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Density Functional Theory with Modified Dispersion Correction for Metals Applied to Molecular Adsorption on Pt(111)

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Abstract

We have performed density functional theory calculations using our modified DFT-D2 dispersion correction for metals to investigate adsorption of a range of molecules on Pt(111). The agreement between our calculations and experimental adsorption energies ranging from 0 to 3 eV was excellent with a mean absolute deviation of 0.19 eV and a maximum deviation of 0.37 eV. Our results show that the DFT-D2 semiempirical dispersion correction can provide accurate results also for describing adsorption on metals, provided that relevant physical properties of the system are taken into account, such as shorter ranged dispersion because of screening by the conducting electrons and a lower polarizability of the core electrons in metals compared to isolated atoms.

Introduction

Density functional theory (DFT) is a workhorse in condensed matter theory, including modeling of adsorption phenomena and heterogeneous catalytic reactions on solid surfaces. While generally very successful, one very important type of interaction that is not included in local density functionals is London dispersion, or van der Waals (vdW) interactions, that arises from interaction between induced dipoles. Dispersion interactions play an important role in conformational properties as well as thermochemistry [1], and are not only important for systems dominated by non-bonded interactions. A lot of scientific effort currently goes into improving the description of dispersion interaction in DFT via new approaches and new functionals, some of which has been reviewed recently by Klimeš and Michaelides[2]. In their review, they concluded that treating adsorption of organic molecules on metals using dispersion corrected DFT, while important, is currently quite challenging.

One approach for including dispersion in DFT is by using non-local vdW functionals (e.g. [3-6]), which directly calculate the dynamic electron correlation responsible for the vdW forces [7]. A simpler, complimentary method for including dispersion is to introduce semiempirical corrections [8-11], which have proven very efficient and accurate for molecular systems. Standard semi-empirical corrections on the other hand, have shortcomings and/or give inconsistent results for extended ionic solids (e.g. [12-14]) and metallic systems (e.g. [15-18]). The main reason for the poor performance for these kinds of systems is that semiempirical dispersion methods generally were developed for molecular systems. This is particularly true for the atomic C_6 parameters in the DFT-D2 method, which determine the magnitude of the contribution for each atom type to the total dispersion interaction in the system. The nature of the dispersion interactions is significantly different for ionic solids and metals compared to molecular systems, because the electronic structure and polarizability differs significantly from typical covalent bonds. The electron cloud around a cation is considerably smaller than for the corresponding neutral atom, which results in a C_6 coefficient that is about an order of magnitude lower than the atomic coefficient [12, 14]. For metals, the situation is even more complex. Electronic screening of the dispersion interactions from the conducting electrons becomes important [13, 19, 20] and it leads to shorter-ranged interactions and a weaker dispersion interaction overall.

While quite elaborate theoretical methods have been suggested to take into account the screening effect of metals on dispersion interactions, [19, 20], in a previous paper, we suggested a simple and straightforward model that took into account the main physical effects of the metallic electronic states of the system[13]. Our recent simple modification to the DFT-D2 method performed very well for bulk properties (lattice constants and cohesive energies) as well as for adsorption properties for CO and benzene on a range of metals, and thiol physisorption and chemisorption on gold. Inspired by a recent comparison between various vdW functionals for describing molecular adsorption on Pt(111) [21], we here evaluate how well our modified DFT-D2 method performs for the same system. The set of molecules investigated is chosen because reliable experimental data exist for adsorption energies for a range of molecules on Pt(111). Additionally, the adsorption energies cover a very wide range, from about 0 eV to almost 3 eV, making it a challenging data set to model.

Computational Details

The details of the simple metal dispersion method can be found in [13], but are outlined here and we herafter denote it DFT-mtnD2, where mtn stands for “metal to noble gas”. We first make a few assumptions regarding the dispersion interactions: We assume that the only effect of the conducting valence electrons (the metallic states) is to screen the dispersion interactions, making them more short-ranged. As a simple model of the increased screening from the valence electrons, we introduced a 12 Bohr cutoff for dispersion interaction. The cutoff value was chosen such that properties for Au matched for the PBE-mtnD2 and the revPBE-mtnD2 methods. If the balance between dispersion and conventional DFT is right, results from different functionals should in general differ as little as possible[1]. The hard cutoff could potentially lead to instabilities in the geometry optimization, but only in a few cases did the default BFGS optimization algorithm fail. In all those instances, switching to damped dynamics geometry optimization enabled the geometry optimization to finish normally. A smooth switching function would alleviate this problem, but has not been implemented yet.

