Ab initio Free Energy Predictions with Chemical Accuracy: Adsorption and Catalysis in Nanoporous Materials

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Rational design of materials for adsorption and catalysis

Compared to solid supported catalysts which have complex structures that are not ordered into unit cells, reticular materials like zeolites and metal-organic frameworks (MOFs) combine the advantages of reduced complexity and periodicity with a large structural variability and scalability. In zeolites, the networks of corner-sharing TO_4-tetrahedra ($T=Si$, Al^-) form a large variety of frameworks with different pore topologies and sizes [1]. The frameworks can have different Si/Al ratios and their negative charge can be compensated by different (metal) cations. Compensation with protons results in the large family of Brønsted acid catalysts. For the cosmos of one-, two- and three-dimensional reticular structures, I refer to the contributions of Yaghi (3.0) and Fujita (3.1) in this volume.

The rational design of materials is based on understanding gained from experiments and computation. An example is the development of the SAPO-34 catalyst for the UOP/HYDRO Methanol-to-Olefine process [2]. The small pore size leads to high selectivity for ethene and propene production, and the optimized acid function leads to much less formation of paraffinic by-products. In more recent work on MOFs [3], machine learning in combination with Monte Carlo simulations has been used to identify a top-performing material for H_2 storage within a data base of more than 50,000 experimental structures. The material was synthesized and the measured isotherms agreed well with the predictions. The latter example demonstrates the increasing importance of data science as the fourth pillar of science in addition to experiment, computation, and theory.

The design of improved materials and – not less important – the understanding of existing ones requires the *ab initio* prediction of adsorption constants with no other input than the positions of the atoms. Adsorption isotherms describe the adsorbed amount (given as loading Θ) as function of the gas pressure p

$$\Theta = K p / (K p + 1).$$

The adsorption (Henry) constant K is obtained from the Gibbs free energy of adsorption:

$$\Delta G_a = -RT \ln K$$

To be useful, Gibbs free energy predictions have to be chemically accurate (≈ 4 kJ/mol). For realistic models of molecule-surface interactions with hundreds of atoms in the simulation cell, this is a challenging problem of computational quantum chemistry.

Divide-and-conquer approach for *ab initio* calculation of Gibbs free energies

Free energy simulations require (i) a method to calculate the potential energy surface (PES), and (ii) a method to sample the PES. The computer time for both parts scales non-linearly with the number of atoms in the simulation cell. To make accurate calculations for large simulation cells affordable, we use a divide-and-conquer approach. We have developed methodology that relies on the Taylor expansion of the PES around equilibrium structures [4,5].

(i) For calculating the PES, we use wave-function methods as high-level methods in hybrid QM:QM calculations (QM – quantum mechanics). Specifically, we use 2nd order Møller-Plesset Perturbation Theory (MP2). As low-level QM method, we employ density functional theory with some account of dispersion (DFT+D), the work horse in solid state and surface calculations.

(ii) We calculate *anharmonic* vibrational frequencies for each degree of freedom separately. The one-dimensional potentials are sampled in *curvilinear* coordinates.

$$K = (Q_a/Q_0)\exp(-\Delta E/RT) = \exp(-\Delta S/R)\exp(-\Delta E/RT)$$

$$k = (kT/h)(Q^{\neq}/Q_0)\exp(-\Delta E^{\neq}/RT) = (kT/h)\exp(-\Delta S^{\neq}/R)\exp(-\Delta E^{\neq}/RT)$$

$$Q = \Sigma_i \exp(-\varepsilon_i/k_BT)$$

$$\Delta G = \quad -RT \ln(Q_1/Q_0) + \Delta E_{ZPV} \quad + \quad \Delta E$$

	Vibrational energies	Energy of stat. points
Standard	**harmonic**	**DFT+D**
This work	**anharmonic**	**hybrid MP2:DFT+D** **+ ΔCCSD(T)**

Chemical accuracy (1 kcal/mol ≈ 4 kJ/mol)
periodic boundary conditions, 1000 atoms per unit cell

Fig. 1. Implemented methods for calculating equilibrium and rate constants compared to the standard approach for molecule – surface interactions.

