

The Role of vdW Interactions in Coverage Dependent Adsorption Energies of Atomic Adsorbates on Pt(111) and Pd(111)

Hari Thirumalai^a, John R. Kitchin^{a,*}

^a*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213*

Abstract

Adsorption, a fundamental process in heterogeneous catalysis is known to be dependent on the adsorbate-adsorbate and surface-adsorbate bonds. van der Waals (vdW) interactions are one of the types of interactions that have not been examined thoroughly as a function of adsorbate coverage. In this work we quantify the vdW interactions for atomic adsorbates on late transition metal surfaces, and determine how these long range forces affect the coverage dependent adsorption energies. We calculate the adsorption energies of carbon, nitrogen, oxygen, sulfur, fluorine, bromine and chlorine species on Pt(111) and Pd(111) at coverages ranging from $\frac{1}{4}$ to 1 ML using the BEEF-vdW functional. We observe that adsorption energies remain coverage dependent, and this coverage dependence is shown to be statistically significant. vdW interactions are found to be coverage dependent, but more significantly, they are found to be dependent on molecular properties such as adsorbate size, and consequently, correlate with the adsorbate effective nuclear charge.

*Corresponding author

Email address: jkitchin@andrew.cmu.edu (John R. Kitchin)

We observe that these interactions account for a reduction in the binding energy of the system, due to the destabilizing attractive interactions between the adsorbates which weaken its bond with the surface.

Keywords: density functional theory, late transition metals, adsorption energies, van der Waals interactions, coverage dependence

1. Introduction

Adsorption on metal surfaces is a key elementary step in catalytic mechanisms. Transition metals are an important class of catalysts and a vast amount of research has been devoted to understanding adsorption processes on these systems [1–7]. It has been found that the activity of a catalyst can often be described by a few simple low coverage adsorption energies [8, 9]. However, under certain conditions, the coverage of adsorbates on the surface can be high. It is known that the adsorption energies of many adsorbates are coverage dependent because there is bonding competition with the surface, and the existence of adsorbate-adsorbate interactions [10, 11].

The coverage dependence of the adsorption energies of simple adsorbates has received considerable attention over the last few years. Schneider and coworkers [11, 12] predicted that higher coverages were suitable for the catalytic oxidation of NO, due to a favorable decrease in the binding energy of oxygen at those coverages. Hammer investigated the process of nitrogen dissociation on a precovered Ru(0001) surface and showed that binding energies rapidly become unfavorable with increasing coverage [13]. Miller showed changes and predicted adsorbate induced changes in the surface electronic structure governed by the d-band model [14], and also purported the exis-

tence of configurational correlations among late transition metals for coverage dependent adsorption of oxygen atoms [6]. Xu showed the existence of configurational and adsorbate configurational correlations among the same group of metals [15]. In most cases, these investigations focus on the properties of the surfaces in question, and not so much on the properties of the adsorbate. They mostly employed the DFT-GGA functionals which have some limitations, e.g. with respect to van der Waals forces. The bond forming ability of an adsorbate with a surface depends also on its own electron sharing properties such as its atomic size, electronegativity and electron affinity. These properties will also, in high coverage scenarios, affect the behavior of other nearby adsorbates on account of long range forces like van der Waals forces.

van der Waals (vdW) forces have a universal presence in all molecules and solids. They were first identified in 1873 by Johannes van der Waals at Leiden University [16]. vdW forces are relevant and important for varied systems, but their variation and difference in complexity from one environment to another still pose challenges in research. They are present in soft matter systems, surfaces, DNA, graphenes [17], fullerenes [18], etc. They are long range in nature, and are weak when compared to chemical bonding, but not necessarily negligible. The description of vdW forces from first principles calculations and Density Functional Theory (DFT) has proved to be challenging.

Since the late 90's, interest in describing vdW forces has picked up immensely. Various research groups have, with varying degrees of success, included vdW forces in DFT calculations. vdW forces are long range forces and they are said to be included in the correlation energy contribution of the

exchange-correlation functional [19]. The commonly used functionals such as the PBE [20] (GGA) functional and the LDA [21] fail to accurately account for these interactions. The LDA fortuitously shows a better agreement with some experimental values for systems with known vdW interactions, but, the exponential decline of the local density interaction is inherently wrong in describing these long range forces, while GGA underestimates the vdW contributions to binding energies [22]. Over the last decade, there have been attempts to bridge this gap in description and various approaches have been developed [19, 23–25].

A promising development towards the accurate description of vdW interactions was the introduction of the Langreth-Lundquist vdW density functional (vdW-DF) [26], which depends non-locally on the electron density. In this functional, the nonlocal correlation energy E^{nl-c} is added to a GGA exchange and local density approximation [27]. This approach has enabled a more accurate description of many systems [22, 28–30]. A series of optimized vdW functionals within the framework of the vdW-DF functional have also been developed [31–34].

In the present work, the Bayesian Error Estimation Functional with van der Waals Correlation (BEEF-vdW) [35] was used. This functional is constructed using the E^{nl-c} contribution from the vdW-DF functional. Developed recently, this functional has shown accurate results for a wide range of systems, while showing a good transferability between systems like hydrocarbon synthesis [36], adsorption on graphene [37], and adsorption on transition metals [38]. It also generates error ensembles around the ground state energy, which can provide valuable insight into the errors present in

DFT calculations and in the systems under investigation.

Our primary objective was to investigate and quantify the vdW interactions present in the coverage dependent adsorption of atomic adsorbates including carbon, nitrogen, oxygen, sulfur, fluorine, chlorine and bromine at increasing coverages of $\frac{1}{4}$ ML, $\frac{1}{2}$ ML, $\frac{3}{4}$ ML and 1 ML. Previous work by Xu et al. [15] has shown that there is a breakdown of configurational correlations between adsorption energies on the hollow and atop sites as coverages increase. We wanted to investigate if the inclusion of vdW interactions would improve the correlations between these geometrically dissimilar sites. We found that the adsorption energies remain coverage dependent for adsorption at the hollow sites, while there is no such dependency for adsorption on the atop sites when vdW contributions are included. The inclusion of vdW interactions results in the systematic decrease in binding energies of the adsorbates (less negative E_{ads}) from that shown in previous work [15] using the Perdew-Burke-Ernzerhof (PBE) [20] functional. We quantified the vdW interactions for each system and we find that they correlate with adsorbate size and the adsorbate effective nuclear charge Z_{eff} . Finally, the errors obtained from the calculations were analyzed and statistically support that a coverage dependence does indeed exist within the 95% confidence interval. We finally discuss the reasons for the behavior shown by these adsorbates.

2. Methods

The calculations required for this work were performed using the Vienna Ab-initio Simulation Package [39–41]. VASP solves the Kohn-Sham equations [42] in an iterative manner within a planewave basis set, while

employing periodic boundary conditions. The interaction between the core and valence electrons was described by the application of the projector augmented wave (PAW) method [43]. The exchange correlation functional used was the Bayesian Error Estimation Functional with van der Waals Correlation (BEEF-vdW) [35]. The construction of this functional is represented in equation 1.

$$E_{xc} = \sum_{m=0}^{M_x-1} a_m E_m^{GGA-x} + \alpha_c E^{LDA-c} + (1 - \alpha_c) E^{PBE-c} + E^{nl-c} \quad (1)$$

This functional can be considered as a linear combination of the Perdew-Burke-Ernzerhof (PBE) [20], the Perdew-Wang LDA correlation [44] and the vdW-DF2 type nonlocal correlation [45].