As a result of the approximation that the valence electrons only screen the dispersion interaction and don't contribute to the polarizability of the atoms, only the core electrons of the atoms in the metal contribute to the dispersion interactions. Because only the core electrons were assumed to contribute to the polarizability, the atomic C_6 parameters for all metals were replaced with the noble gas in the row above in the periodic table. Importantly, theoretical work that includes the effects of screening more rigorously via Lifshitz-Zaremba-Kohn theory[19] shows that the many-body effect of the metallic screening can be rewritten in terms of pairwise potentials with reduced atomic C_6 parameters, justifying our approach.

Several modified PBE functionals such as RPBE[22] and revPBE[23] have been shown to perform better for adsorption energies on solids than the original PBE[24] method, which tends to predict too strong adsorption energies for many molecules. Therefore, in this paper we evaluate the accuracy of the revPBE-mtnD2 method for molecular adsorption properties on Pt(111).

We used Quantum Espresso 5.1.2 [25] to perform the density functional theory plane-wave calculations using ultrasoft pseudopotentials. We used a 4x4 unit cell of Pt(111) with four atomic layers in the z-direction, of which the bottom layer was frozen in bulk positions during the geometry optimizations. We used a 2x2x1 k-points Monkhorst-Pack grid, 25 Ry kinetic energy cutoff and 250 Ry density cutoff. The adsorption energy of cyclohexene on Pt(111) was converged to within 0.02 eV with respect to k-points and kinetic energy cutoff. The modified file mm_dispersion.f90 used in this work is included as supporting information and works when compiling version 5.3 of Quantum Espresso. The CO and benzene data was taken from our previous work[13]. The CO adsorption used a different, smaller unit cell than the present work.

Adsorption energies were calculated using standard methods, i.e.

$$E_{ads} = E_{slab+molecule} - (E_{slab} + E_{molecule})$$

which means that the more negative the adsorption energy is the stronger the molecule binds.

Results and Discussion

The adsorption geometries for the five largest molecules in our study (cyclohexene, ethylidyne+H, C_6H_9+H, benzene and naphthalene) are shown in Figure 1. The optimized geometries are in agreement with previous studies[21, 26]. The optimized molecular geometries for all molecules in the study are available as .xyz files in the supporting information. We observe that the interaction between aromatic molecules (benzene and naphthalene) and the Pt(111) surface is strong enough that the positions of the hydrogen atoms deviate significantly from the molecular plane spanned by the carbon atoms. The strong interaction also results in high adsorption energies (Table 1). Atomic O and H bind in the three-fold hollow sites, while CO is known to bind in the top site [27-29].

