

PE OLDE DISPERSION CORRECTIONS IN DENSITY FIELD THEORY

Samuel James Frost

Abstract

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§ 1. INTRODUCTION

The electronic structure of a molecule, or system of molecules, is an important property of much interest to scientists of all fields. As such many methods have been devised to calculate these structures to help aid scientists in their research of complicated systems, where direct measurement of certain properties may not be practical or even possible. One of these is methods is DFT, which uses electron density to calculate the energy at each nuclear position. A geometry optimisation can then be run which will find the minimum energy configuration. [1] This method can be used to find all sorts of useful properties, such as molecular geometries, thermodynamic properties, reaction barriers, etc.[2]

It may seem that the most important part of a system of molecules is the intramolecular covalent and ionic bonds. Whilst they do play a large role in determining the structure of the molecule these do not paint the full picture. Fluctuations of electron density cause pockets of slight negative and positive charge, this has a knock on effect to neighbouring electrons which

causes both inter and intramolecular attraction, along with further fluctuations in electron density. This phenomenon is known as van der Waals (also London dispersion) forces; despite being incredibly weak (many orders of magnitude weaker than covalent bonds), it plays an important role in chemistry. DFT methods have previously failed in considering these crucial van der Waals forces at long ranges, making them appear much weaker than in reality. Whilst this may not be a problem for basic solid state physics, where almost purely ionic crystals are concerned, it is a major problem in other areas of science. A lack of proper London dispersion forces causes a multitude of problems: DNA, which is held together with hydrogen bonds, will lack the strength to keep its form and as such will unwind; polar molecules, such as those commonly found in biology and organic chemistry, will have their thermodynamic properties miscalculated; molecules adsorbing to metal surfaces will adsorb to the wrong site, and give weaker energies than in actuality; complicated molecular crystals will pack incorrectly, giving the wrong optimised geometry. With this in mind, it is obvious that DFT is in dire need of a solution, but before one can find a solution one needs to actually find the problem.

The total electronic ground state energy of an atom, molecule, or ion, can be written as follows

$$E_{\text{tot}} = E_T + E_V + E_J + E_X + E_C \quad (1.1)$$

E_T is the total kinetic energy of the electrons, and is always positive, E_V is the total potential energy due to the attraction of the electron to the positive nuclear centre(s), this is also always negative. E_J is the *average* energy of the Coloumb repulsion between pairs of electrons, and is always positive, this doesn't paint the full picture however. It does not take into account the instantaneous influence of electrons on one another when they are in close proximity. Electrons will always try to repel each other, they will avoid each other, there-

fore the movements of one electron depends on the others, they are *correlated*, this lowers the energy of the system as it reduces the repulsion between electrons. E_J does not take this into account as it is only modelled as the electrons moving in the average potential field of all the other electrons, and therefore does not include individual correlation effects. To fix this the negative E_X and E_C correction terms are introduced, and are often lumped together into a single term dubbed the exchange correlation energy E_{XC} . E_X , the exchange energy, accounts for the much stronger correlated motion of electron sharing the same spin, caused by the Pauli exclusion principle, and removes the non-physical self repulsion terms included in E_J . E_C , the correlation energy, is much smaller and accounts for the weaker correlated motion of electrons with opposite spin.

It is the exchange correlation energy which represents van der Waals interactions between atoms and molecules, so its accurate calculation is vital to many systems. The calculation of the exchange correlation energy is a formidable task however, and thus many approximations have to be made. This has led to DFT methods such as LDA (local-density approximation) and GGA (generalised gradient approximation) (such as PBE). These type of functionals give semi-accurate results in solid state physics, where dispersion interactions are less important and normally of shorter range, as opposed to bio-organic molecules where dispersion forces play a key role over long distances (e.g. DNA).[3] The LDA functional assumes that the exchange correlation energy depends on the local electron density at a single point in space only, which is modelled as a uniform electron gas.[4] The slightly more complex GGA method uses both the local electron density at each point, but also its *gradient*, giving better results.[5][6] A consequence of this is that only local (i.e. short range) contributions to the exchange correlation energy are considered. Therefore there is a lack of long range electron correlation, which means that long range van der Waals forces are not considered. This causes systems to underbind, meaning weaker van der Waals interactions are simulated, which obviously gives incorrect results.

