

DISPERSION CORRECTIONS IN DENSITY FIELD THEORY

Samuel James Frost

Abstract

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetur.

CONTENTS

1. INTRODUCTION	1
2. SEMI-EMPIRICAL CORRECTIONS	2
2.1 DFT-D ₂	2
2.1.1 Theory	2
2.1.2 Application	3
2.2 DFT-D ₃	3
2.2.1 Theory	3
2.2.2 Application	4
3. NON-LOCAL CORRELATION FUNCTIONALS	4
3.1 vdW-DF ₂	5
3.2 VV ₁₀	5
3.2.1 Performance and Application	6
4. EXCHANGE-DIPOLE MOMENT MODEL	6
4.1 Theory	6
4.2 Application	8

§ 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 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 de-

termining 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, therefore 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)[3] and GGA (generalised gradient approximation)[4], [5] (such as PBE[6]). 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).[7] 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.[3] The slightly more complex GGA method uses both the local electron density at each point, but also its *gradient*, giving better results.[4][5] 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-EMPIRICAL CORRECTIONS

§ 2.1. DFT-D2.

§ 2.1.1. **Theory.** In 2006 Stefan Grimme published DFT-D2[8], 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. [8]

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

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 PBEo functional[9]. 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

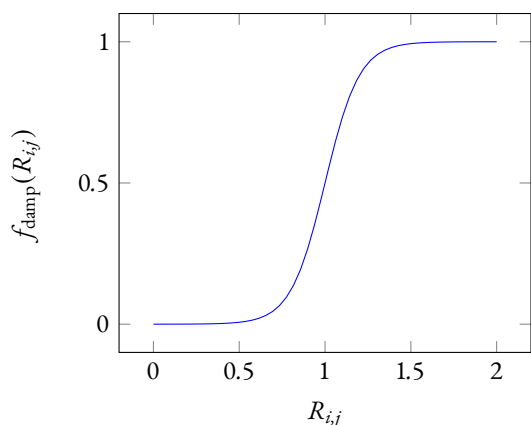


Figure 1: The Fermi damping function which ensures that the van der Waals correction energy doesn't grow too large as $R_{ij} \rightarrow 0$

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 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[10] 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. It can also lead to inaccurate results for systems

which differ greatly from the training data.[11][12][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.[13] 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".[14] In a limited study involving a Ag(111) surface and aromatic molecules, Schiavo *et al.* attempted to reparametrise 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.[10] 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.[15]

§ 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. [12] 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

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

where $R_{A,\text{cov}}$ 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.[9] An altered Casimir-Polder expression is used to find the new dispersion coefficient.

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

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.[16] 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.[17] 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.[17]

FIND DISAGREEING EVIDENCE

§ 3. NON-LOCAL CORRELATION FUNCTIONALS

Unlike the semi-empirical correction terms 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, non-local correlation methods help 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

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

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 which then induces electron 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. All modern non-local correlation functionals take this

form, which is based off the work of Dobson and Dinte (DD) [18], and, Andersson, Langreth, and Lundqvist (ALL)[19]. In order for a non-local correlation functional to be "seamless" it must not operate in the same region as the local correlation functional as to avoid double counting.

§ 3.1. **vdW-DF2.** In 2004 Dion *et al.* introduced the first non-local correlation method, vdW-DF1. [20] This proved a success, especially in areas such as adsorption to surfaces and graphene interactions, where previous methods had failed. [21] However, it still vastly underestimated hydrogen bonding, and overestimate molecular separation. The derivation of the kernel for both vdW-DF1 and vdW-DF2 is large and tedious, and as such not included in this limited review, however it can be found in reference [20]. For a similar but simpler example based on the same principles, see section 3.2.1.

To fix the issues with vdW-DF1, Lee *et al.* proposed an improved model in 2010, vdW-DF2. [22] The revPBE[23] exchange functional which was used in the original was replaced with the less repulsive rPW86 functional. [24] Along with this a reparameterisation was performed on the constant controlling the size of the exchange functional. This indeed fixed most of the problems with vdW-DF1, performing especially well on small molecules. Some problems still remained for large bulk molecules and adsorption to metals.