Our systems were modeled by considering a supercell consisting of a (111) oriented face-centered-cubic (fcc) slabs and adsorbate molecules placed on top of it. A slab was represented by a 2×2 surface unit cell, and consisted of 4 layers. A plane wave cutoff of 520 eV was used along with a k-point Monkhorst-Pack mesh [46] of $(12 \times 12 \times 1)$. A Gaussian smearing width of 0.01 was chosen for the relaxations. The slab was surrounded by 6 Å of vacuum on both sides. The bottom two layers were fixed, allowing the top two layers and the adlayer to relax. Lattice constants for the two metals, Pt and Pd were calculated using the Stabilized Jellium Equation of State (SJEOS) [47], and the BEEF-vdW functional. From the fit, we obtained the lattice constants as $a_{Pt} = 3.9934$ Å and $a_{Pd} = 3.9791$ Å. These are in reasonable agreement with experimental lattice constants $a_{Pt} = 3.9161$ Å and $a_{Pd} = 3.8823$ Å [48]. The adsorbates considered in this work were carbon, nitrogen, oxygen, sulfur, fluorine, chlorine and bromine, and they

were adsorbed in configurations of increasing monolayer coverage, $\frac{1}{4}$ ML, $\frac{1}{2}$ ML, $\frac{3}{4}$ ML and 1 ML. The adsorption sites chosen were the hollow and the atop sites. The structures were allowed to relax till the convergence criteria of 0.05 eV for forces was attained in the iterative process. The energies of the adsorbates were calculated in their gas phase, and in a box of dimensions $5 \times 6 \times 7$ Å. The systems were modeled in a way similar to that shown in figure 1.

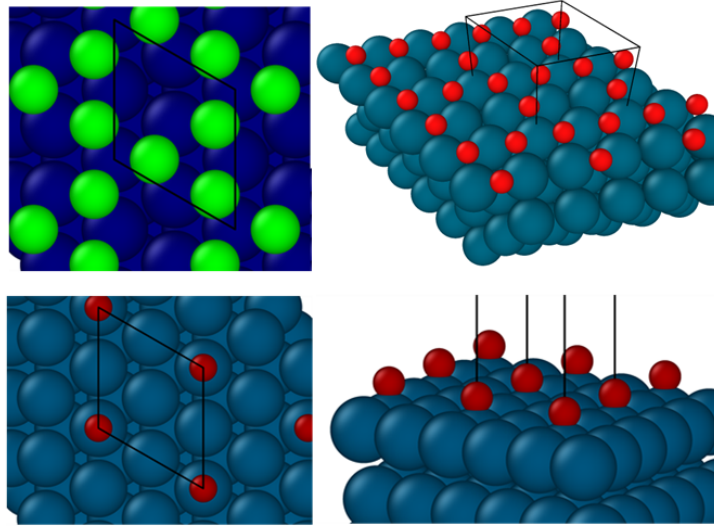


Figure 1: The system models under consideration. Top row, left to right : chlorine adsorbed at a coverage of $\frac{3}{4}$ ML, hollow sites on Pd(111) and oxygen adsorbed at a coverage of $\frac{3}{4}$ ML, hollow sites on Pt(111). Bottom row, left to right: nitrogen adsorbed at a coverage of $\frac{1}{4}$ ML, atop sites on Pt(111).

The energy of adsorption ΔE_{ads} was calculated using equation 2

$$\Delta E_{ads}(eV) = \frac{1}{n} \cdot (E_{adsorbed\ slab} - E_{clean\ slab} - n \cdot E_{adsorbate}^{gas}) \quad (2)$$

where ΔE_{ads} is the adsorption energy of the species adsorbed, per atom of

the species, and n is the number of the atoms of the species adsorbed on the surface. For example, three adsorbate atoms are adsorbed in the $\frac{3}{4}$ ML configuration, and four atoms are adsorbed in the 1 ML configuration, on the 2×2 surface. The BEEF-vdW functional employed has the capability of generating an ensemble of errors around the ground state energy, which enables us to derive a standard deviation in the computed adsorption energy. In subsequent calculations, one standard deviation, or a confidence interval of 68.27 % was used in the error bars. In addition to the standard deviation, we also utilized the non-local correction part of BEEF-vdW functional to analyze the vdW energy contributions captured by the calculations [28]. It is to be noted that the E^{nl-c} contribution to the exchange correlation energy includes a non local correction, which corresponds to the interaction beyond the LDA correlation, thus including long range interactions like vdW forces. The E^{nl-c} value can be obtained directly from the calculations, and the vdW contributions to the adsorption energy can be calculated as given in equation 3

$$\Delta E_{ads}^{nl-c}(eV/) = \frac{1}{n} \cdot (E_{adsorbed\ slab}^{nl-c} - E_{clean\ slab}^{nl-c} - n \cdot E_{adsorbate}^{gas, nl-c}) \quad (3)$$

which is an expression analogous to equation 2, except that the total energies are replaced by the corresponding non-local contributions from the calculations. The database of energies from these calculations can be accessed via the supporting information file. All the plots used in this work can be generated from data in the file.

3. Results and Discussion

We considered the adsorption of a range of adsorbates, carbon, nitrogen, oxygen, sulfur, fluorine, chlorine, and bromine on the fcc(111) metals Pt and Pd, to determine if the inclusion of vdW interactions in these calculations brought about any changes in adsorption energies or in other trends. Previous work in coverage dependent adsorption has lead to a variety of deductions and correlations. The existence of correlations in coverage dependent atomic adsorption energies has been previously reported [5, 10]. The existence of configurational correlations [6, 15] in these adsorbates was also reported. We goal was to determine if these observations would be affected by the inclusion of vdW interactions. Figure 2 a) shows the adsorption energy of each species on Pt(111) hollow sites, and figure 2 b) on Pt(111) atop sites, as a function of coverage. Figure 3 shows adsorption energies for adsorbates on the a) hollow sites and b) atop sites of Pd(111). We can observe clearly that the adsorption energies for the fcc sites are linearly dependent on coverage, which is consistent with previous results [10]. The error bars suggest in most cases that the coverage dependence is statistically significant. For example, there is a high degree of confidence the adsorption energy at 1 ML is weaker than that at $\frac{1}{4}$ ML for the hollow sites. For the atop sites, it is not always clear coverage dependence is significant.

