

Performance of density functionals compared to the Quantum Monte Carlo method: case study of H₂ adsorption on silicon

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Accurate calculations of surface reaction energetics from first principles is a key issue in numerous fields of applied research, e.g. in studies on heterogeneous catalysis and simulations of molecular beam epitaxy. The reliability of the calculations depends critically both on the geometrical model used to describe the surface, as well as on the level of theory at which electronic exchange and correlation effects are treated. While density functional theory lends itself to calculations using periodic slab models, some functionals (B3LYP) and most approaches that allow for a systematically improved treatment of electronic correlation effects are better suited for cluster models. In the present study, we shall employ both cluster and slab models in conjunction with density functional theory (PW91) for calculations of the geometrical properties of reactant, product and transition states of a surface reaction, and for cluster size convergence studies. In addition, we use B3LYP and Quantum Monte Carlo (QMC) calculations performed on the clusters to monitor necessary corrections due to an improved treatment of exchange and correlation effects.

As an example for a surface reaction involving hydrogen transfer, we have studied the dissociative adsorption of H₂ at the Si(100) surface. For this system, a huge amount of experimental data is available, while attempts to describe the reaction pathway theoretically have fueled a still ongoing debate. For the reaction energy in this covalently bonded system, our QMC calculations predict both reaction energies and barriers in clear excess of LDA values, while popular semi-local density functionals (PW91, BP, BLYP) yield a Si-H binding energy even lower than the result obtained within the local-density approximation (LDA), and adsorption barriers which are clearly too low compared to experimental data. We convinced ourselves of the validity of the QMC method by comparing to the more traditional treatment of correlations within the configuration-interaction method where literature results were available (i.e. for small clusters). For larger clusters, results obtained with the B3LYP hybrid functional are in fair agreement with, though still distinctly lower than, the energetics from the QMC calculations. The rather high adsorption barriers found both in QMC and B3LYP are in better agreement than previous DFT results with the observed low sticking coefficient of H₂ on Si(001).