To fix this shortcoming of DFT, many solutions have been devised over the recent years. This literature review will focus on two main types of dispersion correction: the semi-empirical correction term, and the non-local density functional. The former applies a correction term, which is derived through fitting to empirical data, to a given LDA or GGA functional. This correction term helps to add on longer range forces to the energy already calculated by the functional. The calculation of this correction term does not change the scaling factor of the functional, and as such, the semi-empirical

correction term methods are a very cheap fix. The latter is a different type of functional entirely. It relies only on the electron density, and considers *every point in space*, and as such are dubbed non-local density functionals. As electron correlation can affect electrons on the other side of a molecule this methods helps to ensure that every fluctuation is considered.

§ 2. SEMI-EMPERICAL CORRECTIONS

§ 2.1. DFT-D2.

§ 2.1.1. **Theory.** In 2006 Stefan Grimme published DFT-D2[7], the successor to his more limited DFT-D method. The main setback of this original method was the narrow scope of the atoms as it could model, only Hydrogen and Carbon through to Neon. This, paired with very large inconsistencies for thermochemical calculations (e.g. energy of atomisation) made it a very limited method in dire need of improvement for it to become widespread.

The basis of the DFT-D2 dispersion correction is in the pairwise attraction between distinct atoms i and atoms j for all N atoms in the system. [7]

$$E_{\text{disp}} := -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{C_6^{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}) \quad (2.2)$$

Where C_6^{ij} is the dispersion coefficient for the pair of atoms i and j , s_6 is the scaling factor depending on the functional used, and R_{ij} is the interatomic separation. C_6^{ij} is calculated by the taking the geometric mean of the single atoms

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \quad (2.3)$$

These atomic C_6 values are themselves computed through the PBE0 functional[8]. They are the same irrespective of the chemical environment, C_6 for carbon in methane is the same as in benzene, when obviously the dispersion interactions differ, this glaring hole is fixed in DFT-D3, where the chemical environment is considered.

$$C_6^i = 0.05 N I_i \alpha_i \quad (2.4)$$

N is a scaling factor which depends on the row of the periodic table, taking on the value of the atomic mass of the element at the end of the row (e.g. for row 4 $N = 36$). I is the first ionisation potential and α the static dipole polarisability, both of which are found with the PBE0 functional. These atomic dispersion coefficients

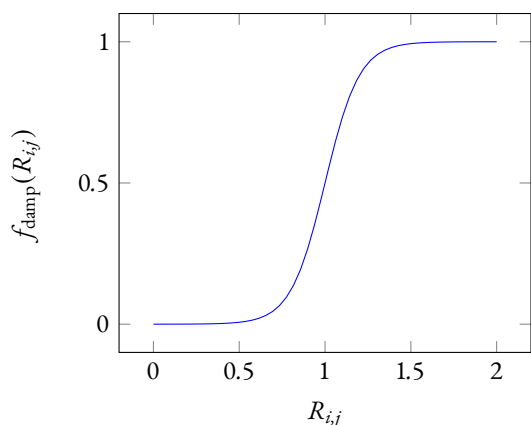


Figure 1: The Fermi damping function which ensures that the van der Waals correction energy doesn't grow too large as $R_{ij} \rightarrow 0$

are only available up to Xenon, a large improvement on DFT-D.