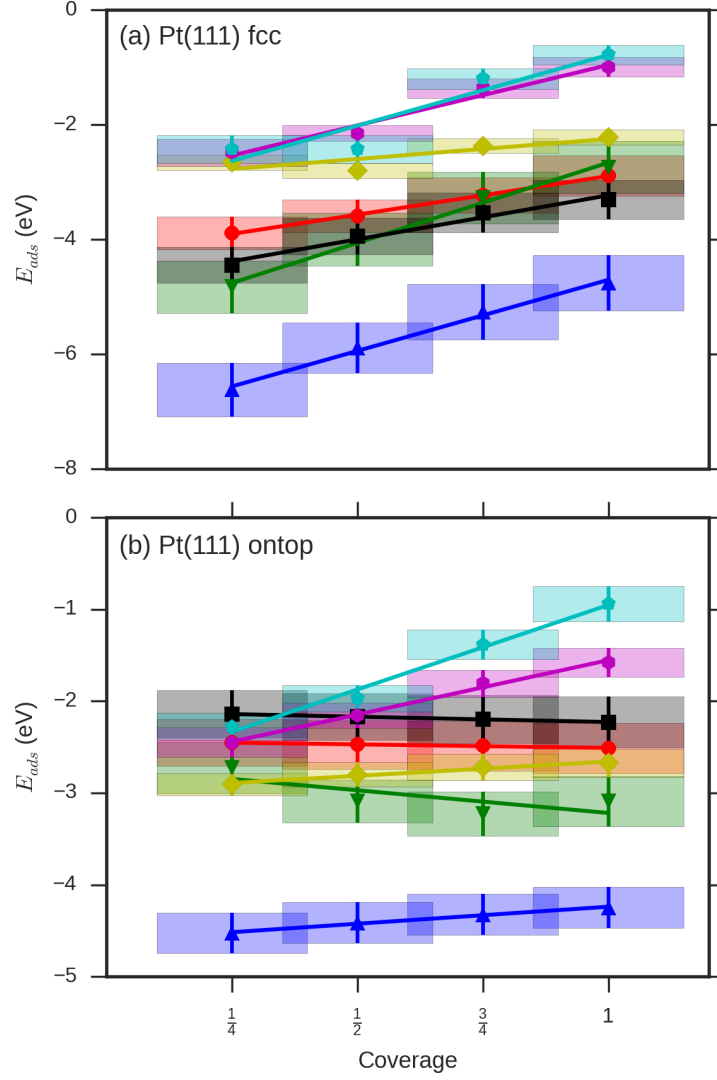


Figure 2: Energies of adsorption of adsorbate species on a) hollow sites and b) atop sites of Pt(111). The adsorbates are oxygen (red circles), sulfur (green triangles), carbon (blue triangles), nitrogen (magenta hexagons), fluorine (yellow rhombus), chlorine (black squares) and bromine (cyan pentagons). The linear fits to the data points are solid lines of the same color as the corresponding adsorbate. The first standard deviation obtained for each system is shown in similarly colored error bars.

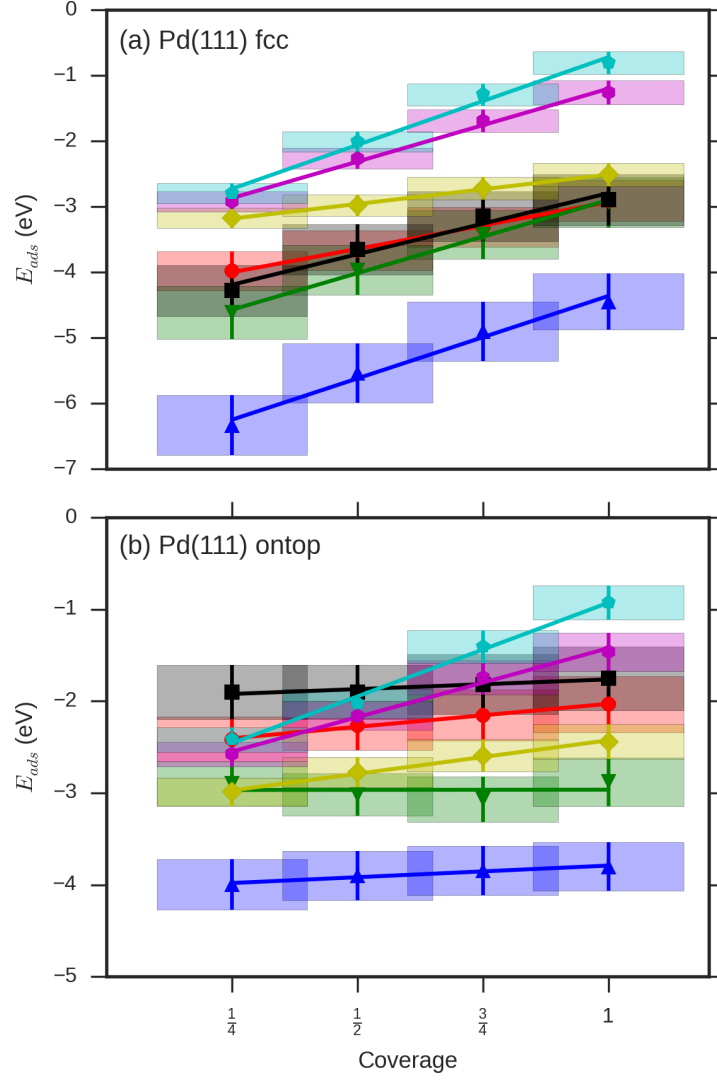


Figure 3: Energies of adsorption of adsorbate species on a) hollow sites and b) atop sites of Pd(111). The adsorbates are oxygen (red circles), sulfur (green triangles), carbon (blue triangles), nitrogen (magenta hexagons), fluorine (yellow rhombus), chlorine (black squares) and bromine (cyan pentagons). The linear fits to the data points are solid lines of the same color as the corresponding adsorbate. The first standard deviation obtained for each system is shown in similarly colored error bars.

Next, we discuss the errors in adsorption energy calculated by the BEEF-vdW functional. These have been depicted as the first standard deviation on the adsorption energy obtained at each coverage. Figures 2 and 3 show these errors in adsorption energy as transparent colored boxes. It can be seen that, in the range of the first standard deviation, these errors could be used to account for various discrepancies in calculations, which can arise from usage of a different XC functional etc... The first standard deviation includes all these variations, which makes the use of the BEEF-vdW functional quite attractive. The main conclusion from these figures is the validation of the concept of coverage dependent adsorption energy model for adsorption on the hollow sites. On visual inspection of the plots for adsorption at hollow sites, we say that within the 68% confidence interval or the first standard deviation, the energy of adsorption at the $\frac{1}{4}$ ML coverage is different from that at $\frac{1}{2}$ ML and so on. It can be observed here that there is a definite slope to the linear coverage fit, with the fit passing through, or very close to the four data points. There is a small probability that the energy of adsorption for a system at $\frac{1}{2}$ ML of adsorption could erroneously be that at $\frac{1}{4}$ ML or $\frac{3}{4}$ ML. This validation is significant because it provides a theory derived statistical evidence of the existence of this linear coverage dependence, which has often been observed and used in kinetic models. There appears to be no general linear trend observed for species adsorbing on the atop sites, and a substantial overlap of errors at each coverage suggest that the adsorption energies on the atop site are independent of coverage.

