

Chemical Accurate Calculations on Metal Surfaces

Accurate Description of Dispersion Interactions for the Adsorption of Alkanes on Metal Surfaces

C. Sheldon, J. Sauer, Institut für Chemie, Humboldt-Universität zu Berlin

In Short

- Accurate adsorption energies.
- Modelling large metallic systems using RPA.
- Adsorption of the first four *n*-alkanes onto Pt(111).

Heterogeneous catalysis accounts for many of the reactions that occur in the chemical industry. A sizeable number of these catalysts are (noble) metals, such as Au and Pt, and are usually employed as supported nanoparticles. The shape of these nanoparticles depends on their preparation as well as their reaction conditions. Importantly, for close-packed cubic systems, the (111) face is the most stable orientation and, therefore, this is the most frequently exposed face of nanoparticles, e.g. Pt₁₀ clusters on the CeO₂(111) surface.

It hardly comes as a surprise then that the study of molecules on single crystal surfaces as model systems is a vibrant area of research, both experimentally and theoretically. The first step of the catalysis is adsorption onto the metal surface and so a good description of this is crucial. At present, quantum chemical methods can model this with some degree of success. However, an important contributor for the adsorption of many molecules, the van der Waals-type dispersion interaction, is not accurately described by current methods at suitable cost.[1] To achieve better results, ideally within the range of chemical accuracy (~ 4 kJ mol⁻¹), these dispersive interactions must be properly considered.[2]

The importance of achieving chemical accuracy becomes apparent even when simply considering the Arrhenius equation:

$$k = Ae^{E_a/RT}$$

where k is the rate constant, A is the pre-exponential constant, E_a is the activation enthalpy, R is the gas constant, and T is the temperature.

A relatively small difference of only a few kJ mol⁻¹ in the activation enthalpy E_a can be exponentially magnified when raised to the power.

An exemplary reaction, where dispersion interactions play the major role in adsorption, is the dehydrogenation step within the reformation process.

This is typically carried out on a noble metal surface and, frequently, the (111) face of platinum.

Importantly, the adsorption of alkanes on Pt(111) has reliable experimental data sets available, necessary for testing computational approaches against.[3] Currently, there is significant discrepancy between computational and experimental values with respect to the adsorption energy, and inconsistency in the treatment of coverages, leaving ample room for improvement.

The post-HF methods, such as MP2 and CCSD(T), account for these dispersive interactions, by correctly describing the R^{-6} asymptote of the potential energy curve.[4] Contrastingly, the computationally cheaper approximations to density functional theory (DFT), e.g. the generalised-gradient approximation (GGA) or meta-GGAs, fail to show this, meaning that corrections must be made to take this into account. A noteworthy exception to this is the Random Phase Approximation (RPA), which inherently accounts for the dispersion.

A variety of dispersion corrections exist, including force field-type corrections, which are independent of the density (a few density-dependent variants are also available), and the so-called van der Waals functionals that aim to treat the dispersion explicitly.

In the literature, many approaches have been attempted to varying degrees of success, largely through application of dispersion corrections to GGA functionals, as shown in Figure 1. However, these all fall short of attaining chemical accuracy and, for alkanes, the adsorption energies given become increasingly inaccurate as the chain lengths.

While it would be desirable to use high-level post-HF methods to solve this problem, these are cur-

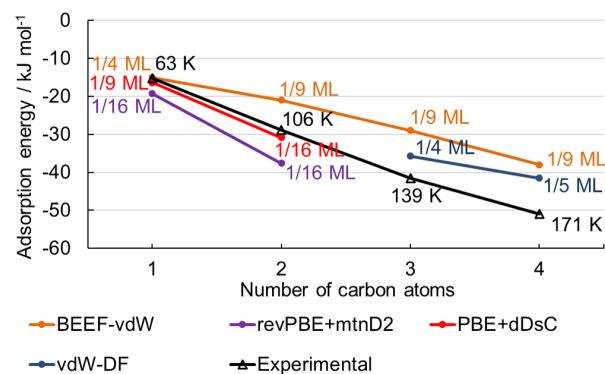


Figure 1: Experimental adsorption enthalpy, with temperature of desorption, and computational adsorption enthalpies, coverage in monolayers (ML) for *n*-alkanes on the Pt(111) surface.[3,7–9]

