

An overview of calculation schemes for inclusion of dispersion interactions, done in the course of preparing the manuscript published under DOI 10.1063/1.5030539, which description ended up too detailed to be included in the said manuscript.

Andrei Postnikov, andrei.postnikov@univ-lorraine.fr

The last decade has witnessed tremendous effort in development of various correction methods to account for the missing London dispersion interactions in conventional Kohn-Sham DFT calculations. Two types of approaches are used. One can use specific non-local correlation functional that approximately accounts for dispersion interactions, as originally developed by Dion *et al.*¹ and improved in subsequent works.^{2,3} The other group of methods encompasses additive correction schemes, in which dispersion energy is included on top of “conventional” DFT results. These methods (a hierarchy of which is briefly addressed below) typically allow a relatively easy implementation in the codes, and do not increase the calculation time considerably. A number of such schemes became available in the VASP package.^{4–8} We note that there is no implicit potential, band structures etc. associated to these schemes, but just the total energy (elaborated, in some cases, to yield corresponding forces). Consequently, the properties affected concern just the equilibrium geometry.

The need to account for disperse interactions, not automatically included in the current XC schemes, can be met by a number of “technical” solutions. We note however that they are not suggestions for a true XC *functional* with its implicit potential, band structures etc., but just an additional term to total energy (elaborated, in some cases, to yield corresponding forces). The application of the schemes discussed below affects the equilibrium geometry.

In the **DFT+D2** approach of Grimme⁹,

$$E_{\text{DFT+D2}} = E_{\text{DFT}} - s_6 \sum_{\substack{\text{A,B} \\ \in \text{cell}}} \sum'_{\boldsymbol{\tau}} \frac{C_6^{\text{AB}}}{|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|^6} f_{\text{dmp}}(|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|), \quad (1)$$

where the summation is over (A,B) atom pairs, including lattice translations $\boldsymbol{\tau}$ besides those (hence \sum') whereby an atom would interact with itself. The damping function of distance $f_{\text{dmp}}(r)$ will come about in all schemes; its role is to remove the unphysical divergence of $\sim r^{-6}$ at small distances and smoothly pass into a constant at distances where the vdW radii of close atoms would touch. In the original D2 scheme (and in many others since then), the

damping is taken of Fermi-type, $f_{\text{dmp}}(r) = [1 + e^{-d(r/R^{\text{AB}} - 1)}]^{-1}$. The dispersion coefficients

$$C_6^{\text{AB}} = \sqrt{C_6^{\text{A}} C_6^{\text{B}}} \quad (2)$$

and vdW radii $R^{\text{AB}} = R^{\text{A}} + R^{\text{B}}$ are constructed from single-atom parameters; s_6 and d are global constants – see Ref. 4 for details of realisation in VASP.

The **DFT+D3** approach by Grimme *et al.*¹⁰ adds the term inversely proportional to the 8th power of interatomic distance, with appropriately parametrised (and different from that in the DFT+D2 scheme) damping function, that was originally due to Chai and Head-Gordon.¹¹ Moreover, three-atom interactions were suggested to be included:

$$\begin{aligned} E_{\text{DFT+D3}} &= E_{\text{DFT}} - \sum_{\substack{\text{A,B} \\ \in \text{cell}}} \sum'_{\boldsymbol{\tau}} \sum_{n=6,8} s_n \frac{C_n^{\text{AB}}}{|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|^n} f_{\text{dmp},n}(|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|), \\ &\quad - \sum_{\substack{\text{A,B,C} \\ \in \text{cell}}} \sum'_{\boldsymbol{\tau}_1, \boldsymbol{\tau}_2} \frac{C_9^{\text{ABC}}}{(r_{BC} r_{CA} r_{AB})^3} (3 \cos \vartheta_{CAB} \cos \vartheta_{CBA} \cos \vartheta_{ACB} + 1) f_{\text{d}(3)}(\bar{r}); \\ f_{\text{dmp},n}(r) &= \left[1 + 6 \left(\frac{r}{s_{r,n} R_0^{\text{AB}}} \right)^{-\alpha_n} \right]^{-1}. \end{aligned} \quad (3)$$

– Check the 3-at. terms – formula and realisation in VASP! [Ref.?] –

The calculation of the dispersion coefficients C_n^{AB} , the choice of cutoff radii R_0^{AB} with their scaling factors $s_{r,n}$, the “steepness parameters” α_n and the other atom-dependent parameters are discussed in Ref. 10.