§ 3.2. **VV10.** Introduced by Vydrov and Van Voorhis, VV10 was introduced in 2010 as the successor to their method from the previous year, VV09, which was based on Dion *et al.*'s vdW-DF1 method.[25][26] Despite being the simplest, VV10 is the most accurate in the VV family.[9]

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.[27] 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. This caused strong overbinding in hydrogen bonded complex.[27] Long-range corrected (LC) hybrid exchange functionals have been shown to reduce SIE. [28] The

use of LC hybrids has also shown to be effective at describing the repulsive parts of the van der Waals potential. [29] VV used the LC- ω PBE exchange functional using the parameterisation of $C = 0.0089$, $b = 6.3$, and $\omega = 0.45$, this alternative long-range corrected method is known as LC-VV10, and generally fixes the overbinding of hydrogen bonds.

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.[30] 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 unreparamaterised PBE, VV10 needs to be damped much heavier, as such $b \approx 8$. [9]

§ 3.2.1. Performance and Application. In 2012 Vydrov and Van Voorhis compared VV10, LC-VV10 (using the parameterisations mentioned in section 3.1.1), another non-local density functional, vdW-DF2 [22], and meta-hybrid GGA functionals which have no non-local correlation, Mo6-2X [31] and ω B97X-D [32]. They calculated the binding energy at fixed equilibrium distance using the highly accurate (less than 1% uncertainty) S66[33], [34] test set. It contains the binding energy for 66 weakly bound molecular systems, split into three groups: 23 dispersion dominated systems, 23 hydrogen-bonded systems, and 20 with mixed behaviour. The mean errors of the results can be seen in figure 2.

vdW-DF2 tended to underbind, especially on the mixed aromatic systems, but tended to perform better on smaller systems, leaving it with an average mean error of $-0.48 \text{ kcal mol}^{-1}$, the largest of the group. VV10 performs especially well with dispersion dominant and mixed systems, with some slight overbinding, it had the second most accurate result for dispersion based systems, $-0.20 \text{ kcal mol}^{-1}$, and the most accurate for mixed systems, $0.15 \text{ kcal mol}^{-1}$. A noteworthy increase over the meta-GGA functionals also tested. As mentioned in section 3.1.1, VV10 tends to overbind hydrogen-bonded molecules, giving a result ($0.53 \text{ kcal mol}^{-1}$) significantly worse than the meta-hybrid GGA functionals, this is caused by the use of the semilocal rPW86 exchange component. When a long-range corrected exchange func-

tional is used as is the case of LC-VV10 and ω B97X-D, the hydrogen-bonded mean error is greatly reduced, this is evidence by LC-VV10's mean hydrogen bonded error being over half as low as regular VV10. A notable decrease in the mean error of LC-VV10 is observed for dispersion dominant systems too, with the mean error being exactly half as small as VV10. Overall, LC-VV10 performs best out of all the functionals tested, with nearly half as small mean error than the next best functional. This shows as clear success of VV10, and especially of LC-VV10 over its non-local density functional ancestors. The improved accuracy comes at the cost of higher computational time [35], quadrature grid optimisations can help to alleviate some of this cost however. For LC-VV10, the most intensive step was found to actually be the exchange component, not the non-local correlation.

Although the focus of this paper is on van der Waals interactions, that is not a functional's only use, and so if the correction is to be of any value it must obtain accurate results for strongly bound (i.e. ionic and covalent) systems as well. In their 2010 paper Vydrov and van Voorhis[26] measured the equilibrium bond lengths[36] of 20 closed shell ionic and covalent molecules, which consisted mostly of diatomics and molecules with high symmetry whose geometry is reliant on only one bond length. VV10 achieved the same mean error as PBE of 0.017 \AA (bond lengths tend to range from $1-3 \text{ \AA}$). The other non-local density functional vdW-DF2 gave a result slightly higher at 0.021 \AA ; rPW86-PBE, which is without the non-local correlation term, was only slightly worse with an error of 0.0018 \AA . The same was done for atomisation energies[37], of which VV10 performed relatively well with a mean error of $2.9 \text{ kcal mol}^{-1}$, whilst rPW86-PBE and PBE had mean errors of $-2.0 \text{ kcal mol}^{-1}$ and $10.4 \text{ kcal mol}^{-1}$ respectively. Another successful result.