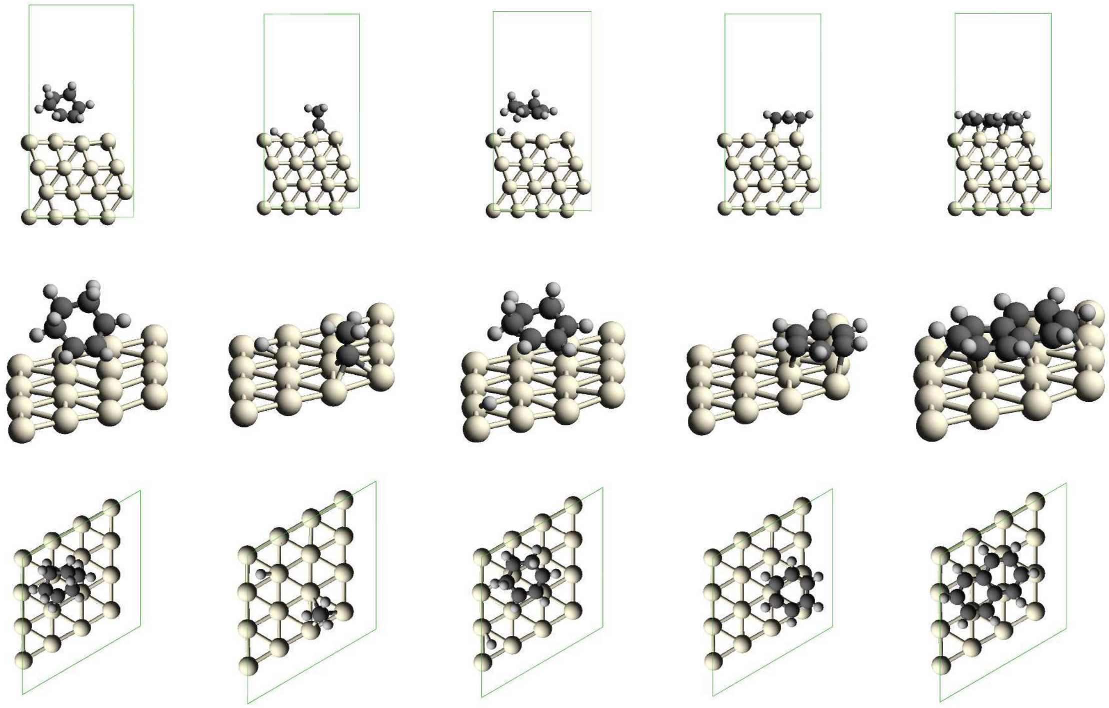

Figure 1. revPBE-mtnD2 optimized molecular geometries (from left to right) for cyclohexene, ethylidyne+H, C_6H_9+H, benzene and naphthalene. All molecules are shown along the (100) direction (top row), the (401) direction (middle row) and the (001) direction (bottom row). The unit cells are shown in green.

The adsorption energies for the range of molecules investigated here are presented in Table 1 along with the experimental values taken from [21] (which in turn were obtained from [30-40]). Our DFT predictions compare quite favorably to experiments (Table 1): the mean deviation is -0.11 eV, the mean absolute deviation is 0.19 eV and the maximum deviation is 0.37 eV, all across a range of adsorption energies from 0 to 3 eV. All of the statistical averages point to as good as or better agreement with experimental data for the revPBE-mtnD2 method than more elaborate and modern vdW functionals [21]. The non-zero mean deviation implies that the dispersion interaction parameters for Pt could potentially be altered slightly in order to optimize the adsorption energies further, but because the agreement is already acceptable, such a level of fine-tuning is outside the scope of this investigation, especially considering that a mean deviation of -0.11 eV is within DFT uncertainties from the functional itself [41]. A comparison between experiments and our method is also shown in Figure 2, where most points lie very close to the y=x line. The adsorption of saturated and aromatic hydrocarbons is well described on average. The adsorption energy of CO, cyclohexene and the C-H bond cleavage dissociation products of ethane and cyclohexene (ethylidyne and C_6H_9 in Table 1) are overestimated (bound too strongly) by 0.3-0.4 eV, and thus fall below the line in Figure

2. The deviation from experiment is systematic and shows a consistent deviation for all molecules with the same type of chemical bond to the surface. For CO it has been shown that the overbinding is a result of a too low HOMO-LUMO gap, which manifests as too strong interactions with the metal [29, 42], primarily via electron backbonding from the metal into the LUMO. The LUMO is a π* orbital both in CO and alkenes with a single double bond and therefore it is quite reasonable that the same systematic error occurs for both CO and alkenes.

For the same set of molecules on Pt(111), we observe that our results with revPBE-mtnD2 compare well to the optPBE-vdW and the PBE-dDsC functionals [21]. The three functionals treat dispersion interaction differently; yet still have similar strengths such as the error being independent on molecular size, which is a strong indication that dispersion is treated accurately with these methods. This behavior differs from PBE and BEEF-vdW, which suffer from increasing deviation from experiments with increased molecular size. The overbinding of CO and ethylidyne are less severe for revPBE-mtnD2 and opt-PBE-vdW than for PBE-dDsC. One plausible explanation is that PBE overbinds strongly even without any dispersion interactions added, and when dispersion is added, the adsorption energy can only become stronger.

Table 1. Adsorption energies for a range of molecules on Pt(111) as predicted by revPBE combined with our modified DFT-D2 dispersion correction for metals (revPBE-mtnD2) and compared to experimental data. In the last column, where the deviation between calculations and experiments are presented, DFT overbinding is shown in red and values where DFT predicts too weak binding are shown in blue.

