

# DISPERSION CORRECTIONS IN DENSITY FUNCTIONAL THEORY

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# WHAT IS DFT?

- ▶ A computational chemistry method which uses the principles of quantum mechanics to model the electronic structure of a chemical system, thus pulling out many important properties
- ▶ Uses functionals of the local electron density, more accurate 'GGA' methods which use a *gradient* of the electron density exist e.g. PBE & BLYP

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- ▶ DFT cannot accurately model dispersion interactions
- ▶ This causes DNA to unravel and graphene sheets to repel each other

# STEFAN GRIMME TO THE RESCUE

- ▶ In 2006 Stefan Grimme introduced DFT-D2, a method of correcting a functional to include dispersion interactions<sup>1</sup>
- ▶ A more extensive and accurate based off of his previous DFT-D method
- ▶ This method was so cheap and accurate that it's still used to this day

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<sup>1</sup>Semiempirical GGA-type density functional constructed with a long-range dispersion correction, <https://doi.org/10.1002/jcc.20495>

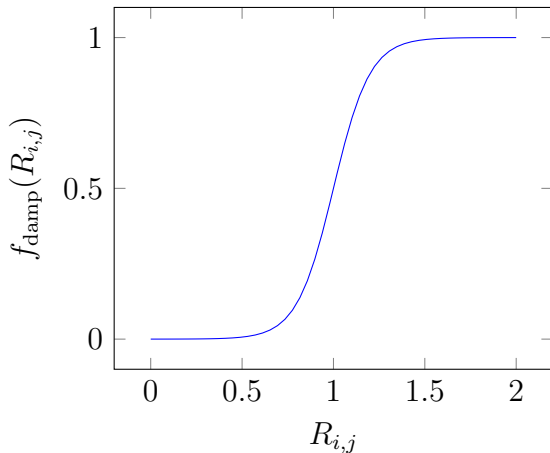
# HOW DOES DFT-D2 WORK?

- ▶ Pairwise attraction between distinct atoms  $i$  and  $j$  for all  $N$  atoms, where  $R_{i,j}$  is their separation

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

- ▶  $C_6^{i,j} = \sqrt{C_6^i C_6^j}$  is the *dispersion coefficient*
- ▶  $C_6^i = 0.05 N I_i \alpha_i$ , where  $N$  is a scaling factor depending on its row,  $I$  is the first ionisation energy and  $\alpha$  is the polarisability

# FERMI DAMPING FUNCTION



$$f_{\text{damp}}(R_{i,j}) = \frac{1}{1 + \exp(-d(R_{i,j}/R_r) - 1))}$$

# EFFECTIVENESS

## BLACK PHOSPHORUS

With the correct functional, DFT-D2 can help predict the exact equilibrium distance between sheets!<sup>2</sup>

	LDA	LDA-D2	PBE	PBE-D2	optB86b-vdW
$d_0$ / Å	2.93	2.89	3.42	3.09	3.09

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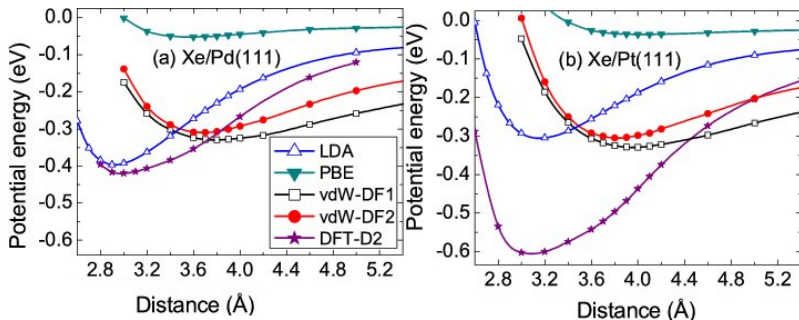
<sup>2</sup>Effect of van der Waals interaction on the structural and cohesive properties of black phosphorus



# INEFFECTIVENESS

## METALS GASSES

- DFT-D2 overestimates vdW interactions on metal surfaces  
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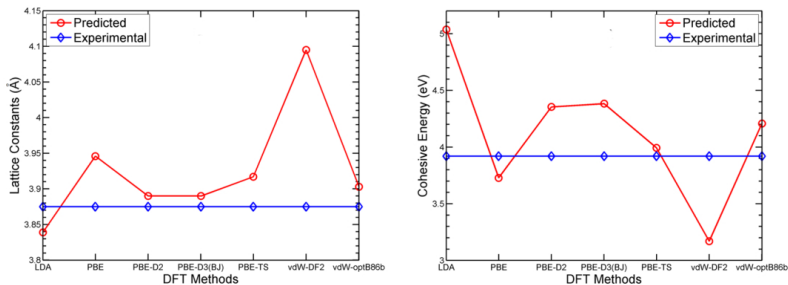


<sup>3</sup>The Role of van der Waals Interactions in the Adsorption of Noble Gases on Metal Surfaces, 10.1088/0953-8984/24/42/424211

# INEFFECTIVENESS

## EXTREME CONDITIONS

- Under extreme conditions DFT-D2 can begin to break down, and actually give worse results than no dispersion correction at all<sup>4</sup>



**FIGURE:** Shown here is the lattice constant and cohesive energy for Paladium Hydride under extreme stress

<sup>4</sup>Breaking Badly: DFT-D2 Gives Sizeable Errors for Tensile Strengths in Palladium-Hydride Solids

# OTHER CRITICISMS

- ▶ The aforementioned  $s_6$  scaling factor and  $d$  in the fermi damping function are both *fit* to emperical data
- ▶ The  $C_6$  constant does not account for the *environment* of the atom,  $C_6$  for carbon in methane is the same as  $C_6$  for carbon in benzene

- ▶ DFT-D3 uses the coordination number of the atom to help account for the chemical environment<sup>5</sup>
- ▶ Uses higher order terms *e.g.*  $C_8$

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<sup>5</sup>Density functional theory with London dispersion corrections,  
10.1002/wcms.30

# NON-LOCAL DENSITY DEPENDENT CORRECTIONS

- ▶ Only depend on the electron density at two coordinates, DFT functionals normally depend on a single location in space<sup>6</sup>
- ▶ Derived entirely from first principles, in contrast to DFT-D2/3 which depend on many experimental values and even requires fitting parameters
- ▶ Incredibly expensive to run, can take months to run even on expensive hardware, in contrast to DFT-D2 which can easily run on your laptop

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<sup>6</sup>Dispersion-Corrected Mean-Field Electronic Structure Methods

# CONCLUSION

- ▶ For fast results under normal conditions, DFT-D2/3 or any other semi-empirical method is ideal, especially for those on a budget
- ▶ For accurate results and edge cases, non-local density dependent corrections may be favourable

*The End*

*Fin.*