$f_{\text{damp}}(R_{ij})$, which can be seen in figure: 1, is a Fermi damping function which ensures that the dispersion correction goes to zero as R_{ij} decreases. Without this damping function the $1/R_{ij}^6$ term would grow too large as $R_{ij} \rightarrow 0$, causing a singularity to form. This would in turn cause van der Waals interactions to be dwarfed by other forces, making molecules effectively stick together and never come apart.

$$f_{\text{damp}}(R_{ij}) := \frac{1}{1 + \exp(-d(R_{ij}/R_r - 1))} \quad (2.5)$$

Here, R_r is the sum of the atomic van der Waals radii of the two atoms, which is derived from Restricted Open-shell Hartree-Fock calculations, in DFT-D2 $d = 20$, a small value compared to DFT-D, giving stronger corrections at intermediate distances.

The scaling parameter s_6 and the constant Fermi damping function constant d are both reliant on the functional used. They can both be changed however to fit different environment types if necessary, *e.g.* one may use a different s_6 value for the adsorption to silver[9] than one may use for modelling noble gasses.

These constants are through least-squares fit optimisation against the energy deviations of a large set of highly accurate training systems, which leads some to believe it to be unacceptable from a theoretical standpoint.[10][11][2] For methods with little empiricism, see section 3.

This dispersion correction, E_{disp} , is simply added on to the Kohn-Sham energy obtained from the chosen functional. **talk about the dashed line fig 2 from**

grimme's review paper

Maybe talk about empiricism more

§ 2.1.2. **Application.** One area where DFT-D2 fails is under extreme conditions, Ilawe *et al.* found that DFT-D2 begins to break down for Palladium Hydrides under large amounts of stress, giving errors close to 40% when compared with experimental data.[12] This, coupled with its general poor performance when heavy metals surfaces are involved make for some very poor results. *REFERENCE THIS* Researching how different computational methods model the adsorption of noble gasses to heavy metals, Chen *et al.* found that DFT-D2 vastly overestimates the energy of adsorption by a factor of two, leading to the conclusion that "the DFT-D2 method, at least with recommended parameterisation, is not suitable for investigating noble gas adsorption on metals".[13] In a limited study involving a Ag (111) surface and aromatic molecules, Schiavo *et al.* attempted to reparameterise DFT-D2 to better suit adsorption to metal surfaces. Fitting R_r against MP2 data, causing an increase in R_r , was found to limit overbinding whilst still semi-accurately describing the geometry.[9] This method could be applied to other metal surfaces and adsorbants in the future.

Kim *et al.* compared the results of the equilibrium spacing for sheets of black phosphorus with and without multiple dispersion corrections applied. For PBE with no correction there was a 10% difference compared with experimental data, however with DFT-D2 applied that dropped down to only 0.5%, obviously a very successful result for DFT-D2.[14]

§ 2.2. DFT-D3.

§ 2.2.1. **Theory.** As mentioned earlier, DFT-D2 does not consider the chemical environment of the atom. Covalent bonds change the electronic structure, half occupied atomic orbitals become lower energy molecular orbitals. This lowers the polarisability of the atom, meaning a smaller C_6 constant is needed. DFT-D3 considers the coordination number of the atom, giving a more accurate result. [11] D3 also uses higher order correction terms (which correspond to a higher order distance factor too), however these generally stop at C_8 , as any higher has shown to give unstable results for larger molecules.

The coordination number for an atom A in a molecule with N atoms is given by

$$\text{CN}^A = \sum_{B \neq A}^N \frac{1}{1 + e^{-16(4(R_{AB,\text{cov}} + R_{AB,\text{cov}})/(3R_{AB}) - 1)}} \quad (2.6)$$

where R_A, cov is the covalent radius and R_{AB} the distance between the two atoms.

For the dispersion coefficient of a specific system the electric dipole polarisability $\alpha^A(i\omega)$ is calculated for the free atom as well as differently coordinated hydrides, A_mH_n and B_kH_l using the PBE38 hybrid functional.[8] An altered Casimir-Polder expression is used to find the new dispersion coefficient.

$$C_6^{AB}(\text{CN}^A, \text{CN}^B) = \frac{3}{\pi} \int_0^\infty \frac{1}{\omega} \left(\alpha^{A_mH_n}(i\omega) - \frac{n}{2} \alpha^{H_2}(i\omega) \right) \times \frac{1}{k} \left(\alpha^{B_kH_l}(i\omega) - \frac{l}{2} \alpha^{H_2}(i\omega) \right) d\omega \quad (2.7)$$

Here the A_mH_n reference compound corresponds to the required coordination number of the atom A , the contribution of the hydrogen atoms to the polarisability is then subtracted from this.