§ 4. EXCHANGE-DIPOLE MOMENT MODEL

§ 4.1. Theory. Becke and Johnson proposed a model[38] in which the cause of dispersion interactions comes from an exchange-hole induced dipole moment.[39]–[41] The exchange hole, otherwise known as a Fermi hole, originates from the Pauli exclusion principle, and stops two electrons of the same spin, σ , from occupying the same space. Thus there is an area around an electron where there is a zero probability of there being another electron. If there is an electron of spin σ at point \vec{r} , then the amount to which the hole depletes the probability of finding another electron

	vdW-DF2	VV10	LC-VV10	ω B97X-D	Mo6-2X
Hydrogen Bonded Systems					
MAE	0.62	0.53	0.20	0.16	0.32
MAPE	5.8	6.4	2.3	2.2	3.9
Dispersion Based Systems					
MAE	0.33	0.20	0.10	0.50	0.29
MAPE	8.7	7.9	3.3	17.2	10.2
Mixed Behaviour Systems					
MAE	0.49	0.15	0.17	0.20	0.26
MAPE	9.0	6.3	3.3	8.5	7.1

Figure 2: Errors of the binding energy at equilibrium distance for the functionals benchmarked against the S66 test set for weakly bounded systems in Ref [27], where MAE is the mean absolute error in kcal mol⁻¹ and MPE is the mean absolute percentage error.

with the same spin at point \vec{r}' is given by

$$b_{X,\sigma}(\vec{r}, \vec{r}') = -\frac{1}{\rho_{\sigma}(\vec{r})} \sum_{ij} \phi_{i\sigma}(\vec{r}') \phi_{j\sigma}(\vec{r}') \phi_{i\sigma}(\vec{r}) \phi_{j\sigma}(\vec{r}) \quad (4.23)$$

As such, if $\vec{r} = \vec{r}'$ then

$$b_{X,\sigma}(\vec{r}, \vec{r}) = -\rho_{\sigma}(\vec{r}) \quad (4.24)$$

thus, the probability of finding two electrons at the same point is *zero*. The sum is over occupied real orbitals, i and j , of spin σ , where ρ_{σ} is the total spin- σ electron density. The existence of an electron at \vec{r} reduces the chance to find another electron at \vec{r}' ,

As the electron moves through space so does its hole; the electron and its hole are charge neutral overall. The shape of the hole depends on the position of the electron, \vec{r} , this shape is almost never spherically symmetric about the electron, except for the case of a uniform electron gas. This lack of symmetry creates an exchange hole dipole moment, given by

$$\vec{d}_{X,\sigma}(\vec{r}) = \left(\frac{1}{\rho_{\sigma}(\vec{r})} \sum_{ij} \int \phi_{i\sigma}(\vec{r}') \phi_{j\sigma}(\vec{r}') \vec{r}' \phi_{i\sigma}(\vec{r}) \phi_{j\sigma}(\vec{r}) d\vec{r}' \right) - \vec{r} \quad (4.25)$$

☞ Some papers may use μ for the dipole moment instead of d

This exchange dipole moment, $\vec{d}_{X,\sigma}(\vec{r})$, in atom A, will induce a dipole moment in another atom, B, and vice versa. This dipole-dipole interaction is proportional to the square of the respective exchange dipole moment. The square of the *atomic* exchange dipole moment is given by

$$\langle d_X^2 \rangle_A = \sum_{\sigma} \int d\vec{r} w_A(\vec{r}) \rho_{\sigma}(\vec{r}) d_{X,\sigma}^2(\vec{r}) \quad (4.26)$$

