

Molecule – metal surface interactions: Can we compute them accurately?

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Heterogeneous catalysis is one of the industrially most relevant chemical processes. Nevertheless, theoretical modelling thereof is still limited due to the system size and the approximations that are necessary in such calculations. Specifically, one of the most fundamental ingredients for the accurate modelling of heterogeneous catalysis is the availability of highly accurate potential energy surfaces. Within density functional theory, these can - unfortunately - depend heavily on the exchange-correlation functional. It is therefore an urgent goal to either improve the accuracy of density functional theory (DFT) calculations or to make high-level ab initio calculations possible for larger systems. In this endeavour, also the use of non-standard methods such as quantum Monte Carlo and the combination of different levels of theory in an embedding approach will become more and more important.

Here, we present benchmark diffusion Monte Carlo (DMC) calculations for the dissociative chemisorption of H₂ on Cu(111) [1] and demonstrate the successful combination of density functional embedding theory with DMC. The computationally extremely challenging ab initio calculations for the H₂ on Cu(111) system agree to within 1.6±1.0 kcal/mol with a chemically accurate semi empirical value, giving hope that DMC is able to provide ab initio reference data for electronic structure calculations of molecule - surface interactions at chemical accuracy (see Fig. 1). The calculations are

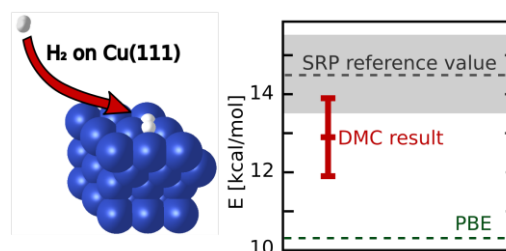


Figure 1: Reaction barrier height for the dissociative adsorption of H₂ on Cu(111): comparison of DMC with a semi empirical reference and a standard DFT calculation.

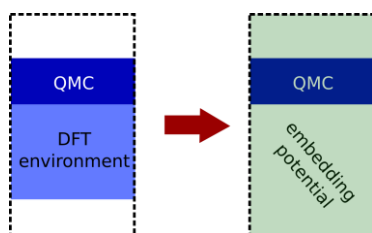


Figure 2: Schematic of periodic density functional embedding. Combining two methods that can both treat periodicity, such as DMC-in-DFT allows for the embedding of 2D periodic structures.

at the cutting edge of what is computationally feasible within a pure DMC approach at the present time. To allow for a further improvement of the results and for more computationally feasible calculations, we have recently developed and tested an interface between density functional theory embedding potentials [2] and DMC (see Fig. 2). The use of density functional embedding for DMC will allow for smaller time-step errors and smaller locality errors and will hopefully allow for sufficient data generation to train DFT functionals.

References:

- [1] Katharina Doblhoff-Dier, Jörg Meyer, Philip E. Hoggan, and Geert-Jan Kroes, *J. Chem. Theory Comput.*, **13**, 3208 (2017).
- [2] Florian Libisch, Chen Huang, and Emily A. Carter, *Acc. Chem. Res.* **47**, 2768 (2014).