These C_6 values are precomputed for every possible coordination number and atom pair. In the actual calculation the dispersion coefficient is evaluated as the Gaussian average of the previous values. This means that only the geometry of a molecule is required to calculate its dispersion coefficient. From here we can calculate the higher order C_8 dispersion coefficient.

$$C_8^{AB} = 3C_6^{AB} \sqrt{Q_A Q_B} \quad (2.8)$$

$$Q_A = \sqrt{Z_A} \frac{\langle r_A^4 \rangle}{\langle r_A^2 \rangle} \quad (2.9)$$

Where $\langle r_A^4 \rangle$ and $\langle r_A^2 \rangle$ are multipole-type expectation values and Z_A is the atomic number of atom A . C_8 is the highest order dispersion coefficient calculated however, C_{10} is ignored and instead absorbed into the s_8 scaling factor.

§ 2.2.2. Application. GGA functionals such as PBE tend to underestimate the cohesive energy of a chemical. Boungou *et al.* calculated the cohesive energy of silver using the PBE functional and compared it with the D3 correction applied, finding errors of 12% and 1% respectively.[15] Kovacs *et al.* ran some comparisons of different functionals paired with dispersion corrections on noble gasses, a common benchmark for dispersion corrections. For the neon dimer, BLYP-D3 was 5% (absolute) more accurate than BLYP-D2, and for the interaction energy, was 50% (also absolute) more accurate.[16] This is clearly a great improvement over the previous method, and for interactions where simple van

der Waals interactions are concerned, shows how robust the updated method is. However, careful consideration for the correct functional should be had, as more basic functionals, such as PBE, returned values twice as large as the experimental data.[16]

FIND DISAGREEING EVIDENCE

§ 3. NON-LOCAL DFT FUNCTIONALS

Unlike the semi-empirical *corrections* introduced in section 2, the methods outlined in this section are not corrections to, but are functionals themselves. These non-local density methods use the electron density at *every* point in space, hence their name; unlike the non-local methods such as LDA and GGA, which only use local points in space. Including points thought to be too far away in space to have any affect allows them to account for very long range correlation effects, the kind which cause the biologically important long range van der Waals forces, which local functionals cannot properly calculate. Paired with other LDA or GGA functionals, VV10 helps to complete the model at longer ranges in a seamless fashion. Although the final integral is very cumbersome, it relies only on the electron density, along with one or two fitted adjustable parameters, and as such uses very little empiricism, which may be desirable from a theoretical point of view. They are only used to find the correlation energy, and as such need to be paired with an exchange functional, and a local density approximation correlation function. The final energy is therefore

$$E_{\text{XC}}^{\text{NL}} = E_{\text{X}} + E_{\text{C}}^{\text{LDA}} + E_{\text{C}}^{\text{NL}} \quad (3.10)$$

The non-local correlation energy (in natural units) is defined as

$$E_{\text{C}}^{\text{NL}} = \frac{1}{2} \int dr dr' \rho(r) \Phi(r, r') \rho(r') \quad (3.11)$$

where $\Phi(r, r')$ is the *correlation kernel* (a functional to be integrated), and $\rho(r)$ is the electron density at point r . This allows for a perturbation at a point r then induces an exchange correlation at a far away point r' **The kernel is the heart of that which makes the functional distinct, and varies from functional to functional.**

§ 3.1. VV10.