We generally observed that the adsorption energies calculated with the BEEF-vdW functional were weaker than those calculated with the PBE func-

tional, especially at lower coverages. To quantify the general reduction in adsorption energy due to the inclusion of long range forces like vdW interactions, we compared the energies of adsorption obtained in this work, with those obtained in the work done by Xu and coworkers, who used the GGA-PBE functional [15]. This is shown in the parity plot in figure 4. On close inspection, we observe that the inclusion of vdW forces through the BEEF-vdW functional results in less negative adsorption energies than what is reported in the earlier work, and that the deviations are coverage dependent. The variation of E_{ads} values reported in this work decreases with increasing coverage, and at very high coverage is nearly equivalent to those reported in earlier work. These results are not entirely intuitive; vdW interactions are usually believed to be attractive, yet including them here weakens adsorption energies. However, the PBE functional is known to overbind adsorbates, and these deviations therefore do not have any physical meaning. They simply show that the quantitative coverage dependent trends in adsorption energies are different if one uses the PBE functional, or the BEEF functional.

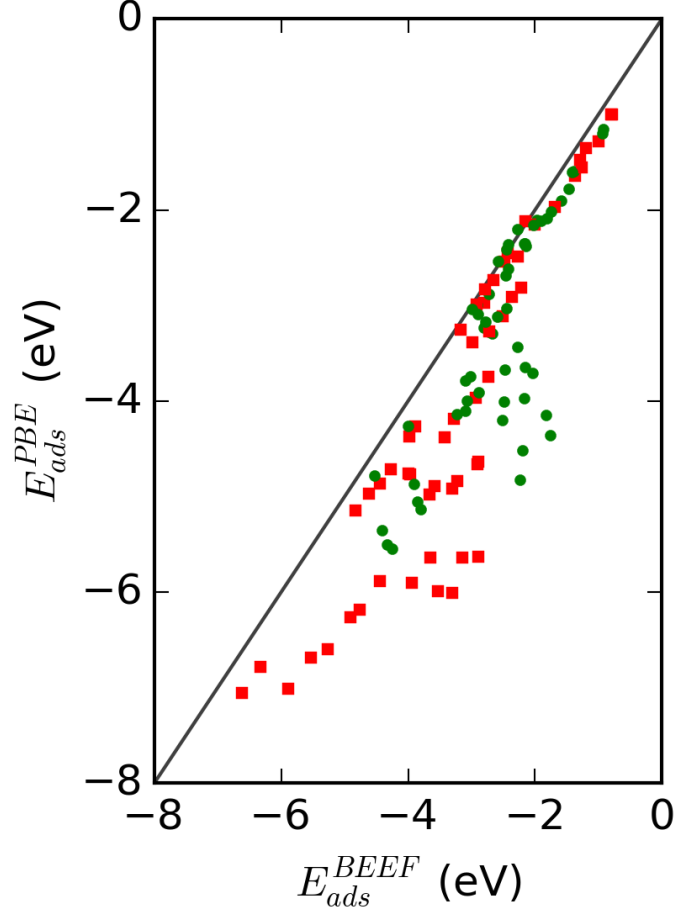


Figure 4: Parity plot showing the energies of adsorption obtained in this work, with respect to those obtained in Ref 15. Red squares indicate adsorption at the hollow sites and green circles indicate adsorption at the atop sites.

The decrease in binding strength due to the presence of multiple adsorbates on the surface occurs because the interactions of adsorbates with the surface and with each other are affected by vdW interactions. Adsorbates have only a limited number of valence electrons and any additional interac-

tions it experiences only weakens its general bonding capability. This is the basis of the Bond-order Bond-length correlations [49, 50]. The effect of vdW interactions can also be rationalized by the Effective Medium Theory (EMT) [51]. This theory states that the bonding of an atom to other atoms in its vicinity can be simply be approximated as the interaction of the atom with an effective medium (homogeneous electron gas). The density of this medium is given by the spherical average n of the density provided by the surrounding atoms [52]. The ground state of this atom can be obtained by virtue of an optimum electron density n_0 . This electron density is obtained by an adsorbate, through its interactions with the surface and other adsorbates. vdW interactions are said to exist in the space of surface-adsorbate, as well as adsorbate-adsorbate interactions, and can be considered as attractive forces. It is intuitive that these interactions, however small or large, contribute to the optimum electron density n_0 , and hence, the electron density required from the surface atoms n_{surf} participating in bond formation is lower. The metal surface is nearly an infinite sink of electrons, and so, n_{surf} is a key contributor to the optimum electron density of the adsorbate. Hence, the reduction in its contribution results in lower adsorption energetics, weaker bonding and larger bond lengths. We also try to account for lower energies of adsorption on atop site, when compared to hollow sites. Hollow sites are three-fold sites, where the adsorbate bonds to three metal atoms, while atop sites are one-fold sites and the adsorbate bonds to one metal atom. Naturally, the contribution to n_0 from threefold sites is more than that from the one-fold sites, and this reduction in contribution, in addition to the prevalent vdW forces accounts for weaker adsorption energetics on atop sites.

We next quantify the vdW interaction contributions to the adsorption energies. The non-local correlation energy E^{nl-c} was determined for each calculation for each adsorbed system, and plotted with respect to coverage. It should be noted that this quantity contains the vdW contribution to the total energy, but also contains some double counting contributions from the correlation energy. The contributions were calculated by using equation 3. The plot is shown a) for hollow sites in Fig. 5 b) for atop sites of Pt(111) and for Pd(111) in Fig. 6.