	DFT (eV)	Experiment (eV)	DFT-exp. (eV)
methane	-0.20	-0.18	-0.02
ethane	-0.39	-0.33	-0.06
H (from ½ H_2)	-0.46	-0.39	-0.07
O (from ½ O_2)	-0.98	-1.10	0.12
cyclohexene	-1.61	-1.27	-0.34
Ethylidyne + H	-1.71	-1.36	-0.35
CO	-1.66	-1.37	-0.29
C_6H_9 + H (from cyclohexene)	-1.80	-1.43	-0.37
benzene	-1.69	-1.72	0.03
naphtalene	-2.54	-2.76	0.22
Mean deviation			**-0.11**
Mean absolute deviation			**0.19**
Mean absolute relative deviation			**17%**
Maximum absolute deviation			**0.37**

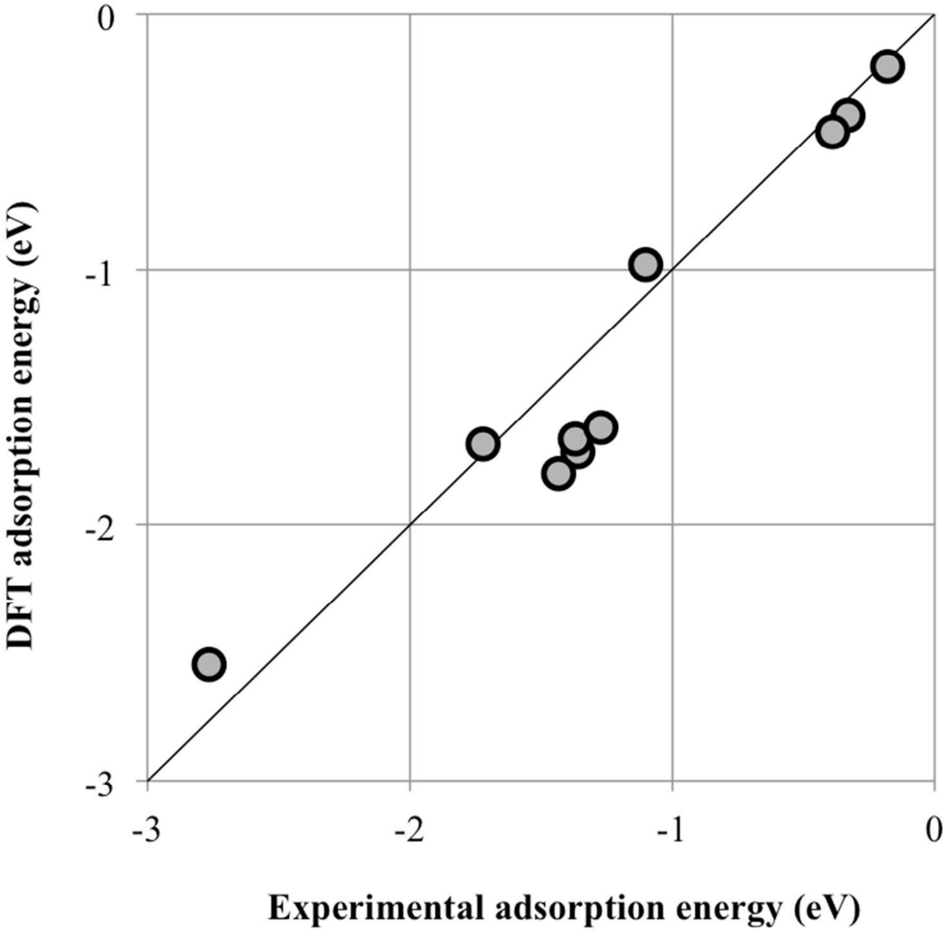

Figure 2. Comparision of experimental adsorption energies and DFT energies predicted by the revPBE-mtnD2 method. The straight line is the y=x line.

One advantage of semiempirical implementations of London dispersion in DFT compared to vdW functionals is that the dispersion contribution can be separated out and compared to the non-dispersive energy. In Table 2 we show that the dispersion contribution to the total adsorption energy ranges from 20% up to 100%, with an average of 70% for the molecules investigated here. Dispersion forces are thus predicted not only to be important, but to actually dominate the adsorption behavior on Pt(111) for a range of molecules with varying chemistry. The relative dispersion contribution to the total adsorption energy varies depending on the density functional used [13]. For more repulsive functionals like revPBE the dispersion contribution is higher than for PBE, which contains some small degree of long-range interactions in its construction [1]. The percentage of dispersion contribution in Table 2 should be treated as qualitative or semi-quantitative rather than absolute, considering that the dispersion correction is semi-empirical to begin with. The number still gives valuable insight into which forces are involved in bonding an adsorbate to the metal surface.

