname refers to the system name of the machine. Alternatively, you can create a file *.dftd3par.local* in the directory where you run your calculation. The layout of these files is:

```
s6 sr6 s8 sr8 alpha6 version
```

for zero-damping (**version** = **3**, note that generally **sr8** = **1**) or

```
s6 a1 s8 a2 alpha6 version
```

for BJ-damping (**version** = **4**). Note that **alpha6** is not used with BJ-damping. If you want to use the old D2 correction with your own parameters, the input is equal to the zero damping, with **version** = **2**. For example,

```
1.0   1.261   1.703     1.0  14 3
```

would result in a calculation with zero-damping and the parameters of the B3-LYP functional. For a constantly updated list of supported functionals, see Ref.[9]
Important: GGA and hybrid functionals should only used with $s_6 = 1.0$ to ensure asymptotically correct behavior.

The modified zero-damping scheme D3M (see Eq. 9) corresponds to **version** = **5** and the format to read-in own parameters is:

`s6 sr6 s8 beta alpha6 version`

1.6 Program Options

`-func <functional name in TM style>`

Choose one of the implemented functionals. No default. For a list of parameterized functionals, refer to our web-site.[9] HF can be invoked by `-func hf`.

`-bj`

Use Becke-Johnson damping.

`-zero`

Use zero-damping.

`-bjm`

Use D3M(BJ), i.e., Becke-Johnson damping with the refitted parameters by Sherrill and coworkers.[6]

`-zerom`

Use modified zero-damping of Sherrill and coworkers (D3M).[6]
If the `-func` option is used, `-bj`, `-zero`, `-bjm`, `-zerom` or `-old` must be chosen.

`-anal`

Performs a detailed analysis of pair contributions. If the file *fragment* with atom numbers (one fragment per line) is found, a fragment based analysis is performed. You can specify atom ranges in your fragment file:

```
2-4
5-7
1,8,9
```

would establish three fragments. Any atoms not specified will be automatically added to an extra fragment.

`-noprint`

Suppress printout.

`-old`

Switch to old DFT-D2 version.[10]

`-grad`

Calculate the D3 gradient. The gradient will be written to *dftd3_gradient* (in a.u.).

`-tz`

Use special parameters for calculations with triple-zeta basis sets. Preliminary results in the SI of Ref.[1] indicate that results are slightly worse than with the default parameters and QZVP type basis sets. This option should be carefully tested and is only available with zero-damping.

`-cutoff <value>`

This defines a cutoff value for the dispersion interaction. The default value is 95 a.u.

`-cnthr <value>`

This defines a cutoff value for the calculation of the CN. The default value is 40 a.u. and sould be kept fixed.

`-pbc`

This keyword switches on the periodic boundary conditions. It has to be given together with an input file in VASP format. The coordinate file has to follow the format of a *POSCAR* file (see Ref. 11).If the element types are not specified in the 6th line (VASP v.5.3), they have to be specified in the first line. If combined with the `-grad` option, an additional file containing the cell gradient in a.u. will be written to *dftd3_cellgradient*.

1.7 Example calls

In the following, we list some example calls of the *dftd3* program.

```
dftd3 coord -func tpss -bj
```

This will calculate a dispersion correction for the **TPSS** functional, with Becke-Johnson damping, using coordinates from the file *coord*.

```
dftd3 POSCAR -pbc -func pbe -bj -grad
```

This will do a dispersion correction for the **PBE** functional, with Becke-Johnson damping and periodic boundary condition. Unit cell and atomic coordinates are taken from the file *POSCAR*. The atomic- and cell gradient are written in the files *dftd3_gradient* and *dftd3_cellgradient*.

```
dftd3 water.xyz -func b3-lyp -zero -anal
```

This will do a dispersion correction for the **B3-LYP** functional, with zero-damping, using coordinates from the file *water.xyz*. It will do a pair-wise analysis of the dispersion contributions as well as a distance-based analysis. If the file *fragment* is found, it will also do a fragment-based analysis of the dispersion energy.

```
dftd3 coord -func pbe -old -grad
```

This will calculate a DFT-D2 correction for the **PBE** functional, using coordinates from the file *coord*. It will also calculate the gradient, and add it to the file *gradient*, if existent. Otherwise, the gradient will be written to *dftd3_gradient*.

References

[1] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

[2] Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *122*, 154101.

[3] Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*, 024101.

[4] Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2006**, *124*, 174104.

[5] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem.* **2011**, *32*, 1456.

[6] Smith, D. G. A.; Burns, L. A.; Patkowski, K.; Sherrill, C. D. *J. Phys. Chem. Lett.* **2016**, *7*, 2197.

[7] Risthaus, T.; Grimme, S. *J. Chem. Theory Comput.* **2013**, *9*, 1580.

[8] Moellmann, J.; Grimme, S. *J. Phys. Chem. C* **2014**, *118*, 7615.

[9] AK Grimme Homepage. `http://www.thch.uni-bonn.de/tc/`.

[10] Grimme, S. *J. Comp. Chem.* **2006**, *27*, 1787.

[11] VASP manual. `http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html`.