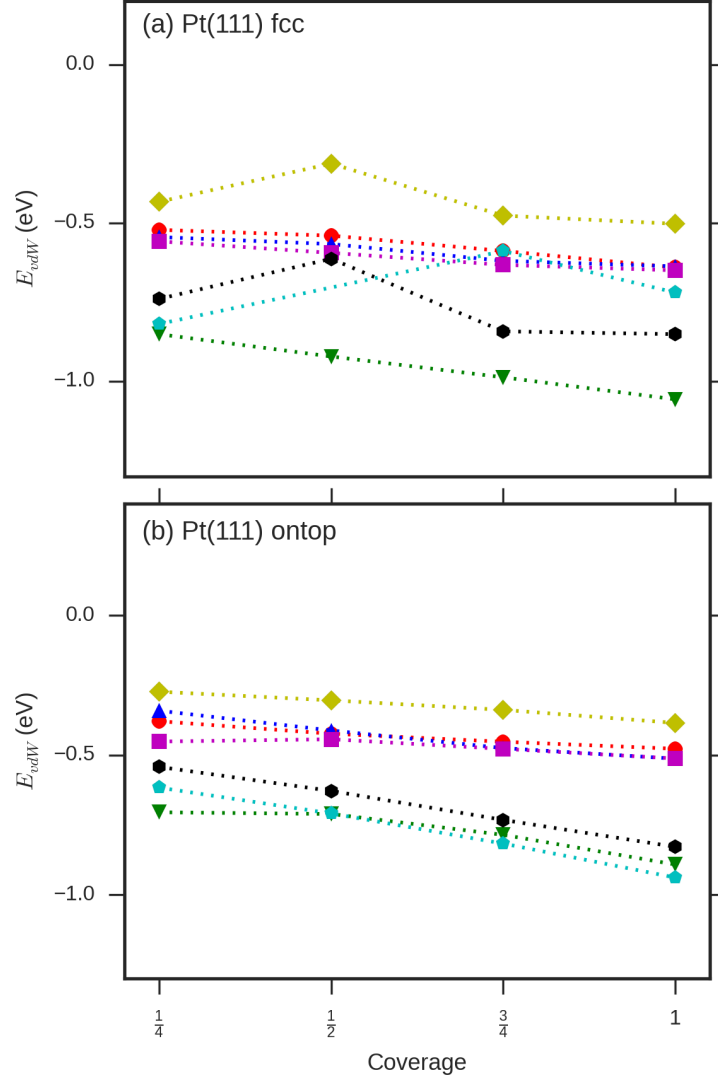


Figure 5: vdW interactions for adsorption on a) hollow sites and b) atop sites of Pt(111). The adsorbates are oxygen (red circles), sulfur (green triangles), carbon (blue triangles), nitrogen (magenta hexagons), fluorine (yellow rhombus), chlorine (black squares) and bromine (cyan pentagons). The dotted lines serve to highlight the trend

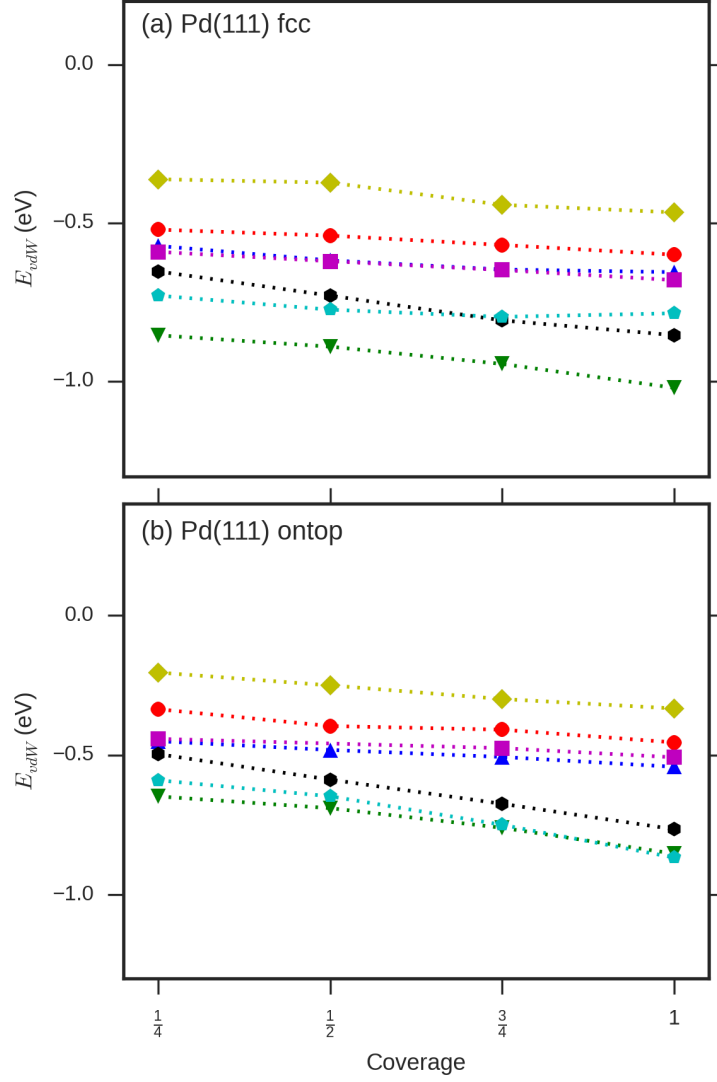


Figure 6: vdW interactions for adsorption on a) hollow sites and b) atop sites of Pd(111). The adsorbates are oxygen (red circles), sulfur (green triangles), carbon (blue triangles), nitrogen (magenta hexagons), fluorine (yellow rhombus), chlorine (black squares) and bromine (cyan pentagons). The dotted lines serve to highlight the trend.

A more negative value corresponds to a higher magnitude of attractive

vdW interactions. We see that the vdW contribution generally increases (gets more negative) with an increase in number of adsorbate atoms. A closer look at the data points suggests that larger adsorbates like sulfur, chlorine and bromine show a larger vdW contribution with increasing coverage than the smaller adsorbates. This can be explained by the fact that larger adsorbates have electron clouds that occupy a larger volume and are more polarizable. The significance of these weak interactions increase with increasing coverage and their contribution to the vdW interactions increases.

For the adsorption at the hollow sites, the interactions due to vdW forces in the oxygen and nitrogen adlayers on Pt and Pd are approximately constant with increasing coverage, likely due to screening by the metal electron density. The interactions in the fluorine adlayer follow a trend similar to the other halogens under consideration. The vdW interactions at $\frac{1}{4}$ ML for fluorine is the least, on both Pt and Pd. This suggests that its interaction with the surface is extremely unidirectional, with the the binding energy mostly accounted for by the bonding to the three-fold site. This rationale can be clearly seen for fluorine adsorption across different systems we have considered, where it shows the lowest vdW contributions among all the adsorbates.

The halogens all follow similar trends except for hollow site adsorption on Pt(111), with chlorine and bromine showing larger vdW contribution at each coverage than fluorine. This behavior is concurrent with the larger size-higher polarizability of the chlorine atom, compared to the fluorine atom. Sulfur, for both metals shows the highest contributions at the hollow sites, and a minor increase with increase in coverage. Bromine shows an even higher contribution than chlorine. We attribute this to to a trade-off be-

tween the atomic size of chlorine and its electronegativity, while in bromine, polarizability dominates, which accounts for higher vdW contribution. Adsorption of fluorine and chlorine at the hollow sites of Pt(111) denotes a peculiar case, where the adatoms started off at the hollow sites and finally converge at an atop site. This behavior is a direct contradiction of existence of relaxed adatoms on hollow sites reported in literature [15, 53]. The inclusion of vdW interactions in the calculations can be seen as a driving forces for this occurrence, and evidence of this is seen in the vdW contributions for these particular systems, which show reduced attractive vdW interactions. Wu et al. [54] reported that Cl-Cl interaction depends strongly on the distance between two adatoms, and showed that the interaction was smallest at the atop positions. Our results, for the case of Pt(111) corroborate this particular finding.

All of the observations presented earlier are also observed on the atop sites, except for the behavior of the small adsorbates carbon, nitrogen, and oxygen which also show a larger increase in vdW contribution with increasing coverage. This was not observed in the plots for adsorption at the hollow sites. The bond formed by these adsorbates on atop site is not as stable as that formed at the hollow site, and this bond is prone to the destabilizing effect of increased vdW interactions, which is possibly due to increased adsorbate-adsorbate interactions. One final observation we would like to make is that there is a negligible difference in the quantification of these interactions, between the hollow and the atop sites. This leads us to believe that vdW interactions are mainly dependent on adsorbate properties, and in the systems examined here do not depend on the nature of the surface.