$w_A(\vec{r})$ is the Hirshfeld partitioning[42] weight for an atom A. This helps to account for the molecular environment of an atom, by estimating changes in the atomic volume and thus changes the polarisability. Where

$$w_A(\vec{r}) = \frac{\rho_A^{\text{atom}}(\vec{r})}{\sum_B \rho_B^{\text{atom}}(\vec{r})} \quad (4.27)$$

The exchange-hole dipole moment induced in atom B from atom A, at length R , will have a potential energy of

$$U^{AB} = -2 \langle d_X^2 \rangle_A \alpha_B / R^6 \quad (4.28)$$

where the reverse interaction is

$$U^{BA} = -2 \langle d_X^2 \rangle_B \alpha_A / R^6 \quad (4.29)$$

α is the polarisability of a given atom modified to account for chemical environment where

$$\alpha_A = \alpha_A^{\text{free}} \frac{\int d\vec{r} w_A(\vec{r}) \rho(\vec{r}) r^3}{\int d\vec{r} \rho_A^{\text{free}}(\vec{r}) r^3} \quad (4.30)$$

$\langle d_X^2 \rangle$ is given by the integral

$$\langle d_X^2 \rangle = \int \rho_{\alpha}(\vec{r}) d_{X\alpha}(\vec{r}) d\vec{r} + \int \rho_{\beta}(\vec{r}) d_{X\beta}(\vec{r}) d\vec{r} \quad (4.31)$$

where ρ_{α} is the density of spin up electrons, and ρ_{β} the density of spin down. $d_{X\sigma}(\vec{r})^2$ is the squared *exact* exchange-hole dipole moment of σ spin electron at point \vec{r} found in equation 4.25. This is a cumbersome integral however, as such Becke and Roussel derived an approximation to this exact model, dubbed BRX, of the form

$$d_{BRX,\sigma}^2(\vec{r}) = \left(\frac{e^{-x}}{8\pi\rho_{\sigma}(\vec{r})} \right)^{2/3} x^2 \quad (4.32)$$

Where x is depend on the electron density and its gradient, for more details see reference [38]. As this method is much faster than the exact equation in equation 4.25, from here on out $d_{X,\sigma}$ will refer to $d_{BRX,\sigma}$, as it sees the most usage by far.

Using second-order perturbation theory[39] the dispersion energy can be written as

$$E_{\text{disp}} = -\frac{C_6}{R^6} \quad (4.33)$$

This is same principle as the methods mentioned in section 2, but with a different derivation of the C_6 constant, which is written as

$$C_6^{AB} = \frac{\langle d_X^2 \rangle_A \langle d_X^2 \rangle_B \alpha_A \alpha_B}{\langle d_X^2 \rangle_{A\alpha_B} + \langle d_X^2 \rangle_{B\alpha_A}} \quad (4.34)$$

With a suitable damping function applied, like the one seen in equation 2.5 and figure 1, we can write our final dispersion energy as a sum over atoms A and B as

$$E_{\text{disp}} = -\sum_{A,B} \frac{C_6^{AB}}{R^6} f_{\text{damp}}(R) \quad (4.35)$$

In 2007, Becke and Johnson updated their approach[43] by adding higher order coefficients into the mix, derived from the exchange quadrupole and octupole moments, taking C_8 and C_{10} coefficients respectively. These coefficients can be found in reference [43] This new approach takes the form of

$$E_{\text{disp}} = -\sum_{A,B} \sum_{n=6,8,10} \frac{C_n^{AB}}{R^n} f_{\text{damp,BJ}}^n(R) \quad (4.36)$$

Where a novel damping function developed by Becke and Johnson is being used [44]

$$f_{\text{damp,BJ}}^n(R) = \frac{R^n}{R^n + (a_1 R_0 + a_2)^n} \quad (4.37)$$

$$R_0 = \frac{1}{3} \left(\sqrt{\frac{C_8^{AB}}{C_6^{AB}}} + \sqrt{\frac{C_{10}^{AB}}{C_6^{AB}}} + \sqrt[4]{\frac{C_{10}^{AB}}{C_6^{AB}}} \right) \quad (4.38)$$

Where a_1 and a_2 depend on the functional being used.

