

Empirical Dispersion Correction Within ONETEP

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1 Theory

1.1 Energy

The modification to the total DFT energy when correcting for dispersion is given by,

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \quad (1)$$

where the dispersion energy correction is given by [1, 2]:

$$E_{disp} = -\frac{1}{2} \cdot s_6 \cdot \sum_{i=1}^{N_{at}} \sum_{j=1}^{N_{at}} \sum_L^* \frac{C_{6,ij}}{R_{ij}^6} f_{damp}(R_{ij}) g_{smooth}(R_{ij}) \quad (2)$$

where:

- s_6 is a DF-dependent global scaling factor,
- $C_{6,ij}$ is a dispersion coefficient for the atom pair ij ,
- L denotes all translations of the unit cell within the van der Waals radial cutoff R_{cut} ,
- $*$ denotes $i \neq j$ in $L = 0$
- R_{ij} is the distance $|\vec{R}_i^0 - \vec{R}_j^L|$ between atom i in the parent cell $L = 0$ and the atom j in all possible translations L ,
- $f_{damp}(R_{ij})$ is a damping function that is unity at large distances and zero at small distances [2, 3],
- $g_{smooth}(R_{ij})$ is smoothening function for truncating the interactions beyond van der Waals radial cutoff.
- The dispersion coefficients and the form of the damping function are dependent upon the empirical vdW correction model adopted. The damping functions for the different models are given below:

Index	Description	Damping function $f_{damp}(R_{ij})$	vdW radii $(R_{0,ij})$
1	Damping function of Elstner [4].	$(1 - \exp^{-c_{damp}(R_{ij}/R_{0,ij})^7})^4$	$\frac{R_{0,i}^3 + R_{0,j}^3}{R_{0,i}^2 + R_{0,j}^2}$
2	First damping function of Wu and Yang [5].	$(1 - \exp^{-c_{damp}(R_{ij}/R_{0,ij})^3})^2$	$\frac{R_{0,i}^3 + R_{0,j}^3}{R_{0,i}^2 + R_{0,j}^2}$
3	Second damping function of Wu and Yang [5].	$\frac{1}{1 + \exp^{-c_{damp}(R_{ij}/R_{0,ij}-1)}}$	$\frac{R_{0,i}^3 + R_{0,j}^3}{R_{0,i}^2 + R_{0,j}^2}$
4	Damping function of D2 correction of Grimme [3].	$\frac{1}{1 + \exp^{-c_{damp}(R_{ij}/R_{0,ij}-1)}}$	$R_{0,i} + R_{0,j}$

where c_{damp} is a damping constant (referred to as d within the literature of Grimme [3] and c_{damp} by Hill [2]) and $R_{0,ij}$ is determined by the vdW radii of the atomic pair i and j .

- The smoothening function has the following form for all dispersion models:

$$g_{smooth}(R_{ij}) = 1 - e^{-(R_{ij}-R_{cut})^2} \quad (3)$$

- where, R_{cut} is the radial cutoff for van der Waals interactions, and can be set by the following keyword in the input file:
`vdw_radial_cutoff: x units.`
[Real physical, default `vdw_radial_cutoff: 100 bohr`].

1.2 Forces

During geometry optimization, the van der Waals forces are calculated from the derivative of the dispersion energy with respect to the ionic coordinates $\{s_i\}$:

$$\frac{\partial E_{disp}}{\partial s_i} = -\frac{1}{2} \cdot s_6 \cdot \sum_{j=1}^{N_{at}} \sum_L^* \frac{C_{6,ij}}{R_{ij}^6} \left[f(R_{ij})g'(R_{ij}) + g(R_{ij}) \left(f'(R_{ij}) - \frac{6f(R_{ij})}{R_{ij}} \right) \right] \frac{\partial R_{ij}}{\partial s_i} \quad (4)$$

2 Activating the dispersion corrections

Four vdW correction options have been implemented within ONETEP. Activation of the vdW corrections within ONETEP is achieved using the `DISPERSION` keyword followed by the dispersion index. eg. For the D2 correction of Grimme [3],

```
DISPERSION 4
```

The exchange-correlation functionals available with optimized parameters for the dispersion models are given below:

Index	Keyword	Available XC Functionals
1	ELSTNER	BLYP, PBE, PW91, REVPBE, RPBE, XLYP.
2	WUYANG1	BLYP, PBE, PW91, REVPBE, RPBE, XLYP.
3	WUYANG2	BLYP, PBE, PW91, REVPBE, RPBE, XLYP.
4	GRIMMED2	BLYP, PBE, B3LYP.

The $C_{6,ij}$ coefficients and the coefficients of the damping function of dispersion corrections 1–3 are optimized for each xc functional to minimize the root mean square difference of the interaction energy from the literature values for a selection of dispersion-dominant biological complexes from the JSCH-2005 and S22 sets [6] and the database of Morgado [7]. For the D2 correction of Grimme the parameters are optimized as described in the literature [3].

The s_6 parameters are unity for dispersion corrections 1–3 and are fitted by least squares optimization of interaction energy error for 40 noncovalently bound complexes for the D2 correction of Grimme.

In the case of using an unoptimized functional not given within the list, default unoptimized c_{damp} , $C_{6,ij}$) and $R_{0,i}$ values are adopted for the damping functions of Elstner or Wu and Yang as described by Hill [2] and a default s_6 value of 1.00 is adopted for Grimme’s D2 correction model.

3 Overriding dispersion correction parameters

It is possible to override the default parameters of the dispersion damping functions. This option allows the user to specify parameters for elements and functionals for which values are not given. The atom-dependent variables $C_{6,i}$ (used to calculate $C_{6,ij}$), $R_{0,i}$ (related to the atomic vdW radius of an atom i), and n_{eff} (used in the calculation of $C_{6,ij}$ for all damping functions excluding the D2 correction of Grimme) are modified using the `vdw_params` block. This override block applies the parameter changes to atoms by their atomic number (`nzatom`). eg. To override the dispersion parameters associated with nitrogen,

```
%block vdw_params
! nzatom, c6coeff, radzero, neff
7      21.1200  2.6200  2.5100
%endblock vdw_params
```

To override the damping constant c_{damp} associated with a damping function, the keyword `vdw_dcoeff` followed by the modified damping constant parameter is used. eg.

```
vdw_dcoeff 11.0
```

4 Boundary Conditions

The boundary conditions are set by the following keyword:

```
vdw_bc P/O P/O P/O
```

which accepts a string which should contain three characters (which may be separated by spaces), specifying the BCs along the x , y and z directions of the simulation cell. ‘P’ for periodic and ‘O’ for open. In case, the keyword is not specified, BCs set same as `ion_ion_bc`.

References

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