One such adsorbate property of interest is the adsorbate effective nuclear charge Z_{eff} . The effective nuclear charge is the valence shell charge an electron experiences after accounting for the shielding of charge by the inner electrons of the atom. As the atom under consideration gets bigger in size, it possesses more inner electrons which result in larger shielding, and consequently, a lower Z_{eff} . Z_{eff} also increases across a period, due to the addition of valence electrons and nuclear protons, while keeping the filling of the inner shells constant. The shielding effect increases as $s < p < d < f$. Our calculations show that vdW contributions for an adsorbate correlates well with its Z_{eff} which increases as $F > O > N > C$, in the same period, and $[F > O > N > C] > Cl > Br > S$ for all the adsorbates considered. This correlation gives credence to the fact that coverage dependent adsorption energetics does depend on the molecular properties of the adsorbate.

4. Conclusions

To summarize, we performed a set of calculations of atomic adsorbates on Pt(111) and Pd(111) surfaces, with a wide range of adsorbates, at various coverages starting from $\frac{1}{4}$ ML up to 1 ML. Our main objective was to investigate the inclusion of long range forces like vdW interactions in the energetics of the adsorption process and its impact on the coverage dependence of the adsorption energy. We found that vdW forces are indeed quite important in adsorption energetics, and particularly more significant in quantity at higher coverages. We also noticed larger vdW contributions for larger adsorbates like as sulfur, chlorine and bromine. This observation was explained in the context of the Effective Medium Theory and bond order-bond length correla-

tions. These interactions are found to strongly correlate with the molecular properties of the adsorbate namely, its effective nuclear charge Z_{eff} . Lastly, we also employed the Bayesian error ensemble generated by the BEEF-vdW functional to statistically validate the observed linear coverage dependence for adsorption at hollow sites for both Pt(111) and Pd(111).

5. References

References

- [1] H. Conrad, G. Ertl, J. Küppers, E. Latta, [Interaction of NO and O₂ With Pd\(111\) Surfaces. I](#), Surface Science 65 (1) (1977) 235–244. doi:
[10.1016/0039-6028\(77\)90304-1](https://doi.org/10.1016/0039-6028(77)90304-1).
URL [http://dx.doi.org/10.1016/0039-6028\(77\)90304-1](http://dx.doi.org/10.1016/0039-6028(77)90304-1)
- [2] H. Conrad, G. Ertl, J. Küppers, E. Latta, [Interaction of NO and O₂ with Pd\(111\) surfaces. ii](#), Surface Science 65 (1) (1977) 245–260. doi:
[10.1016/0039-6028\(77\)90305-3](https://doi.org/10.1016/0039-6028(77)90305-3).
URL [http://dx.doi.org/10.1016/0039-6028\(77\)90305-3](http://dx.doi.org/10.1016/0039-6028(77)90305-3)
- [3] D. H. Parker, M. E. Bartram, B. E. Koel, [Study of High Coverages of Atomic Oxygen on the Pt\(111\) Surface](#), Surface Science Letters 217 (3) (1989) A372. doi:[10.1016/0167-2584\(89\)90123-0](https://doi.org/10.1016/0167-2584(89)90123-0).
URL [http://dx.doi.org/10.1016/0167-2584\(89\)90123-0](http://dx.doi.org/10.1016/0167-2584(89)90123-0)
- [4] E. Lundgren, A. Mikkelsen, J. N. Andersen, G. Kresse, M. Schmid, P. Varga, [Surface Oxides on Close-Packed Surfaces of Late Transition](#)

- [Metals](#), Journal of Physics: Condensed Matter 18 (30) (2006) R481–R499. doi:10.1088/0953-8984/18/30/r01.
URL <http://dx.doi.org/10.1088/0953-8984/18/30/r01>
- [5] N. İnoğlu, J. R. Kitchin, [Simple Model Explaining and Predicting Coverage-Dependent Atomic Adsorption Energies on Transition Metal Surfaces](#), Physical Review B 82 (4) (2010) 045414. doi:10.1103/physrevb.82.045414.
URL <http://dx.doi.org/10.1103/physrevb.82.045414>
- [6] S. D. Miller, N. Inoglu, J. R. Kitchin, [Configurational Correlations in the Coverage Dependent Adsorption Energies of Oxygen Atoms on Late Transition Metal Fcc\(111\) Surfaces](#), J. Chem. Phys. 134 (10) (2011) 104709. doi:10.1063/1.3561287.
URL <http://dx.doi.org/10.1063/1.3561287>
- [7] J. A. Herron, S. Tonelli, M. Mavrikakis, [Atomic and Molecular Adsorption on Pd\(111\)](#), Surface Science 606 (21-22) (2012) 1670–1679. doi:10.1016/j.susc.2012.07.003.
URL <http://dx.doi.org/10.1016/j.susc.2012.07.003>
- [8] P. Gava, A. Kokalj, S. de Gironcoli, S. Baroni, [Adsorption of Chlorine on Ag\(111\): No Subsurface Cl At Low Coverage](#), Physical Review B 78 (16) (2008) 165419. doi:10.1103/physrevb.78.165419.
URL <http://dx.doi.org/10.1103/physrevb.78.165419>
- [9] A. J. Medford, A. C. Lausche, F. Abild-Pedersen, B. Temel, N. C. Schjødt, J. K. Nørskov, F. Studt, [Activity and Selectivity Trends in Syn-](#)

- thesis Gas Conversion To Higher Alcohols, Topics in Catalysis 57 (1-4) (2013) 135–142. doi:[10.1007/s11244-013-0169-0](https://doi.org/10.1007/s11244-013-0169-0).
URL <http://dx.doi.org/10.1007/s11244-013-0169-0>
- [10] J. R. Kitchin, Correlations in Coverage-Dependent Atomic Adsorption Energies on Pd(111), Physical Review B 79 (20) (2009) 205412. doi:[10.1103/physrevb.79.205412](https://doi.org/10.1103/physrevb.79.205412).
URL <http://dx.doi.org/10.1103/physrevb.79.205412>
- [11] R. B. Getman, W. F. Schneider, DFT-based coverage-dependent model of Pt-catalyzed NO oxidation, ChemCatChem 2 (11) (2010) 1450–1460. doi:[10.1002/cctc.201000146](https://doi.org/10.1002/cctc.201000146).
URL <http://dx.doi.org/10.1002/cctc.201000146>
- [12] K. Frey, D. J. Schmidt, C. Wolverton, W. F. Schneider, Implications of Coverage-Dependent O Adsorption for Catalytic NO Oxidation on the Late Transition Metals, Catal. Sci. Technol. 4 (12) (2014) 4356–4365. doi:[10.1039/c4cy00763h](https://doi.org/10.1039/c4cy00763h).
URL <http://dx.doi.org/10.1039/c4cy00763h>
- [13] B. Hammer, Coverage Dependence of N₂ Dissociation At an N, O, Or H Precovered Ru(0001) Surface Investigated With Density Functional Theory, Physical Review B 63 (20) (2001) 205423. doi:[10.1103/physrevb.63.205423](https://doi.org/10.1103/physrevb.63.205423).
URL <http://dx.doi.org/10.1103/physrevb.63.205423>
- [14] S. D. Miller, J. R. Kitchin, Relating the Coverage Dependence of Oxygen Adsorption on Au and Pt Fcc(111) Surfaces Through Adsorbate-Induced