The attentive reader will notice that unlike previous methods mentioned, XDM uses no fitting of parameters. This makes it very theoretically pure. This also makes XDM a good candidate for studying unusual edge case systems, which other highly empirical methods like those in section 2 will fail.

§ 4.2. Application. Otero-de-la-Roza *et al.* tested XDM for bulk ionic crystals[45], although this doesn't

immediately seem like the best use case for a van der Waals correction it is an important to note that even ionic crystals have van der Waals interactions, and so of course it is important that they are modelled correctly. Not only that, but it is important to make sure that XDM does not worsen results of dispersionless functionals. PBE is one of the most popular functionals for cases like this, however for XDM 86bPBE is the recommended functional. For details on the damping function parameters see reference [46]. This is evidenced in the the calculation of the lattice constants for 20 alkali halide. PBE-XDM had a mean error of -0.134 \AA , a similar result with a different sign to PBE-D3 seen in section 2.2, compared to base PBE which had a mean error of 0.164 \AA . Otero-de-la-Roza *et al.* think this poor result is due to PBE's nature to underestimate non-bonded repulsion[46], this will in turn cause PBE-XDM to overbind dispersion forces, causing a much smaller lattice constant. The use of the recommended 86bPBE functional gave a much more impressive result of -0.038 \AA . Unfortunately there is still a systematic underestimation for 86bPBE-XDM, the problem may lie in the delocalisation error for the functional[47]. To remedy this a hybrid functional was tested, 86bPBE-25X-XDM gave a very impressive results of -0.017 , the lowest of all the functionals tested[45].

Adsorption to metals is an area where uncorrected functionals tend to fail, and so is a popular test for the quality of a dispersion correction. In a 2016 paper Christian *et al.* measured[48] the energy of adsorption of benzene to the (111) face of three coinage metals: copper, gold, and silver. 86bPBE-XDM performed extremely well, with all of its values for gold and silver being within the uncertainty, with copper being 0.06 eV outside the margin of uncertainty, giving an overall MAE of 0.04 eV , more accurate than PBE-XDM's 0.10 eV . SCAN-rVV10 tended to overestimate the adsorption energy by the same amount that 86bPBE-XDM underestimated it, giving them the same MAE. Adhikari *et al.* wrote a similar paper in 2021 [49] measuring the adsorption distance of benzene over the same group of metals. Unfortunately data only exists for the adsorption of silver, however using the vdW radii it can be predicted that Ag and Au will have a similar distance, whilst Cu will be significantly shorter. B86bPBE+XDM was in the area of uncertainty for silver, and put copper at 0.32 \AA shorter, thus agreeing with the theory. Both PBE-rVV10 and PBE-D3 performed relatively well, being 0.02 eV from the experimental value and 0.07 eV respectively. However they both failed to put copper at a lower distance. Using SCAN for the exchange correlation functional fixes the order, however they both underestimate the experimental value of silver.

Functional	Adsorption Energy / eV			Adsorption Distance / Å	
	Cu (111)	Ag (111)	Au (111)	Ag (111)	Ordering y/n
PBE					
PBE-D ₂					
PBE-D ₃					
PBE-rVV10					
SCAN-rVV10					
PBE-XDM					
B86bPBE-XDM					