Notes. Easy to implement, computationally efficient undemanding in terms of the basis set quality or the fineness of the numerical integration grid. vdW-DF2 seems to underbind – vydov2012

§ 3.1.1. **Theory.** Introduced by Vydrov and Van Voorhis, VV₁₀ was introduced in 2010 as the successor to their earlier method, VV₀₉.^{[17][18]} Despite being the simplest, VV₁₀ is the most accurate in the VV family.^[8] VV₁₀

After much thought, the correlation kernel is found to be

$$\Phi = -\frac{3}{2gg'(g+g')} \quad (3.12)$$

where

$$g = \omega_0(r)R^2 + \kappa(r) \quad (3.13)$$

$$R = |r - r'|. \quad (3.14)$$

$\omega_0(r)$ above is

$$\omega_0(r) = \sqrt{\omega_g^2(r) + \frac{\omega_p^2(r)}{3}} \quad (3.15)$$

where ω_p is the local plasma frequency and is defined as

$$\omega_p^2(r) = 4\pi\rho \quad (3.16)$$

where ρ is the *total* electron density. The local band gap $\omega_g^2(r)$ is

$$\omega_g^2(r) = C \left| \frac{\nabla\rho(r)}{\rho(r)} \right|^4 \quad (3.17)$$

where C is a parameter to be adjusted. The last term in g is

$$\kappa(r) = b \frac{v_F^2(r)}{\omega_p(r)} \quad (3.18)$$

$$v_F(r) = (3\pi^2\rho)^{1/3} \quad (3.19)$$

where b is another adjustable parameter which helps to control the short range dampening of the $1/R^6$ asymptote. $v_F(r)$ is the local Fermi velocity. Despite the large amount of equations here, it's important to note that everything here relies on only two things, the electron density, $\rho(r)$, at a certain point r , and the *total* electron density. In order for the long range electron correlation energy to go to zero at the electron gas limit, a constant relying on the adjustable parameter b is multiplied by the total number of electrons in the system. This is then added on to the correlation energy to give the new correlation energy.

$$E_C^{VV10} = E_C^{NL} + \beta(b)N_e^- \quad (3.20)$$

Where N_e^- is the number of electrons and

$$\beta(b) = \frac{1}{32} \left(\frac{3}{b^2} \right)^{\frac{3}{4}} \quad (3.21)$$

b and C were originally fit on the S22 data set, giving them values of 5.9 and 0.0093 respectively.^[19] b affects short range dispersion forces greatly, and as such is normally refitted depending on the use case i.e. if it typically overbinds or underbinds for a certain scenario. In the original paper, Vydrov and Van Voorhis pair VV₁₀ with the exchange functional rPW86 and the correlation functional PBE. Using the same parameterisation as the similar vdw-DF2 functional, this gives the final VV₁₀ exchange correlation energy to be

$$E_{XC}^{VV10} = E_X^{rPW86} + E_C^{PBE} + E_C^{VV10} \quad (3.22)$$

The semi-local exchange functional, rPW86, is known to suffer greatly from self-interaction error (SIE), which causes problems with charge transfer complexes and transition states of chemical reactions. Long-range corrected (LC) hybrid exchange functionals have been shown to reduce SIE. ^[20] The use of LC hybrids has also shown to be effective at describing the repulsive parts of the van der Waals potential. ^[21] VV used the LC- ω PBE exchange functional using the parameterisation of $C = 0.0089$, $b = 6.3$, and $\omega = 0.45$. VV₁₀ can be paired with almost any exchange correlation functional, however it is best to use functionals that give little to no major van der Waals forces, as to avoid double counting. Hujo and Grimme were the first to extensively couple the VV₁₀ correlation energy, E_C^{VV10} , to other standard LDA and GGA functionals, adjusting only b with each new functional.^[22] This is dubbed "DFT-NL" in reference to Grimme's other semi-empirical methods mentioned in section 2. The size of the damping parameter b is indicative of the strength of the semi-local density functional. For repulsive functionals such as rPBE, $b \approx 4$, thus giving larger VV₁₀ contributions at short range. Whilst for attractive functionals, such as the un-reparameterised PBE, VV₁₀ needs to be damped much heavier, as such $b \approx 8$.^[8]

§ 3.1.2. Applications.

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