

MM 17: Development of Calculation Methods

Machine Learning, DFT

Time: Wednesday 10:15–12:45

Location: H22

MM 17.1 Wed 10:15 H22

Premature Convergence, It's Nothing to be Embarrassed About: Solving Performance Issues with Swarm-Based Global Optimization to Generate Pt Nanoparticle Ensembles — •JULIAN HOLLAND¹, MALGORZATA MAKOS³, DIFAN ZHANG⁴, MAL-SOON LEE³, ROGER ROUSSEAU³, CHRIS-KRITON SKYLARIS², and VANDA GLEZAKOU³ — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of Southampton, Southampton, UK — ³Oak Ridge National Laboratory, Oak Ridge, USA — ⁴Pacific Northwest National Laboratory, Three Cities, USA

Swarm-based global optimisation (GO) algorithms have proven successful in exploring potential energy surfaces (PESs) of chemical systems. However, they are often limited by their serial implementation. Our GO software, PYGLOBOPT, uses an asynchronously parallel artificial bee colony (ABC) methodology, mitigating this limitation. We enhance PYGLOBOPT further by tuning parameters against a new, general, ensemble generation assessment criterion. Using this criterion, we were also able to demonstrate how to overcome premature convergence, an issue pervading the use of the ABC algorithm for some systems, using a clustering-based methodology. We demonstrate that using the clustering algorithm alongside tuned PYGLOBOPT parameters can lead to a 5-fold increase in the number of unique low-energy structures found as well as more than halving the average energetic distance from the global minimum. We produce ensembles of thermodynamically relevant Pt nanoparticles with varying hydrogenation using our enhanced software and compare to experimental results.

MM 17.2 Wed 10:30 H22

Charge Equilibration in Machine Learning Potentials — •MARTIN VONDRÁK^{1,2}, JOHANNES MARGRAF¹, and KARSTEN REUTER² — ¹Bayreuth University, Bayreuth, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Machine learning (ML) techniques have recently been shown to bridge the gap between accurate first-principles methods and computationally cheap empirical potentials. This is achieved by learning a mapping between a system's structure and its physical properties. To this end, state-of-the-art models typically represent chemical structures in terms of local atomic environments. This inevitably leads to the neglect of long-range interactions (most prominently electrostatics) and non-local phenomena (e.g. charge transfer), resulting in significant errors in the description of e.g. polar molecules or materials in non-isotropic environments. To overcome these issues, we are developing ML frameworks for predicting charge distributions in molecules based on Charge Equilibration (QEq). Here, atomic charges are derived from a physical model using environment-dependent atomic electronegativities. In this presentation, we will demonstrate strategies for creating long-range interatomic potentials on the example of Kernel Charge Equilibration (kQEq) models combined with local Gaussian Approximation Potentials (GAP). An alternative approach, incorporating QEq into the equivariant MACE neural network scheme will also be discussed.

MM 17.3 Wed 10:45 H22

Development of on-the-fly kinetic Monte Carlo framework with neural network potentials for surface chemistry — •TOMOKO YOKAICHIYA, TATSUSHI IKEDA, KOKI MURAOKA, and AKIRA NAKAYAMA — The University of Tokyo, Tokyo, Japan

It is established that adsorbate-adsorbate lateral interactions in heterogeneous catalysis significantly influence adsorption and activation energies. To further our understanding of the degree to which such lateral interactions affect catalytic properties, we develop an "on-the-fly" adaptive kinetic Monte Carlo (kMC) simulation scheme. The scheme proceeds by energetically evaluating each configuration, including its local adsorbate-rich environment, using a neural-network potential then stores them to a database for efficient reuse in later kMC iterations. We apply this scheme to the industry-relevant interactions of H adsorption and diffusion on Pd and Pt surfaces as well as CO oxidation on Pt surfaces. With this scheme, we are able to elicit the extent lateral adsorbate-adsorbate interactions influence surface reactions and diffusion.

MM 17.4 Wed 11:00 H22

DECAF: An Open Source Local Atomic Environment Classifier — •KING CHUN LAI, SEBASTIAN MATERA, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin

Classification of local atomic environments (LAEs) is an inevitable task in most atomic-scale modeling and simulation. The reason is trivial, atoms' characteristics are predominantly determined by neighbors within a limited radius. The task itself, however, is abstract and error-prone due to the diversity of structures and the often ambiguous relationship between geometry and atomic behaviors. To address these issues, we have developed the open-source package DECAF during the last years [1]. DECAF automatically identifies equivalence groups within atomic structure datasets on the basis of the LAEs. We showcase the usage of the DECAF package on a set of nanostructures. We explain the theoretical background as well as the influence of different options to control the outcome. A particular feature is DECAF's ability for out-of-sample classification, identifying LAEs that differ from any groups in the training set. We provide examples where this has been exploited such as automatic process exploration [2] or active learning.

[1] Lai *et al.*, J. Chem. Phys. **159**, 024129 (2023). DOI: 10.1063/5.0160369 Available: <https://gitlab.mpcdf.mpg.de/klai/decap>

[2] Lai *et al.*, ChemRxiv (2024). DOI: 10.26434/chemrxiv-2024-jbzzr7

MM 17.5 Wed 11:15 H22

Accurate TDDFT Excited-State Spectra Across the Full Spectral Range — •MATTHIAS KICK and TROY VAN VOORHIS — Massachusetts Institute of Technology, Cambridge, MA, USA

Theoretically, electronic excitations can be obtained by analyzing the frequency components of the time-dependent dipole moment obtained from real-time time-dependent density functional theory (RT-TDDFT) simulations. Yet, an exact treatment of electronic excitations in large systems with TDDFT is computationally prohibitive. Super-resolution techniques such as compressed sensing typically fail due to the presence of a quasi-continuum of electronic excitations. We present a new approach where we combine exact short-time dynamics with approximate frequency space methods. As a prototypical test system, we use an organic dye-molecule adsorbed on a semi-conductor quantum-dot surface. We calculate the entire electronic absorption spectrum of this system and find that our approach can accurately capture narrow features and a quasi-continuum of states at the same time. We see a reduction of the required amount of data points up to a factor of 20 compared to standard Fourier analysis. By doing so, our method allows us to study electronic properties of large systems in ways that are not currently possible.