REFERENCES

- [1] R. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, en. New York: Oxford Univ. Press, 1989.
- [2] A. Pribram-Jones, D. A. Gross and K. Burke, 'Dft: A theory full of holes?' *Annual Review of Physical Chemistry*, vol. 66, no. 1, pp. 283–304, 2015, PMID: 25830374. DOI: 10.1146/annurev-physchem-040214-121420.
- [3] W. Kohn and L. Sham, 'Self-consistent equations including exchange and correlation effects,' fr, *Phys. Rev.*, vol. 140:A1133–38, 1965.
- [4] A. Becke, 'Density-functional exchange-energy approximation with correct asymptotic behavior,' en, *Phys. Rev. A*, vol. 38, pp. 3098–100, 1988.
- [5] J. Perdew, 'Density functional approximation for the correlation energy of the inhomogeneous gas,' en, *Phys. Rev. B*, vol. 33, pp. 8822–24, 1986.
- [6] P. J. P, B. K and E. M, 'Phys,' hu, *Rev. Lett.*, vol. 77, p. 3865, 1996.
- [7] I. Kaplan, *Intermolecular Interactions*, en. Chichester, England: Wiley, 2006.
- [8] S. Grimme, 'Semiempirical gga-type density functional constructed with a long-range dispersion correction,' *Journal of Computational Chemistry*, vol. 27, no. 15, pp. 1787–1799, 2006. DOI: <https://doi.org/10.1002/jcc.20495>. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/jcc.20495>. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/jcc.20495>.
- [9] —, 'Density functional theory with London dispersion corrections,' *WILEY INTERDISCIPLINARY REVIEWS-COMPUTATIONAL MOLECULAR SCIENCE*, vol. 1, no. 2, 211–228, MAR-APR 2011, ISSN: 1759-0876. DOI: {10.1002/wcms.30}.
- [10] E. Schiavo, A. B. Munoz-Garcia, V. Barone, A. Vittadini, M. Casarin, D. Forrer and M. Pavone, 'Tuning dispersion correction in DFT-D₂ for metal-molecule interactions: A tailored reparameterization strategy for the adsorption of aromatic systems on Ag(111),' *CHEMICAL PHYSICS LETTERS*, vol. 693, 28–33, FEB 2018, ISSN: 0009-2614. DOI: {10.1016/j.cplett.2018.01.005}.
- [11] T. Sato and H. Nakai, 'Density functional method including weak interactions: Dispersion coefficients based on the local response approximation,' *JOURNAL OF CHEMICAL PHYSICS*, vol. 131, no. 22, DEC 14 2009, ISSN: 0021-9606. DOI: {10.1063/1.3269802}.
- [12] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, 'A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements hpu,' *The Journal of chemical physics*, vol. 132, p. 154104, Apr. 2010. DOI: 10.1063/1.3382344.
- [13] N. V. Ilawe, J. A. Zimmerman and B. M. Wong, 'Breaking Badly: DFT-D₂ Gives Sizeable Errors for Tensile Strengths in Palladium-Hydride Solids,' *JOURNAL OF CHEMICAL THEORY AND COMPUTATION*, vol. 11, no. 11, 5426–5435, NOV 2015, ISSN: 1549-9618. DOI: {10.1021/acs.jctc.5b00653}.