A subsequent suggestion by Grimme *et al.*¹² was to modify (yet again) the damping function of the DFT+D3 scheme, following the model suggested by Johnson and Becke¹³, in order to remove the unphysical dip in the dispersion energy near the equilibrium interatomic distance, that generates a slight parasitic repulsion on bringing the atoms closer. In reality, the repulsion at small distances must be brought about within DFT, and does not need any “help” from the dispersion interaction. In the resulting **D3-BJ** scheme (which does not specifically address the 3-atom terms from the DFT+D3),

$$\begin{aligned} E_{\text{DFT+D3-BJ}} &= E_{\text{DFT}} - \sum_{\substack{\text{A,B} \\ \in \text{cell}}} \sum'_{\boldsymbol{\tau}} \left[s_6 \frac{C_6^{\text{AB}}}{|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|^6 + [f(R_0^{\text{AB}})]^6} \right. \\ &\quad \left. + s_8 \frac{C_8^{\text{AB}}}{|\mathbf{r}_A - \mathbf{r}_B + \boldsymbol{\tau}|^8 + [f(R_0^{\text{AB}})]^8} \right], \\ \text{with } f(R_0^{\text{AB}}) &= a_1 R_0^{\text{AB}} + a_2 \quad \text{and} \quad R_0^{\text{AB}} = \sqrt{\frac{C_8^{\text{AB}}}{C_6^{\text{AB}}}}. \end{aligned} \quad (4)$$

Tkatchenko and Scheffler (**TS**, Ref. 14) suggested a different “averaging” of the C_6^{AB} parameters in the generic formula of the Grimme D2 scheme (1) from the individual atomic ones than that given by Eq. (2) by way of taking into account atom polarisabilities, assuming their (simplified) frequency dependence, and hence making the result dependent on the actual charge density distribution. In the TS scheme,

$$C_6^{AB} = \frac{2C_6^A C_6^B}{(\alpha_B^0/\alpha_A^0)C_6^A + (\alpha_A^0/\alpha_B^0)C_6^B}, \quad (5)$$

$\alpha_{A,B}^0$ being the static polarisabilities of respective atoms. Moreover TS addressed the issue of how these parameters have to be modified when coming from isolated (free) atoms to the situation in solid, described by charge density $n(\mathbf{r})$. The “effective” values of $C_6^{A,B}$ are

$$C_6^{A[\text{eff.}]} = \left(\frac{V_A^{[\text{eff.}]} }{V_A^{[\text{free}]} } \right)^2 C_6^{A[\text{free}]} ,$$

where $\frac{V_A^{[\text{eff.}]} }{V_A^{[\text{free}]} } = \frac{\int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}}{\int r^3 n_A^{[\text{free}]}(\mathbf{r}) d\mathbf{r}},$

(6)

the “shrinking” of volume occupied by an atom in molecular or crystalline environment, depends on the “genuine” charge density in the system $n(\mathbf{r})$ and is expressed via the Hirshfeld atomic partitioning¹⁵ weight

$$w_A(\mathbf{r}) = \frac{n_A^{[\text{free}]}(\mathbf{r})}{\sum_{\forall \text{ atoms B}} n_B^{[\text{free}]}(\mathbf{r})}. \quad (7)$$

for a given atom, from the comparison with reference overlapping densities of free atoms. Finally, the vdW radius entering the damping function needs to be modified for an “atom in molecule” with respect to the free-atom situation:

$$R_0^{AB[\text{eff.}]} = R_0^{A[\text{eff.}]} + R_0^{B[\text{eff.}]} ; \quad R_0^{A[\text{eff.}]} = \left(\frac{V_A^{[\text{eff.}]} }{V_A^{[\text{free}]} } \right)^{1/3} R_0^{A[\text{free}]} \quad (8)$$

The realisation of the **TS** scheme in VASP with corresponding tests is described in Ref. 16.

