O 82: Electronic Structure Theory I

Time: Thursday 10:30–12:30 Location: MA 043

O 82.1 Thu 10:30 MA 043

Black-box, accurate, and efficient prediction of band structures with Koopmans functionals — •Edward Linscott[1], Nicola Colonna[1], Junfeng Qiao[2], and Nicola Marzari[1,2] — [1]Paul Scherrer Institut, Villigen, Switzerland — [2]École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Over the past fifteen years we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties in a functional framework.[1] These orbital-density-dependent functionals impose a generalized piecewise linearity condition that ensures that orbital energies match the corresponding electron removal/addition total energy differences (in contrast to semi-local DFT, where a mismatch between the two lies at the heart of the band gap problem and the unreliability of Kohn-Sham band structures more generally). Koopmans functionals prove to be very powerful, yielding band structures and molecular orbital energies with comparable accuracy to self-consistent GW approaches but at greatly reduced computational cost and complexity.[2] This talk will cover the theory of Koopmans functionals and how recent developments – namely, the development of automated workflows via the `koopmans` code[3] and projectability-based Wannierization with manifold remixing[4] – have brought us one step closer to black-box prediction of accurate band structures.

[1] Dabo et al., PRB 82 (2010), Borghi et al., PRB 90 (2014)
[2] Nguyen et al., PRX 8 (2018), Colonna et al., JCTC 15 (2019)
[3] koopmans-functionals.org, Linscott et al., JCTC 19 (2023)
[4] Qiao et al., npj Comput. Mater. 9, 206 & 208 (2023)

O 82.2 Thu 10:45 MA 043

Efficient but accurate approximation to the exact exchange in hybrid density functionals — •Sebastian Kokott[1,2], Volker Blum[3], and Matthias Scheffler[1] — [1]The NOMAD Laboratory at the FHI of the Max Planck Society and IRIS-Adlershof of the Humboldt Universität zu Berlin, Germany — [2]Molecular Simulations from First Principles e.V., Berlin, Germany — [3]Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, USA

We introduce a computationally efficient screening for the Coulomb potential of the exact exchange terms in hybrid density functionals. The proposed approach approximates the long-range exact exchange contributions and noticeably speeds up its numerical evaluation. The method is implemented in the all-electron electronic structure code FHI-aims. We test and demonstrate the approach for prototypical semiconductors and organic crystals using the PBE0 functional. The results show that the accuracy is affected only little, but computational costs for dense materials are reduced significantly. Further, we explore how this methods enables large-scale hybrid DFT simulations.

O 82.3 Thu 11:00 MA 043

Surrogate models for the electron density and related scalar fields — Joseph Abbott[1], •Raymond Chong[1], Alan Lewis[2], and Michele Ceriotti[1] — [1]Laboratory of Computational Science and Modeling (COSMO), IMX, École Polytechnique Fédérale de Lausanne, Switzerland — [2]University of York, United Kingdom

The electron density is a central quantity in electronic structure calculations and a fundamental property of molecules and materials, allowing access to in principle any ground state electronic property. Density-functional theory (DFT) is an ab initio method that calculates the electron density of a system by solving self- consistently the Kohn-Sham equations. However, the cubic scaling in system size makes calculations for large systems intractable. As a complementary approach, machine learning (ML) surrogate models are being developed that directly predict the self-consistent electron density at a fraction of the cost of DFT, and with more favourable linear scaling. One framework in particular focuses on learning the coefficients of basis functions fitted to the real-space density using a local equivariant ML model.

An end-to-end pipeline for the training and prediction of the the electron density is presented here. Built on top of a modular and scalable software stack, the 'bypassing' of the Kohn-Sham equations to access the density of larger systems becomes increasingly possible. Furthermore, the framework can be applied to scalar field related to the electron density, opening the door to interesting applications such as the ML-driven imaging of scanning tunneling microscopy (STM).

O 82.4 Thu 11:15 MA 043

Conventional definitions of the absolute energy reference can lead to suboptimal machine learning performance for the electronic density of states — •Wei Bin How, Sanggyu Chong, Federico Grasselli, Kevin Kazuki Huguenin-Dumittan, and Michele Ceriotti — Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The electronic density of states (eDOS) provides a simple and clear picture of the distribution of energy states for electrons, granting key insights regarding the behaviour of electrons in the material. Currently, the most popular way to obtain the eDOS is through DFT calculations, but the cubic scaling behaviour of DFT has motivated a push to apply machine learning to obtain the eDOS at a much lower cost. However, when constructing the dataset for the machine learning problem, one has to choose an energy reference for the dataset. Current conventions define the energy reference of the eDOS of bulk systems using either the average Hartree potential in the cell or the Fermi level of the entire system. As the absolute value of these quantities are typically not well defined for bulk systems, eDOSes of different bulks have to be interpreted individually. However, machine learning methods typically treat these energy references as absolute which may hinder prediction performance. In this talk, we explore two different ways to provide an optimal absolute energy reference for machine learning and showcase the significant improvement in performance over conventional definitions.