- [14] D.-L. Chen, W. Saidi and K. Johnson, 'The role of van der Waals interactions in the adsorption of noble gases on metal surfaces,' *Journal of physics. Condensed matter: an Institute of Physics journal*, vol. 24, p. 424 211, Oct. 2012. DOI: 10 . 1088 / 0953 - 8984 / 24 / 42 / 424211.
- [15] H. Kim, 'Effect of van der Waals interaction on the structural and cohesive properties of black phosphorus,' *JOURNAL OF THE KOREAN PHYSICAL SOCIETY*, vol. 64, no. 4, 547-553, FEB 2014, ISSN: 0374-4884. DOI: {10 . 3938 / jkps . 64 . 547}.
- [16] C. C. Boungou, G. B. Bouka-Pivoteau, B. R. Malonda-Boungou, M. N'dollo, P. S. Mousounda, A. T. Raji and E. Kanga, 'Adsorption and coadsorption of H and Li on Ag(100) surface: DFT studies including dispersion correction,' *COMPUTATIONAL CONDENSED MATTER*, vol. 28, SEP 2021, ISSN: 2352-2143. DOI: {10 . 1016 / j . cocom . 2021 . e00582}.
- [17] A. Kovacs, J. C. Dobrowolski, S. Ostrowski and J. E. Rode, 'Benchmarking density functionals in conjunction with Grimme's dispersion correction for noble gas dimers (Ne-2, Ar-2, Kr-2, Xe-2, Rn-2),' *INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY*, vol. 117, no. 9, MAY 5 2017, ISSN: 0020-7608. DOI: {10 . 1002 / qua . 25358}.
- [18] J. Dobson and B. Dinte, *Constraint satisfaction in local and gradient susceptibility approximations: Application to a van der Waals*, en.
- [19] Y. Andersson, D. Langreth and B. Lundqvist, 'I. van der Waals interactions in density-functional theory,' en, *Phys. Rev. Lett.*, vol. 76, p. 102 105, 1996.
- [20] M. Dion, H. Rydberg, E. Schroder, D. Langreth and B. Lundqvist, 'Van der Waals density functional for general geometries,' *PHYSICAL REVIEW LETTERS*, vol. 92, no. 24, JUN 18 2004, ISSN: 0031-9007. DOI: {10 . 1103 / PhysRevLett . 92 . 246401}.
- [21] D. C. Langreth, B. I. Lundqvist, S. D. Chakarova-Kack, V. R. Cooper, M. Dion, P. Hyldgaard, A. Kellkanen, J. Kleis, L. Kong, S. Li, P. G. Moses, E. Murray, A. Puzder, H. Rydberg, E. Schroder and T. Thonhauser, 'A density functional for sparse matter,' *JOURNAL OF PHYSICS-CONDENSED MATTER*, vol. 21, no. 8, FEB 25 2009, ISSN: 0953-8984. DOI: {10 . 1088 / 0953 - 8984 / 21 / 8 / 084203}.
- [22] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, 'Higher-accuracy van der Waals density functional,' *PHYSICAL REVIEW B*, vol. 82, no. 8, AUG 4 2010, ISSN: 1098-0121. DOI: {10 . 1103 / PhysRevB . 82 . 081101}.
- [23] Y. Zhang and W. Yang, hu, *Phys. Rev. Lett.*, vol. 80, p. 890, 1998.
- [24] K. Lee, É. Murray, L. Kong, B. Lundqvist and D. Langreth, 'Higher-accuracy van der Waals density functional,' en, *Phys. Rev. B: Condens. Matter Mater. Phys.*, vol. 82, p. 081 101, 2010.
- [25] O. A. Vydrov and T. Van Voorhis, 'Non-local van der Waals Density Functional Made Simple,' *PHYSICAL REVIEW LETTERS*, vol. 103, no. 6, AUG 7 2009, ISSN: 0031-9007. DOI: {10 . 1103 / PhysRevLett . 103 . 063004}.
- [26] —, 'Nonlocal van der Waals density functional: The simpler the better,' *JOURNAL OF CHEMICAL PHYSICS*, vol. 133, no. 24, DEC 28 2010, ISSN: 0021-9606. DOI: {10 . 1063 / 1 . 3521275}.
- [27] —, 'Benchmark Assessment of the Accuracy of Several van der Waals Density Functionals,' *JOURNAL OF CHEMICAL THEORY AND COMPUTATION*, vol. 8, no. 6, 1929-1934, JUN 2012, ISSN: 1549-9618. DOI: {10 . 1021 / ct300081y}.
- [28] O. Vydrov and G. Scuseria, fr, *J. Chem. Phys.*, vol. 125, p. 234 109, 2006.
- [29] T. Sato, T. Tsuneda and K. Hirao, fr, *J. Chem. Phys.*, vol. 126, p. 234 114, 2007.
- [30] W. Hujo and S. Grimme, 'Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions,' *JOURNAL OF CHEMICAL THEORY AND COMPUTATION*, vol. 7, no. 12, 3866-3871, DEC 2011, ISSN: 1549-9618. DOI: {10 . 1021 / ct200644w}.
- [31] Y. Zhao and D. Truhlar, 'Chem,' en, *Acc.*, vol. 120, p. 215 241, 2008.
- [32] J.-D. Chai and M. Head-Gordon, 'Phys,' fr, *Chem. Chem. Phys.*, vol. 10, p. 6615 6620, 2008.
- [33] J. Rezac, K. Riley and Hobza, en, *P. J. Chem. Theory Comput.*, vol. 7, p. 2427 2438, 2011.