15 min. break

MM 17.6 Wed 11:45 H22

Beyond-DFT Machine-Learning Interatomic Potentials and Applications to Covalent-Organic Frameworks — •YUJI IKEDA, AXEL FORSLUND, and BLAZEJ GRABOWSKI — University of Stuttgart, Germany

Covalent-organic frameworks (COFs) are nanoporous crystalline materials composed of covalent organic secondary building units (SBUs), primarily composed of light elements such as C, N, O, and H. Many COFs exhibit a quasi-two-dimensional layered structure, stabilized by van der Waals (vdW) interactions. Machine-learning interatomic potentials (MLIPs) offer an exciting opportunity to explore COFs, enabling access to extended time and length scales in molecular dynamics (MD) simulations. To accurately model vdW interactions, MLIPs must be trained on datasets that include these effects, often derived from vdW-DFT functionals. However, vdW-DFT methods are essentially semi-empirical, with parameters calibrated for experimental agreement, raising concerns about their transferability. Instead, we propose generating training data from post-Hartree-Fock methods, such as coupled-cluster (CC) calculations, which are non-empirical and provide beyond-DFT accuracy. By utilizing MLIPs trained on these high-accuracy datasets, we aim to investigate the structural properties

of COFs in unprecedented detail.

MM 17.7 Wed 12:00 H22

Performance and limits of finite-temperature DFT for SiO₂ — •AXEL FORSLUND, JONG HYUN JUNG, BLAZEJ GRABOWSKI, and YUJI IKEDA — Institute for Materials Science, University of Stuttgart, Germany

Silicon dioxide (SiO₂) is a widely studied compound, yet far from fully understood. It exists in a variety of different phases, several of which are dynamically stabilized. These structures require dynamic vibrations of the atoms to not transform, and pose a challenge from an atomistic modeling point of view. Even in recent publications where state-of-the-art machine-learning interatomic potentials (MLIPs) have been used, the predictions differ significantly from experiments. For example, the transition between the two dynamically stabilized phases beta-quartz and cristobalite is very sensitive, and a single meV/atom shift can change the transition by 100 K. Not only the accuracy of the MLIP and the method for free-energy calculations matters, but also the underlying *ab initio* data play a crucial role. We demonstrate this sensitivity, and provide a simplified, yet precise method of estimating the quartz-cristobalite transition temperature. This approach is accurate enough to closely estimate the transition temperature using new density-functional-theory (DFT) functionals, and we demonstrate this for several functionals and on-top corrections. Our method is also efficient enough for using the random-phase approximation (RPA), which provides a transition temperature in very good agreement with the average CALPHAD value, and thus serves as a benchmark for the development of improved DFT functionals.

MM 17.8 Wed 12:15 H22

DSKO: Dancing through DFTB Parametrization — •ARTEM SAMTSEVICH, YIHUA SONG, CHRISTOPH SCHEURER, KARSTEN REUTER, and CHIARA PANOSSETTI — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Density Functional Tight-Binding (DFTB) offers a computationally efficient alternative to *ab initio* methods, bridging between the accuracy of DFT and the speed of semiempirical models. The approximate nature of DFTB makes its reliability highly dependent on parameter

quality. While recent advancements have significantly improved the parametrization of the so-called repulsive potential, the parametrization of the so-called electronic part of the DFTB interaction remains relatively simplistic and underdeveloped.

Here, we present our in-house DFTB Slater-Koster Optimizer (DSKO), a novel DFTB parametrization framework that aims at producing highly accurate and transferable electronic parameter sets, under rigorous physical constraints. By incorporating robust optimization algorithms and physics-informed loss functions, DSKO generates parameters that align well with high-level DFT references, particularly in predicting electronic properties like density of states (DOS) and band gaps. The versatility of DSKO facilitates the application of DFTB to a wide spectrum of materials science challenges, from catalysis to energy storage, paving the way for routine high-fidelity semiempirical simulations.

MM 17.9 Wed 12:30 H22

A Fundamental Study of Slater-Koster Tables in Density Functional Tight-binding within Trial Nickel Oxides Systems — •YIHUA SONG, ARTEM SAMTSEVICH, CHRISTOPH SCHEURER, KARSTEN REUTER, and CHIARA PANOSSETTI — Fritz Haber Institut

Density-Functional Tight Binding (DFTB), a semiempirical approximation to Density Functional Theory (DFT), is widely used thanks to its undoubtful computational efficiency, which allows to access large scale systems out of reach for DFT, while keeping adequate accuracy and direct electronic structure information. To be mentioned, even with non-spin polarized and non +U reference, the optimized parameters are able to be highly transferable to spin-polarized, DFTB+U and large scale calculations without any pain. The speed advantage in DFTB originates from precalculating distance dependent two-center interaction integrals for each atomic species pair, following the Slater-Koster (SK) principle[1]. In a fundamental study of the prototypical system Ni/NiOx, we test the hypothesis of adapting the SK integrals depending on the local environment. Considering a trial structure containing Ni in different oxidation states simultaneously, we find that assigning to each Ni "type" its optimal SK parametrization significantly improves the description of the band structure and density of states. Generalizing this concept opens a promising way towards adaptive, reliable, machine-learnable SK parameters.