In view of the obvious dependence of the partitioning outcome in Eq. (7) on the reference charge densities of free atoms, that might lead to problems when treating systems with different ionicity or bonding character, Bučko *et al.*^{5,6} suggested to use “iterative Hirshfeld partitioning”, earlier proposed by Bultinck *et al.*¹⁷, on top of the TS method. In this approach, the initial composition of “promolecular density” from free-atom parts is practically without importance, since it is iteratively refined in a well defined procedure, which makes

reference to the total charge density and “optimizes” the $n_A^{[\text{free}]}(\mathbf{r})$ contributions, along with their corresponding partitioning weights $w_A(\mathbf{r})$, until the partitioning becomes unambiguous. This scheme is referred to as **TS/HI** in the following.

A bunch of methods, referred to as **MBD** for “many-body dispersion”, bypass the refinement of phenomenological parameters and goes directly for the results expected, under some approximations, from the behavior of polarisability functions. With the model that many-atom system is represented, in what regards its response function, by a system of quantum harmonic oscillators (see details in Ref. 18), the dispersion energy is^{7,19}

$$E_{\text{disp}} = -\frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} [\ln(\mathbf{1} - \mathbf{A}(\omega)\mathbf{T})] , \quad (9)$$

where \mathbf{T} is the dipole interaction tensor, which is (for atoms A,B connected by \mathbf{r}_{AB} ; α and β numbering Cartesian coordinates):

$$\mathbf{T}_{AB}^{\alpha\beta} = f_{\text{dmp}}(|\mathbf{r}_{AB}|) \frac{-3r_{AB}^\alpha r_{AB}^\beta + |\mathbf{r}_{AB}|^2 \delta^{\alpha\beta}}{|\mathbf{r}_{AB}|^5} , \quad (10)$$

and $\mathbf{A} = \delta_{AB}\delta^{\alpha\beta}\alpha_A(\omega)$ is a diagonal matrix of single-atom polarisabilities. The damping function $f_{\text{dmp}}(r)$ in Eq. (10) leaves only the long-range part, i.e., $|\mathbf{r}_{AB}|$ of the order of, or larger than, the “range separation parameter”, that is typically taken slightly smaller than the sum of vDW radii of interacting atoms, see details in Ref. 7. Now, the single-atom polarisabilities $\alpha_A(\omega)$ entering the construction of $\mathbf{A}(\omega)$ must in fact be *screened*, that can be attained by solving the self-consistent screening (SCS) equation, see details in Ref. 18:

$$\alpha_A^{\text{SCS}}(\omega) = \alpha_A^{\text{TS}}(\omega) \left[1 + \sum_{\substack{\text{atoms B} \\ (+\text{transl.})}} \mathbf{T}_{AB} \alpha_B^{\text{SCS}}(\omega) \right] . \quad (11)$$

check the sign: [1+sum ...] in Ref. 18, however [1 – TA] (Eq. 8) in Ref. 7 !

$\alpha^{\text{TS}}(\omega)$ is the model single-atom polarisability assumed in the derivation of TS (Eq. 3 in Ref. 14). After solving the matrix equation (11), the screened expressions for α may replace the bare single-atom polarisabilities α_A in the formulation of the TS scheme, and accordingly modify the definition of the C_6^A and R_0^A parameters, that results in the **TS-SCS** model. Otherwise, with yet the damping function in Eq. (10) somehow specified, the dispersion energy follows from Eq. (9) without assuming any special shape of the radial dependence of the dispersion interaction. This would be (an example of) a genuine MBD scheme; details of its realisation in VASP are outlined in Ref. 7.

An importance to generalize atomic-related polarisability over the case of variable electron number (and hence ionicity), discussed by Gould *et al.*,⁸ resulted in demonstration that the polarizability is piecewise linear in the electron number, and in revision of implementation details of substantial formulae of the MBD scheme, notably Eq. (9,11). The technical details, the realisation within VASP and test results for this scheme labelled **MBD/FI** (for rational Ions) are given in Ref. 8.

The WIEN2k code allows the use of D3 corrections after Grimme *et al.*¹⁰ via inclusion of an auxiliary code; otherwise, non-local corrections are implemented after the scheme by Dion *et al.*¹ and following the “efficient implementation” by Román-Pérez and Soler,²⁰ the details of which, in what concerns the implementation in WIEN2k and extensive tests e.g. against VASP, are explained by Tran *et al.*²¹ A number of non-local kernels is provided in WIEN2k. For practical reasons, we did all the tests concerning the inclusion of vdW interactions in VASP.