O 82.5 Thu 11:30 MA 043

Prediction of the Single Particle Electronic Hamiltonian for Periodic Systems — •Hanna Türk, Divya Suman, Jigyasa Nigam, and Michele Ceriotti — EPFL, Lausanne, Switzerland

The electronic structure of a material provides essential information on a materials properties. For most materials, it can directly be computed by ab initio calculations. However, for complex systems such as material grain boundaries and interfaces, which often govern relevant chemical processes, the required large simulation cells exceed the feasiblity of such methods.

Here, we take a first step to develop a neural network based model to predict the effective single particle electronic Hamiltonian for periodic systems from given atomic environments. This apporach has proven successful for molecules[1], and we now adapt it to bulk materials. By expanding the framework to learn the realspace Hamiltonian, which includes all relevant periodic translations, sampling of the entire k-phase becomes possible. Our versatile framework yields an accurate description of the relevant electronic structure, which can be used to obtain band structures and electronic conductivities. In perspective, the prediction on local environments allows training of a model on small cells, and the trained model can then be used to obtain electronic structure information on larger, more complex systems.

[1] J. Nigam, M. J. Willatt, M. Ceriotti, J. Chem. Phys. 2022, 156, 014115, DOI 10.1063/5.0072784.

O 82.6 Thu 11:45 MA 043

Electronic excited states from physically-constrained machine learning — Edoardo Cignoni[1], •Divya Suman[2], Jigyasa Nigam[2], Lorenzo Cupellini[1], Benedetta Mennucci[1], and Michele Ceriotti[2] — [1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy — [2]Laboratory of Computational Science and Modeling (COSMO), IMX, École Polytechnique Fédérale de Lausanne, Switzerland

The integration of machine learning (ML) techniques with quantum mechanical (QM) calculations has opened new avenues in predicting a variety of electronic properties of molecules. Our work investigates a fundamental question, which is of great relevance to drive these developments: should machine learning (ML) be directly employed to predict desired properties or be synergistically combined with physically-grounded operations? To this end we introduce an integrated modelling approach in which we build a symmetry-adapted ML model that targets the properties of interest while learning the minimal-basis, single-particle electronic Hamiltonian as an intermediate. This approach also enables predictions of properties other than the ones used during the training process, like the molecular excited states. The resulting architecture, therefore, inherits the accuracy of

QM calculations, as well as the transferability to larger, more complex molecules as well as a variety of ground and excited states properties, while being orders of magnitude faster compared to the traditional electronic structure methods.

O 82.7 Thu 12:00 MA 043

Algorithmic inversion on sum over poles to embed interacting many-body systems — •Alessandro Carbone[1], Tommaso Chiarotti[1], Massimo Capone[2], and Nicola Marzari[1,3] — [1]École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — [2]International School for Advanced Studies (SISSA), via Bonomea 265, 34136 Trieste, Italy — [3]Paul Scherrer Institut, 5232 Villigen, PSI, Switzerland

Quantum embedding methods are powerful techniques to study interacting correlated electrons beyond mean-field theories. An established approach is dynamical mean-field theory, which tackles the problem by mapping the strongly correlated electrons into an Anderson impurity model. Here, we explore a different avenue to solve Dyson-like equations at $T = 0K$ — the algorithmic inversion on sum over poles — providing an embedding formulation on the real axis. We first discuss the analytical derivation of the method and compare it with an exact diagonalization of the Anderson model. We then test this solver on a one-dimensional Hubbard ring in a self-consistent framework, and conclude discussing applications to general many-body Hamiltonians and other quantum embedding strategies.

O 82.8 Thu 12:15 MA 043

Total energies from the Klein and the Luttinger-Ward functionals: analytical benchmarking of conserving many-body approximations — •Giovanna Lani[1] and Nicola Marzari[1,2] — [1]École Polytechnique Fédérale de Lausanne, Lausanne — [2]Laboratory for Materials Simulations, Paul Scherrer Institute, Villigen, Switzerland

We investigate analytically the performance of two many-body energy functionals, derived respectively by Klein and Luttinger and Ward, at different levels of diagrammatic approximations (2B, GW and T-matrix), for the calculation of total energies. We benchmark our results on the extended two-site Hubbard model, which is analytically solvable and for which several exact properties can be calculated. Despite its simplicity, this model is prototypical of the H_2 dissociation, a notoriously difficult problem to tackle for most mean-field based approaches. We show that both functionals exhibit good to excellent variational properties, particularly in the case of the Luttinger-Ward one, which is in close agreement with fully self-consistent calculations, and we elucidate the relation between the accuracy of the results and the different input one-body Green's functions. Provided that such input is wisely chosen, we demonstrate how the Luttinger-Ward functional can be used as a computationally less expensive alternative to fully self-consistent many-body calculations, without sacrificing the precision of the results. In virtue of this accuracy, we argue that this functional can also be used to rank many-body approximations at different regimes of electronic correlation, thus bypassing the need for self-consistency.