- Surface Electronic Structure Effects, *Surface Science* 603 (5) (2009) 794–801. doi:[10.1016/j.susc.2009.01.021](https://doi.org/10.1016/j.susc.2009.01.021).
URL <http://dx.doi.org/10.1016/j.susc.2009.01.021>
- [15] Z. Xu, J. R. Kitchin, Probing the Coverage Dependence of Site and Adsorbate Configurational Correlations on (111) Surfaces of Late Transition Metals, *J. Phys. Chem. C* 118 (44) (2014) 25597–25602. doi:[10.1021/jp508805h](https://doi.org/10.1021/jp508805h).
URL <http://dx.doi.org/10.1021/jp508805h>
- [16] H. Hamaker, The London van Der Waals Attraction Between Spherical Particles, *physica* 4 (10) (1937) 1058–1072.
- [17] M. Vanin, J. J. Mortensen, A. K. Kelkkanen, J. M. Garcia-Lastra, K. S. Thygesen, K. W. Jacobsen, Graphene on Metals: A Van Der Waals Density Functional Study, *Physical Review B* 81 (8) (2010) 081408. doi:[10.1103/physrevb.81.081408](https://doi.org/10.1103/physrevb.81.081408).
URL <http://dx.doi.org/10.1103/physrevb.81.081408>
- [18] L. A. Girifalco, Molecular Properties of Fullerene in the Gas and Solid Phases, *J. Phys. Chem.* 96 (2) (1992) 858–861. doi:[10.1021/j100181a061](https://doi.org/10.1021/j100181a061).
URL <http://dx.doi.org/10.1021/j100181a061>
- [19] Y. Andersson, D. C. Langreth, B. I. Lundqvist, Van Der Waals Interactions in Density-Functional Theory, *Phys. Rev. Lett.* 76 (1) (1996) 102–105. doi:[10.1103/physrevlett.76.102](https://doi.org/10.1103/physrevlett.76.102).
URL <http://dx.doi.org/10.1103/physrevlett.76.102>

- [20] J. P. Perdew, K. Burke, M. Ernzerhof, [Generalized Gradient Approximation Made Simple](#), Phys. Rev. Lett. 77 (18) (1996) 3865–3868. doi:[10.1103/physrevlett.77.3865](#).
URL <http://dx.doi.org/10.1103/physrevlett.77.3865>
- [21] J. P. Perdew, [Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas](#), Physical Review B 33 (12) (1986) 8822–8824. doi:[10.1103/physrevb.33.8822](#).
URL <http://dx.doi.org/10.1103/physrevb.33.8822>
- [22] P. O. Bedolla, G. Feldbauer, M. Wolloch, S. J. Eder, N. Dörr, P. Mohn, J. Redinger, A. Vernes, [Effects of Van Der Waals Interactions in the Adsorption of Isooctane and Ethanol on Fe\(100\) Surfaces](#), J. Phys. Chem. C 118 (31) (2014) 17608–17615. doi:[10.1021/jp503829c](#).
URL <http://dx.doi.org/10.1021/jp503829c>
- [23] T. C. Choy, [Van der Waals Interactions in Density Functional Theory](#), Electronic Density Functional Theory, Springer US, 1998, pp. 384–384. doi:[10.1007/978-1-4899-0316-7_29](#).
URL http://dx.doi.org/10.1007/978-1-4899-0316-7_29
- [24] S. Grimme, [Accurate Description of Van Der Waals Complexes By Density Functional Theory Including Empirical Corrections](#), J. Comput. Chem. 25 (12) (2004) 1463–1473. doi:[10.1002/jcc.20078](#).
URL <http://dx.doi.org/10.1002/jcc.20078>
- [25] X. Chu, A. Dalgarno, [Linear Response Time-Dependent Density Functional Theory for Van Der Waals Coefficients](#), J. Chem. Phys. 121 (9)

- (2004) 4083. doi:10.1063/1.1779576.
 URL <http://dx.doi.org/10.1063/1.1779576>
- [26] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, [Van Der Waals Density Functional for General Geometries](#), Phys. Rev. Lett. 92 (24) (2004) 246401. doi:10.1103/physrevlett.92.246401.
 URL <http://dx.doi.org/10.1103/physrevlett.92.246401>
- [27] J. Wellendorff, T. Bligaard, [On the Importance of Gradient-Corrected Correlation for Van Der Waals Density Functionals](#), Topics in Catalysis 54 (16-18) (2011) 1143–1150. doi:10.1007/s11244-011-9736-4.
 URL <http://dx.doi.org/10.1007/s11244-011-9736-4>
- [28] J. Carrasco, J. Klimeš, A. Michaelides, [The Role of Van Der Waals Forces in Water Adsorption on Metals](#), J. Chem. Phys. 138 (2) (2013) 024708. doi:10.1063/1.4773901.
 URL <http://dx.doi.org/10.1063/1.4773901>
- [29] J. Wong, S. Yadav, J. Tam, C. V. Singh, [A Van Der Waals Density Functional Theory Comparison of Metal Decorated Graphene Systems for Hydrogen Adsorption](#), J. Appl. Phys. 115 (22) (2014) 224301. doi:10.1063/1.4882197.
 URL <http://dx.doi.org/10.1063/1.4882197>
- [30] J. Carrasco, W. Liu, A. Michaelides, A. Tkatchenko, [Insight Into the Description of Van Der Waals Forces for Benzene Adsorption on Transition Metal \(111\) Surfaces](#), J. Chem. Phys. 140 (8) (2014) 084704.

[doi:10.1063/1.4866175](https://doi.org/10.1063/1.4866175).

URL <http://dx.doi.org/10.1063/1.4866175>

- [31] O. A. Vydrov, T. V. Voorhis, [Nonlocal Van Der Waals Density Functional Made Simple](#), Phys. Rev. Lett. 103 (6) (2009) 063004. [doi:10.1103/physrevlett.103.063004](https://doi.org/10.1103/physrevlett.103.063004).
URL <http://dx.doi.org/10.1103/physrevlett.103.063004>
- [32] J. Klimeš, D. R. Bowler, A. Michaelides, [Chemical Accuracy for the Van Der Waals Density Functional](#), Journal of Physics: Condensed Matter 22 (2) (2009) 022201. [doi:10.1088/0953-8984/22/2/022201](https://doi.org/10.1088/0953-8984/22/2/022201).
URL <http://dx.doi.org/10.1088/0953-8984/22/2/022201>
- [33] O. A. Vydrov, T. V. Voorhis, [Nonlocal Van Der Waals Density Functional: The Simpler the Better](#), J. Chem. Phys. 133 (24) (2010) 244103. [doi:10.1063/1.3521275](https://doi.org/10.1063/1.3521275).
URL <http://dx.doi.org/10.1063/1.3521275>
- [34] I. Hamada, M. Otani, [Comparative Van Der Waals Density-Functional Study of Graphene on Metal Surfaces](#), Physical Review B 82 (15) (2010) 153412. [doi:10.1103/physrevb.82.153412](https://doi.org/10.1103/physrevb.82.153412).
URL <http://dx.doi.org/10.1103/physrevb.82.153412>
- [35] J. Wellendorff, K. T. Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, K. W. Jacobsen, [Density Functionals for Surface Science: Exchange-Correlation Model Development With Bayesian Error Estimation](#), Physical Review B 85 (23) (2012) 235149.