- ¹ M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (Jun 2004), <https://link.aps.org/doi/10.1103/PhysRevLett.92.246401>
- ² K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **82**, 081101 (Aug 2010), <https://link.aps.org/doi/10.1103/PhysRevB.82.081101>
- ³ J. Klimeš, D. R. Bowler, and A. Michaelides, Phys. Rev. B **83**, 195131 (May 2011), <https://link.aps.org/doi/10.1103/PhysRevB.83.195131>
- ⁴ T. Bučko, J. Hafner, S. Lebègue, and J. Ángyán, The Journal of Physical Chemistry A **114**, 11814 (Nov 2010), <http://dx.doi.org/10.1021/jp106469x>
- ⁵ T. Bučko, S. Lebègue, J. Hafner, and J. G. Ángyán, Journal of Chemical Theory and Computation **9**, 4293 (Oct 2013), <http://dx.doi.org/10.1021/ct400694h>
- ⁶ T. Bučko, S. Lebègue, J. G. Ángyán, and J. Hafner, The Journal of Chemical Physics **141**, 034114 (Jul 2014), <https://doi.org/10.1063/1.4890003>
- ⁷ T. Bučko, S. Lebègue, T. Gould, and J. G. Ángyán, Journal of Physics: Condensed Matter **28**, 045201 (Feb 2016), <http://stacks.iop.org/0953-8984/28/i=4/a=045201>
- ⁸ T. Gould, S. Lebègue, J. G. Ángyán, and T. Bučko, Journal of Chemical Theory and Computation **12**, 5920 (Dec 2016), pMID: 27951673, <http://dx.doi.org/10.1021/acs.jctc.6b00925>

- ⁹ S. Grimme, Journal of Computational Chemistry **27**, 1787 (Nov 2006), ISSN 1096-987X, <http://dx.doi.org/10.1002/jcc.20495>
- ¹⁰ S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of Chemical Physics **132**, 154104 (Apr 2010), <https://doi.org/10.1063/1.3382344>
- ¹¹ J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys. **10**, 6615 (Sep 2008), <https://doi.org/10.1039/B810189B>
- ¹² S. Grimme, S. Ehrlich, and L. Goerigk, Journal of Computational Chemistry **32**, 1456 (May 2011), ISSN 1096-987X, <http://dx.doi.org/10.1002/jcc.21759>
- ¹³ E. R. Johnson and A. D. Becke, The Journal of Chemical Physics **123**, 024101 (Jul 2005), <https://doi.org/10.1063/1.1949201>
- ¹⁴ A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (Feb 2009), <https://link.aps.org/doi/10.1103/PhysRevLett.102.073005>
- ¹⁵ F. L. Hirshfeld, Theoretica Chimica Acta **44**, 129 (Jun 1977), <https://doi.org/10.1007/BF00549096>
- ¹⁶ T. Bućko, S. Lebègue, J. Hafner, and J. G. Ángyán, Phys. Rev. B **87**, 064110 (Feb 2013), <https://link.aps.org/doi/10.1103/PhysRevB.87.064110>
- ¹⁷ P. Bultinck, C. Van Alsenoy, P. W. Ayers, and R. Carbó-Dorca, The Journal of Chemical Physics **126**, 144111 (Apr 2007), <https://doi.org/10.1063/1.2715563>
- ¹⁸ A. Tkatchenko, R. A. DiStasio, Jr., R. Car, and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (Jun 2012), <https://link.aps.org/doi/10.1103/PhysRevLett.108.236402>
- ¹⁹ A. Ambrosetti, A. M. Reilly, R. A. DiStasio, Jr., and A. Tkatchenko, The Journal of Chemical Physics **140**, 18A508 (May 2014), <https://doi.org/10.1063/1.4865104>
- ²⁰ G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (Aug 2009), <https://link.aps.org/doi/10.1103/PhysRevLett.103.096102>
- ²¹ F. Tran, J. Stelzl, D. Koller, T. Ruh, and P. Blaha, Phys. Rev. B **96**, 054103 (Aug 2017), <https://link.aps.org/doi/10.1103/PhysRevB.96.054103>