

Ab initio calculations beyond DFT for molecule - surface interactions

Joachim Sauer

Institut für Chemie, Humboldt Universität zu Berlin

js@chemie.hu-berlin.de

The *ab initio* prediction of molecule-surface energies for realistic models with an accuracy that is comparable to experiment is a challenging problem of computational quantum chemistry. Calculations with periodic boundary conditions are limited to DFT at the GGA or meta-GGA level and do not reach chemical accuracy which is required for a quantitative understanding of heterogeneous catalysis or gas adsorption/separation processes. Taking advantage of the full arsenal of wavefunction electron correlation methods with converging accuracy requires local, finite size models (cluster models). Three examples are given how *molecular quantum mechanics* can be used for molecule-surface interactions .

To combine the best of both approaches we use *hybrid QM:QM calculations* which combine DFT(including dispersion) for the full periodic structure as the low level method with wavefunction methods for the reaction/adsorption site as high-level method.

- (1) For *single-reference cases* the problem is solved. For adsorption of small molecules on flat oxide surfaces (MgO), in zeolites and in metal-organic frameworks (MOFs) as well as for hydrocarbon reactions in zeolites, we have reached chemical accuracy with the QM:QM approach employing MP2 and CCSD(T) as high level methods.
- (2) A large class of solid catalysts are based on *metals*. Even with specially designed functionals, the DFT errors are still large, and RPA is considered as the next step. Our RPA calculations for CH₄ on the Pt(111) surface predict the correct adsorption mode (hcp, tripod) and yield an adsorption energy of 13.5 kJ/mol which agrees within 2.2 kJ/mol with the experimental value of 15.7 kJ/mol. We show that the substantial computational effort can be reduced by several orders of magnitude, if RPA is limited to a cluster model and employed as high-level method in a hybrid RPA:DFT approach. A careful choice of the cluster model and the electronic state is crucial.

To reduce the complexity of catalysts, experiments on gas phase clusters (mass spectrometry, IR spectroscopy) are conducted to study “the active site in isolation”. Their limited size makes high-level calculations and a direct comparison of the results possible. This way, benchmarks are established on which different exchange-correlation functionals can be assessed. Functionals that pass the test can then be applied to periodic models of similar systems.

- (3) Their *multi-reference character* makes transition metal oxides the most challenging type of catalysts. As a model of a “single atom catalysts”, one Al in Al₃O₄⁺ has been replaced with Fe which changes the cone-like C_{3v} structure into a planar bicyclic frame (C_s) for Al₂FeO₄⁺ with a highly reactive terminal Al–O^{•-} radical site. This structural change is driven by a change from the Fe^{+III}/O^{-II} to the Fe^{+II}/O^{-I} valence state. With DFT, the right relative stability of the two isomers is obtained only if functionals with very high admixture of Fock exchange (50%, BHLYP) are employed.

Multi-reference (MR) calculations are required to predict the valence isomer energetics correctly. However, even if the number of atoms is not large, the MR calculations are difficult to converge with the size of the “active space”, i.e., the number of included oxygen orbitals. MRCI and NEVPT2 agree on Fe^{+II}/O^{-I} as the global minimum-energy isomer, but the predicted relative stabilities with respect to the Fe^{+III}/O^{-II} isomer, 52 ± 17 and 69 ± 14 kJ/mol, respectively, still differ by 17 kJ/mol with estimated uncertainties of the same order of magnitude. (Is this the famous 0.2 eV accuracy limit of MR calculations?) This suggests that Al₂FeO₄⁺ is not only an important benchmark for established computational methods, but also a challenging target for benchmarking advanced electronic structure methods.