Fig. 1 summarizes the implemented methods compared to the current standard approach in computational adsorption/catalysis. For small alkanes in zeolite H-chabazite [5], we have demonstrated that both enthalpies and entropies of adsorption can be calculated with chemical accuracy. For this system, the computer time for a full MP2 calculation [6] is five orders of magnitude larger than for a DFT+D calculation (PBE+D2). Our hybrid

MP2:(PBE+D2) calculation is only two orders of magnitude more expensive than the DFT+D calculation.

Ab initio **isotherm predictions with chemical accuracy**

For adsorption of CO and N_2 in Mg-MOF-74, comparison has been made with measured adsorption isotherms. Fig. 4 in ref. [7] shows the isotherms calculated in the harmonic approximation and with anharmonic partition functions. The latter are in very good agreement with experiment. Comparison with isotherms obtained after changing the Gibbs free energy (or energy) of adsorption by 1 and 4 kJ/mol shows that the accuracy of our anharmonic free energy calculations is better than 1 kJ/mol.

We have studied adsorption of CH_4, CO_2, and H_2O in MOFs with regard to storage and separation of small energy-carrying molecules, carbon capture, and water harvesting, see refs. [8-11]. Fig. 2 shows CH_4 molecules adsorbed at different sites in Mg-MOF-74 (which are colored differently) and their contributions to the total (excess) adsorption isotherm [8]. This decomposition provides valuable information for a rational design of improved materials. However, this good agreement is not obtained for the ideal perfect Mg-MOF-74 crystal structure, but only if it is assumed that only 78% of the adsorption sites in the perfect structure are accessible for adsorption of CH_4. This percentage has been determined experimentally (isosteric heats of adsorption as function of loading) and explained with “a reduced rate of diffusion at such loadings” or with the fact that “the remaining metal sites are physically obstructed from access because of defects in the crystal structure” [12].

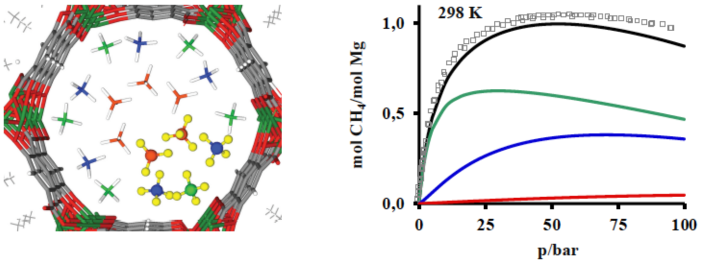

Fig 2. CH_4 adsorption in Mg-MOF-74 at different sites (left), Mg^{2+} – green, linker – blue, second layer – red, and their contributions to the total (black line) excess adsorption isotherm (right) [8]. The experimentally determined availability (78%) of adsorption sites is assumed. Experimental data points [12] are given as squares.

Outlook

Having a method for predicting adsorption isotherms with chemical accuracy for ideal

MOF (or zeolite) structures, *deviations from experiment may indicate imperfections of the sample or the measurements.* Together with progress in experimental structure characterization, this opens the door for understanding the structures of "real" materials which are employed for adsorption and catalysis. A recent example is the combined low-dose HRTEM and computational study on MOF UiO-66 [13] in which "… missing-linker defects were observed in various ... samples, including those that would have typically been assumed to be essentially defect-free, which underlines *that notionally perfect materials can contain defects invisible to most characterization techniques* that may influence observed variance in properties of MOFs such as gas uptake."

Imperfections of the materials may also explain the wide variation of experimental isotherms for H_2O adsorption in Mg-MOF-74, obtained in different laboratories or in the same laboratory using different synthesis procedures, see ref. [14] for the original references. The similarly wide variation of the isotherms predicted with different simulation techniques [14] calls for chemically accurate *ab initio* calculations for this system which are in progress.

Not less important with respect to the rational design of improved materials for water harvesting is the 1:1 connection between points on the isotherm and the structures of the corresponding number of H_2O molecules in the MOF pore which have been determined in parallel with Single Crystal-XRD experiments and quantum chemical calculations [11].

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