**Ab initio Free Energy Calculations with Chemical Accuracy
for Molecule - Surface Interactions**

Solving problems in heterogeneous catalysis (hydrocarbon synthesis by zeolites) and gas separation (CO_2 capture and storage by MOFs - metal-organic frameworks) requires the reliable prediction of rate and equilibrium constants. With this aim in mind we have developed and applied methodology for the quantum mechanical *ab initio* prediction of *free energies* for large periodic systems (order of 1000 atoms) with chemical accuracy (4.2 kJ/mol). We have implemented a hybrid high level – low level approach combining accurate wave-function methods for the reaction site ("MP2") with less accurate, but computationally more efficient density functional theory (DFT) calculations on the full periodic system. This approach is used for structure optimizations, whereas chemical accuracy for the energies is achieved after adding Coupled Cluster corrections with basis set extrapolation. We use molecular statistics (vibrational partition function) for efficient sampling of the potential energy surface. Chemical accuracy is reached with *anharmonic* vibrational frequencies. Calculation of the latter becomes possible by solving one-dimensional Schrödinger equations for each degree of freedom separately.

These methods yield free energies for the interaction of molecules with individual interaction sites. For predicting selectivities for gas separation, e.g. CH_4/CO_2 separation in MOFs, we use Grand Canonical Monte-Carlo simulations on a lattice of these sites. The Hamiltonian is defined by the free energies of adsorption on these sites and the lateral interaction energies of the molecules in the adsorbate layer.