

The Quantum Monte Carlo method and its application to water-gas shift catalysis on Pt(111).

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The present work determines rate-limiting barrier heights and reaction mechanism for the production of hydrogen, using CO co-adsorbed on Pt (111) with water. This reaction is being developed in the renewable energy industry but fundamental studies on the mechanism are usually limited to Density-functional (DFT) work. Here we present an ab initio Quantum Monte Carlo (QMC) benchmark and proposed mechanism for this reaction. This approach is the only method that describes bond dissociation, the limiting factor of these reactions reliably.

A stochastic solution of the time-dependent Schrödinger equation is introduced. This equation is transformed into a diffusion equation by changing the time-variable to the pure-imaginary 'it'. Diffusion and drift is then used to project from a population of real-space instantaneous particle positions, or configurations, the exact ground-state density. Input is a trial wave-function that has a correlation factor (so-called Jastrow factor) optimised in a preliminary variation step (Variation Monte Carlo). This solves the integrals in the energy expectation value and is used to optimise flexible parameters in the Jastrow factor.

These stochastic approaches are currently becoming spectacularly more popular, due to the fact that they are well suited to massively parallel supercomputers. They have become routine for molecular systems, even with 1000 or more electrons.

In the solid state, additional problems have been progressively solved and software such as that adapted and used here; CASINO has been developed with emphasis on periodic systems.

First-principles approaches to key points on reaction paths at metal surfaces are now required to deliver chemical accuracy compared to reliable experiment. This means that such values as the activation barrier must be within 1 kcal/mol of empirical values (we were within 0.2 Kcal/mol). This accuracy level excludes ab initio DFT. Quantum Monte Carlo (QMC) is a promising (albeit lengthy) first-principles method for this and we are now beyond the dawn of QMC benchmarks for these systems, since hydrogen dissociation on Cu(111) has been studied with quite adequate accuracy in two improving QMC studies and compared to molecular beam measurements [1, 2].

A PRACE allocation of 45.6 Mh on Irene knl at the CEA, France made this work possible.

References

[1] Rajesh O. Sharma, Tapio T. Rantala, and Philip E. Hoggan, Quantum Monte Carlo Approach for Determining the Activation Barrier of Water Addition to Carbon Monoxide Adsorbed on Pt(111) within 1 kJ/mol <https://pubs.acs.org/doi/full/10.1021/acs.jpcc.0c07304>

[2] Doblhoff-Dier, K.; Meyer, J.; Hoggan P. E.; Kroes, G-J. Quantum Monte Carlo calculations on a benchmark molecule - metal surface reaction: H₂ + Cu (111). *J. Chem. Theory Comput.* 2017, 13 (7), pp 3208-3219. DOI: 10.1021/acs.jctc.7b00344