Highly accurate simulations and benchmarking of molecule-surface reactions

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PROPOSITIONS

"Highly Accurate Simulations and Benchmarking of Molecule-Surface Reactions."

1. To confirm that the dissociative chemisorption of H_2 on Ni (111) is accurately simulated, a well-defined experiment for incidence energies > 0.20 eV is still desirable (**Chapter 2**).

2. Quantum dynamics molecular beam simulations can be performed efficiently with reduced computation time using the partial Monte-Carlo (PMC) method, which involves averaging over a selection of initial rovibrational states (**Chapter 4**).

3. An improved database of barrier heights can be obtained by replacing the reference barrier heights obtained with a more ad hoc semi-empirical approach with values obtained with the specific reaction parameter approach to density functional theory (**Chapter 3**).

4. The choice of the generic form of the specific reaction parameter density functional is important to ascertain the success of the application of the corresponding semiempirical approach to a specific system (**Chapter 5**).

5. If the difference of the work function of the metal surface and the electron affinity of the incident molecule is less than 7 eV a semi-empirical approach to extracting the barrier height for the dissociative chemisorption of the molecule on that surface will not give accurate results. (N. Gerrits et al., *J. Phys. Chem. Lett., **11**, 10552 (2020)*).

6. Including Van der Waals correlation in the density functional improves the description of the reactivity of a molecule-metal surface reaction even if the van der Waals well is rather shallow (M. Wijzenbroek and G.J. Kroes, *J.Chem.Phys.* **140**, 084702 (2014)).

7. The effect of surface atom motion on the dissociative chemisorption of molecule on metal surface can be taken into account using AIMD with a computational cost to be paid. Machine learning is emerging as both an accurate and a cost-effective alternative (K. Shakouri et al., *J. Phys. Chem. Lett.* **8**, 2131 (2017)).

8. With the increasing number of types of DFT functionals, the description of Jacob's ladder needs to be updated (B. G. Janesko et al., *J.Chem.Phys.* **148**, 104112 (2018)).

9. In the tradition of the peoples of the African woods, one cannot seat oneself under a tree without tasting it's fruits. It follows that a student from such a tradition will attempt to gain maximum experience with the methods available in a theory group.

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Leiden, 4 July 2023