[doi:10.1103/physrevb.85.235149](https://doi.org/10.1103/physrevb.85.235149).

URL <http://dx.doi.org/10.1103/physrevb.85.235149>

- [36] R. Y. Brogaard, R. Henry, Y. Schuurman, A. J. Medford, P. G. Moses, P. Beato, S. Svelle, J. K. Nørskov, U. Olsbye, [Methanol-To-Hydrocarbons Conversion: The Alkene Methylation Pathway](#), Journal of Catalysis 314 (2014) 159–169. [doi:10.1016/j.jcat.2014.04.006](https://doi.org/10.1016/j.jcat.2014.04.006).
URL <http://dx.doi.org/10.1016/j.jcat.2014.04.006>
- [37] S. Rajasekaran, F. Abild-Pedersen, H. Ogasawara, A. Nilsson, S. Kaya, [Interlayer Carbon Bond Formation Induced By Hydrogen Adsorption in Few-Layer Supported Graphene](#), Phys. Rev. Lett. 111 (8) (2013) 085503. [doi:10.1103/physrevlett.111.085503](https://doi.org/10.1103/physrevlett.111.085503).
URL <http://dx.doi.org/10.1103/physrevlett.111.085503>
- [38] H. Yildirim, T. Greber, A. Kara, [Trends in Adsorption Characteristics of Benzene on Transition Metal Surfaces: Role of Surface Chemistry and Van Der Waals Interactions](#), J. Phys. Chem. C 117 (40) (2013) 20572–20583. [doi:10.1021/jp404487z](https://doi.org/10.1021/jp404487z).
URL <http://dx.doi.org/10.1021/jp404487z>
- [39] G. Kresse, J. Hafner, [Ab Initio Molecular Dynamics for Liquid Metals](#), Physical Review B 47 (1) (1993) 558–561. [doi:10.1103/physrevb.47.558](https://doi.org/10.1103/physrevb.47.558).
URL <http://dx.doi.org/10.1103/physrevb.47.558>
- [40] G. Kresse, J. Hafner, [Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium](#),

- Physical Review B 49 (20) (1994) 14251–14269. doi:[10.1103/physrevb.49.14251](https://doi.org/10.1103/physrevb.49.14251).
URL <http://dx.doi.org/10.1103/physrevb.49.14251>
- [41] G. Kresse, J. Furthmüller, [Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set](#), Physical Review B 54 (16) (1996) 11169–11186. doi:[10.1103/physrevb.54.11169](https://doi.org/10.1103/physrevb.54.11169).
URL <http://dx.doi.org/10.1103/physrevb.54.11169>
- [42] W. Kohn, L. J. Sham, [Self-Consistent Equations Including Exchange and Correlation Effects](#), Physical Review 140 (4A) (1965) A1133–A1138. doi:[10.1103/physrev.140.a1133](https://doi.org/10.1103/physrev.140.a1133).
URL <http://dx.doi.org/10.1103/physrev.140.a1133>
- [43] P. E. Blöchl, [Projector Augmented-Wave Method](#), Physical Review B 50 (24) (1994) 17953–17979. doi:[10.1103/physrevb.50.17953](https://doi.org/10.1103/physrevb.50.17953).
URL <http://dx.doi.org/10.1103/physrevb.50.17953>
- [44] J. P. Perdew, Y. Wang, [Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy](#), Physical Review B 45 (23) (1992) 13244–13249. doi:[10.1103/physrevb.45.13244](https://doi.org/10.1103/physrevb.45.13244).
URL <http://dx.doi.org/10.1103/physrevb.45.13244>
- [45] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, [Higher-Accuracy Van Der Waals Density Functional](#), Physical Review B 82 (8) (2010) 081101. doi:[10.1103/physrevb.82.081101](https://doi.org/10.1103/physrevb.82.081101).
URL <http://dx.doi.org/10.1103/physrevb.82.081101>

- [46] H. J. Monkhorst, J. D. Pack, [Special Points for Brillouin-Zone Integrations](#), Physical Review B 13 (12) (1976) 5188–5192. doi:[10.1103/physrevb.13.5188](#).
URL <http://dx.doi.org/10.1103/physrevb.13.5188>
- [47] A. B. Alchagirov, J. P. Perdew, J. C. Boettger, R. C. Albers, C. Fiolhais, [Energy and Pressure Versus Volume: Equations of State Motivated By the Stabilized Jellium Model](#), Physical Review B 63 (22) (2001) 224115. doi:[10.1103/physrevb.63.224115](#).
URL <http://dx.doi.org/10.1103/physrevb.63.224115>
- [48] R. W. G. Wyckoff, R. W. Wyckoff, Crystal structures, Vol. 1, Interscience New York, 1960.
- [49] P. Mishra, D. Rai, [Bond Order-Bond Length Relationship in All-Valence-Electron Molecular Orbital Theory](#), Molecular Physics 23 (3) (1972) 631–634. doi:[10.1080/00268977200100621](#).
URL <http://dx.doi.org/10.1080/00268977200100621>
- [50] R. J. Boyd, S. C. Choi, [A Bond-Length-Bond-Order Relationship for Intermolecular Interactions Based on the Topological Properties of Molecular Charge Distributions](#), Chemical Physics Letters 120 (1) (1985) 80–85. doi:[10.1016/0009-2614\(85\)87017-2](#).
URL [http://dx.doi.org/10.1016/0009-2614\(85\)87017-2](http://dx.doi.org/10.1016/0009-2614(85)87017-2)
- [51] J. K. Nørskov, N. D. Lang, [Effective-Medium Theory of Chemical Binding: Application To Chemisorption](#), Physical Review B 21 (6) (1980)

2131–2136. doi:10.1103/physrevb.21.2131.

URL <http://dx.doi.org/10.1103/physrevb.21.2131>

- [52] F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T. R. Munter, P. G. Moses, E. Skúlason, T. Bligaard, J. K. Nørskov, [Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces](#), Phys. Rev. Lett. 99 (1) (2007) 016105. doi:10.1103/physrevlett.99.016105.

URL <http://dx.doi.org/10.1103/physrevlett.99.016105>

- [53] I. A. Pašti, S. Mentus, Halogen Adsorption on Pt (111) and Palladium Monolayer Electrocatalysts: DFT Study, ECS Transactions 25 (23) (2010) 79–87.

- [54] C. J. Wu, J. E. Klepeis, [Halogen Adsorption on Transition-Metal Surfaces: A Case Study of Cl on Ta\(110\)](#), Physical Review B 55 (16) (1997) 10848–10853. doi:10.1103/physrevb.55.10848.

URL <http://dx.doi.org/10.1103/physrevb.55.10848>