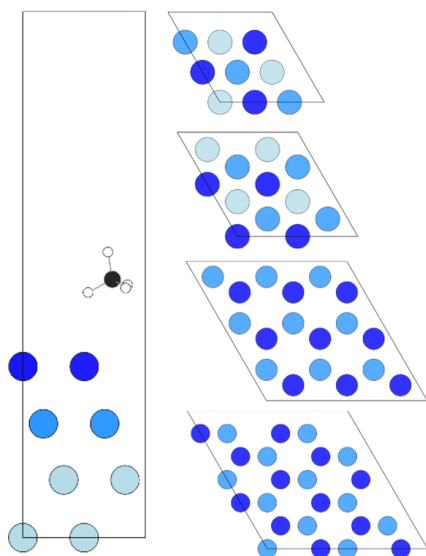


Figure 2: Surface platinum models. The left image shows methane adsorbed onto the Pt(111) surface in a (2×2) supercell. The right-hand side shows, in descending order $(\sqrt{3} \times \sqrt{3})R30^\circ$, (2×2) , (3×3) , and $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ supercells.

rently intractable, as well as many being unsuitable for application to metals. An alternative to both approaches is to use the aforementioned RPA. This occupies the Fifth-Rung of Jacob's Ladder, as applied to DFT, and is thus at the forefront of DFT research. By careful application of RPA, relatively large systems may be studied to within chemical accuracy.[4]

We intend to study the Pt(111) surface through a selection of slab models, shown in Figure 2. These will allow for alkanes of various sizes to be studied, up to *n*-butane, across a range of coverages. The Vienna ab initio Simulation Package (VASP) and its implementation of RPA will be used to this end.[5] The release of VASP 6 will make these RPA calculations even more accessible with its new low scaling RPA algorithm.[6] The HLRN 4 facilities are optimally suited for such a job, making RPA calculations more feasible and affordable.

Finally, we will combine RPA with standard DFT+D (with dispersion corrections) in a hybrid high-level QM : low-level QM approach to achieve chemical accuracy for the van der Waals interaction at reasonable cost.[2] This will be done through high-level correction of platinum clusters, where the difference is taken between RPA and DFT. This will then correct the periodic, low-level DFT representation of the platinum surface. This hybrid method will provide the accuracy of RPA at a much lower cost.

WWW

<http://www.chemie.hu-berlin.de/forschung/>

More Information

- [1] S. Grimme, A. Hansen, J. Brandenburg, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016). doi:10.1021/acs.chemrev.5b00533
- [2] M. Alessio, F. Bischoff, J. Sauer, *Phys. Chem. Chem. Phys.* **20**, 9760 (2018). doi: 10.1039/C7CP08083B
- [3] S. Tait, Z. Dohnálek, C. Campbell, B. Kay, *J. Chem. Phys.* **125**, 234308 (2006). doi: 10.1063/1.2400235
- [4] G. Chen, V. Voora, M. Agee, S. Balsubramani, F. Furche, *Annu. Rev. Phys. Chem* **68**, 421 (2017). doi:10.1146/annurev-physchem-040215-112308
- [5] G. Kresse, J. Furthmüller, *Comp. Mat. Sci.* **6**, 15 (1996). doi:10.1016/0927-0256(96)00008-0
- [6] M. Kaltak, J. Klimeš, G. Kresse, *Phys. Rev. B* **90**, 054115 (2014). doi:10.1103/PhysRevB.90.054115
- [7] J. Wellendorff, T. Silbaugh, D. Garcia-Pintos, J. Nørskov, T. Bligaard, F. Studt, C. Campbell, *Surf. Sci.* **640**, 36 (2015). doi: 10.1016/j.susc.2015.03.023
- [8] M. Andersson, *Phys. Chem. Chem. Phys.* **18**, 19118 (2016). doi:10.1039/C6CP03289C
- [9] S. Gautier, S. Steinmann, C. Michel, P. Fleurat-Lessard, P. Sautet, *Phys. Chem. Chem. Phys.* **17**, 28921 (2015). doi:10.1039/C5CP04534G

Project Partners

Dr. Joachim Paier

Funding

Kekulé Scholarship, Fonds der Chemischen Industrie