- [34] —, en, *P. J. Chem. Theory Comput*, vol. 7, p. 3466 3470, 2011.
- [35] O. A. Vydrov, Q. Wu and T. Van Voorhis, ‘Self-consistent implementation of a nonlocal van der Waals density functional with a Gaussian basis set,’ *JOURNAL OF CHEMICAL PHYSICS*, vol. 129, no. 1, JUL 7 2008, ISSN: 0021-9606. DOI: {10.1063/1.2948400}.
- [36] D. ed., Ed., en. Boca Raton, FL: CRC Handbook of Chemistry and Physics, 2009.
- [37] B. Lynch and D. Truhlar, cs, *J. Phys. Chem. A*, vol. 107, p. 8996, 2003.
- [38] A. Becke and E. Johnson, ‘Exchange-hole dipole moment and the dispersion interaction,’ *JOURNAL OF CHEMICAL PHYSICS*, vol. 122, no. 15, APR 15 2005, ISSN: 0021-9606. DOI: {10.1063/1.1884601}.
- [39] —, ‘Exchange-hole dipole moment and the dispersion interaction,’ en, *J. Chem. Phys*, vol. 122, p. 154 104, 2005.
- [40] —, ‘A post-hartree-fock model of intermolecular interactions,’ en, *J. Chem. Phys*, vol. 123, p. 024 101, 2005.
- [41] —, ‘A post-hartree-fock model of intermolecular interactions: Inclusion of higher-order corrections,’ en, *J. Chem. Phys*, vol. 124, p. 174 104, 2006.
- [42] F. Hirshfeld, ‘Bonded-atom fragments for describing molecular charge densities,’ en, *Theor. chim. acta*, vol. 44, p. 129 138, 1977.
- [43] A. D. Becke and E. R. Johnson, ‘Exchange-hole dipole moment and the dispersion interaction revisited,’ *JOURNAL OF CHEMICAL PHYSICS*, vol. 127, no. 15, OCT 21 2007, ISSN: 0021-9606. DOI: {10.1063/1.2795701}.
- [44] E. Johnson and A. Becke, fr, *J. Chem. Phys*, vol. 123, p. 024 101, 2005.
- [45] A. Otero-de-la-Roza and E. R. Johnson, ‘Application of XDM to ionic solids: The importance of dispersion for bulk moduli and crystal geometries,’ *JOURNAL OF CHEMICAL PHYSICS*, vol. 153, no. 5, AUG 7 2020, ISSN: 0021-9606. DOI: {10.1063/5.0015133}.
- [46] E. Johnson, en, *Non-Covalent Interactions in Quantum Chemistry and Physics*, vol. 5, A. Otero-de-la-Roza and G. DiLabio, Eds., pp. 169–194, 2017.
- [47] A. J. Cohen, P. Mori-Sanchez and W. Yang, ‘Insights into current limitations of density functional theory,’ *SCIENCE*, vol. 321, no. 5890, 792–794, AUG 8 2008, ISSN: 0036-8075. DOI: {10.1126/science.1158722}.
- [48] M. S. Christian, A. Otero-de-la-Roza and E. R. Johnson, ‘Surface Adsorption from the Exchange-Hole Dipole Moment Dispersion Model,’ *JOURNAL OF CHEMICAL THEORY AND COMPUTATION*, vol. 12, no. 7, 3305–3315, JUL 2016, ISSN: 1549-9618. DOI: {10.1021/acs.jctc.6b00222}.
- [49] S. Adhikari, N. K. Nepal, H. Tang and A. Ruzsinszky, ‘Describing adsorption of benzene, thiophene, and xenon on coinage metals by using the Zaremba-Kohn theory-based model,’ *JOURNAL OF CHEMICAL PHYSICS*, vol. 154, no. 12, MAR 28 2021, ISSN: 0021-9606. DOI: {10.1063/5.0042719}.