Table 2. The contribution to the adsorption energy from dispersion, as calculated using our modified DFT-D2 method for metals. Contributions above 100% are shown as 100%.

	DFT (eV)	Dispersion contribution (eV)	Dispersion contribution relative to the total adsorption energy
methane	-0.20	-0.18	90%
ethane	-0.39	-0.55	100%
H (from ½ H_2)	-0.46	-0.16	34%
O (from ½ O_2)	-0.98	-0.20	20%
cyclohexene	-1.62	-1.54	95%
Ethylidyne + H	-1.71	-0.69	41%
CO	-1.66	-0.36	22%
C_6H_9 + H (from cyclohexene)	-1.80	-1.85	100%
benzene	-1.69	-1.72	100%
naphtalene	-2.54	-2.58	100%
Average relative dispersion contribution to the adsorption energy			**70%**

Because the agreement between experiments and predictions is quite reasonable for a wide range of interaction energies, our DFT-mtnD2 method should be suitable for modeling a variety of systems. Importantly, at least in this case, the error is independent of the molecular size. BEEF-vdW and similar specialized functionals that have been extensively investigated, benchmarked or even optimized for certain target systems (mostly smaller molecules), would perform better for those, but going outside of the tested range of molecules, uncertainties can increase substantially. This was shown in a recent study of adsorption on Pt(111), where the maximum error for naphthalene was more than 1 eV for the PBE and BEEF-vdW functionals[21], to be compared to 0.22 eV for revPBE-mtnD2.

The fact that revPBE-mtnD2 performs as well as or better than dedicated vdW functionals [21] for molecular adsorption on Pt(111), shows that revPBE can describe molecular adsorption on a variety of solids quite successfully, including on metal surfaces, provided that proper treatment of dispersion forces is included via semiempirical corrections. This has previously been shown for adsorption on ionic surfaces, where the C_6 dispersion parameter for cations need to be reduced by about an order of magnitude[12, 43], because the polarizability of the electron cloud of a cation is significantly reduced compared to the neutral atom. For metals, the valence electrons are essentially free electrons contributing to the electric conductivity of the metal. This leads to enhanced screening of electronic interactions below the plasma frequency of the metal and as a result, mainly the core electrons contribute to the dispersion[13]. For Au we had to reduce the C_6 parameter[13] by an additional factor of 2 to obtain quantitative agreement with experiments, while in this paper we have shown that for Pt, our initial assumption give good enough results that no fine-tuning is needed or justified. Thus, in the initial assumption Au and Pt would have the same C_6 parameters, but this and our previous study[13] shows that dispersion interactions are in fact stronger for Pt than they are for Au. The more elaborate theories for dispersion interaction within metals also suggest that the strength of the dispersion interaction depends on the metal. It is quite likely that within the DFT-D2 formalism, an optimal C_6 value for each metal could be optimized, but from the data presented here and in [13], we conclude that the influence dispersion has on adsorption energies of molecules on metals is generally described quite well by our model.

Conclusion

Density functional theory with semiempirical dispersion usually performs poorly and inconsistently for metallic systems. Our modification to the DFT-D2 method, revPBE-mtnD2, is based on simple approximations of fundamental physical properties of a metallic system, taking into account the screening of the valence electrons and the lower polarizability of the atoms in the metal. We found that revPBE-mtnD2 performed very well for molecular adsorption on the Pt(111) surface, for a wide range of molecules with adsorption energies ranging from 0 to 3 eV. The mean deviation was -0.11 eV, the mean absolute deviation was 0.19 eV and the maximum deviation 0.37 eV. The -mtnD2 method is easy to implement in existing plane wave codes for which the DFT-D2 method of Grimme is available, changing only the cutoff distance for the dispersion forces and modifying the atomic C_6 parameters by replacing the parameter for the metal with the parameter for the noble gas in the row above.

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All converged geometries are available as xyz files for download, as is the mm_dispersion.f90 file used in this work (compilation has been confirmed to work for Quantum Espresso version 5.3).

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