

# FHI-aims Developers' and Users' Meeting 2023

ELECTRONIC STRUCTURE THEORY WITH NUMERIC ATOM-CENTERED BASIS FUNCTIONS

August 2 – August 4, 2023

Center of Free Electron Laser Science (CFEL), Hamburg, Germany



Organizers:

Mariana Rossi, Volker Blum, Ville Havu, Patrick Rinke, Matthias Scheffler, Sebastian Kokott, Christian Carbogno, Uthpala Herath, Konstantin Lion



# Information for Participants

## 1 Scope

The workshop will cover three days and 20 invited talks, as well as a poster session. Time will be reserved in the afternoons for “Hands-On Discussions”, providing dedicated time for the participants to split up into small groups to focus on topics of specific interest ranging from methodological improvements all the way to code development questions related to specific subgroups of participants and joint programming sessions. Participants are also able to present their own work during the Postersession.

Topics covered are new developments in electronic structure theory with numeric atom-centered orbitals - including, but not limited to:

- Numerical algorithms and new methods for NAOs
- Technical advances in and scalability of electronic structure methods
- External libraries interfacing with FHI-aims
- Recent developments in advanced electronic properties

## 2 Conference Venue

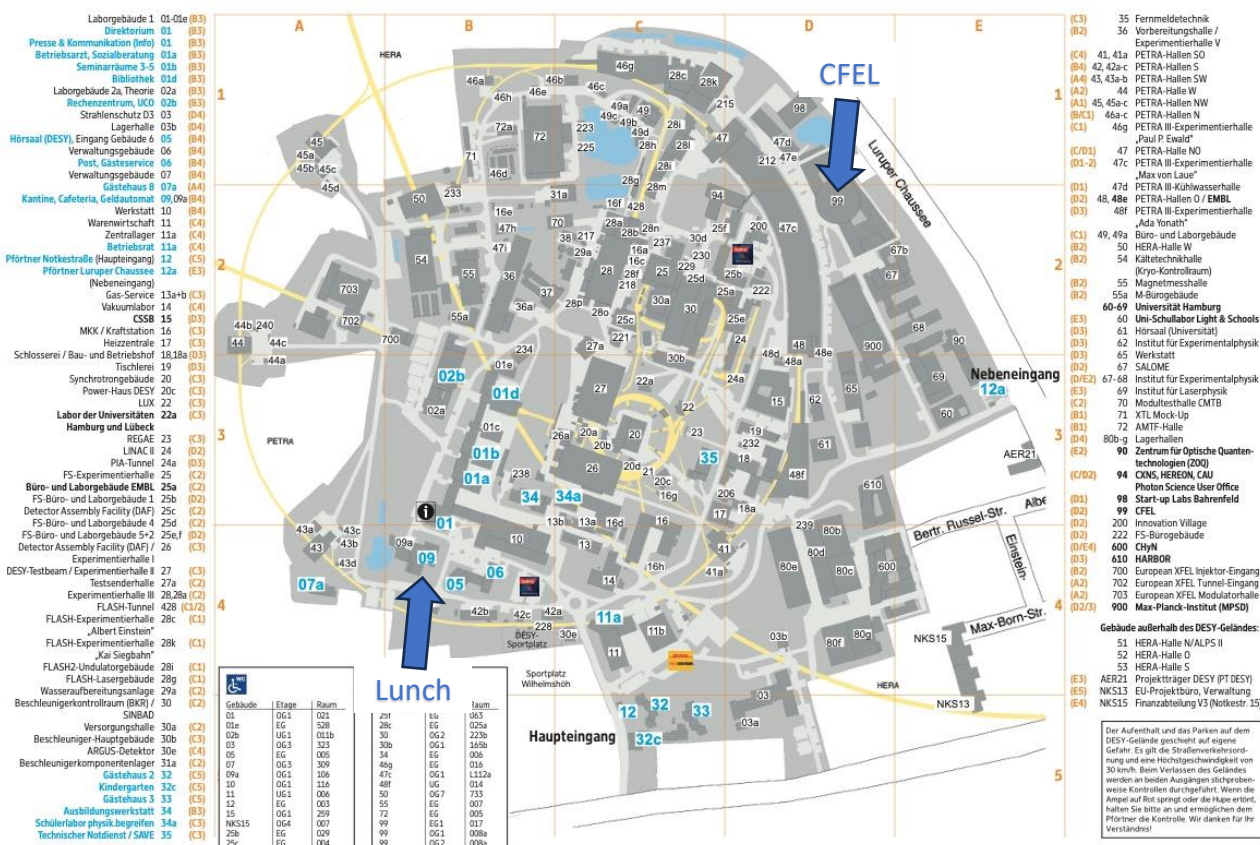
The workshop will be held from August 2 – August 4, 2023 at

[Center of Free Electron Laser Science \(CFEL\)](https://www.cfel.de)

Luruper Chaussee 149, 22761 Hamburg

All talks will take place at Luruper Chaussee 149, CFEL building (building 99), in Seminar rooms I and II, on the ground floor. Find more details at [https://www.cfel.de/about/building/index\\_eng.html](https://www.cfel.de/about/building/index_eng.html) or refer to the campus map below.

Lunch will be served at the [DESY Canteen](#) (building 09/09a), and all participants will be provided with food vouchers. The canteen is a 10-minute walk from the conference building, a walk which we will do together. The meal plan for the conference is available at this [link](#). In addition to the main courses, a variety of side dishes and a salad bar are available.



Oktober 2021

### 3 Program

Wednesday, August 2, 2023		
13:00 – 13:15	Registration	
13:15 – 13:30	Welcome	Mariana Rossi
13:30 – 14:00	FHI-aims overview and GIMS	Volker Blum / Andrey Sobolev
14:00 – 14:30	Current status of Hybrid Density Functionals and ELPA	Florian Merz
14:30 – 15:00	Coffee Break	
15:00 – 15:30	Modelling Core Level X-ray Photoelectron Spectroscopy using the $\Delta$ -Self-Consistent-Field Approach	Juhan Matthias Kahk
15:30 – 16:00	Real-time Nuclear-Electron Orbital Time-dependent DFT	Yosuke Kanai
16:00 – 16:15	Break	
16:15 – 17:30	Hands-on Discussion 1	
17:30 – 18:00	Hands-on Discussion Summary 1	
18:00 – 18:30	Break	
18:30 – 20:30	Poster Session	

Thursday, August 3, 2023		
09:00 – 09:30	Intricacies of DFT+U, not only in a numeric atom centered orbital framework	Matthias Kick
09:30 – 10:00	The exchange-hole dipole moment (XDM) dispersion model implementation in FHI-aims	Alberto Otero de la Roza
10:00 – 10:30	Coffee Break	
10:30 – 11:00	Overview GW: Status of the library GreenX	Dorothea Golze
11:00 – 11:30	Coupled Clusters for Solids	Evgeny Moerman
11:30 – 12:00	Basis-set-error free RPA correlations for atoms and diatomic molecules based on the Sternheimer equation	Xinguo Ren
12:00 – 13:30	Lunch Break	
13:30 – 14:00	Periodic BSE	Ruiyi Zhou
14:00 – 14:30	Machine Learning for the Electronic Structure	Alan Lewis
14:30 – 15:00	Coffee Break	
15:00 – 15:30	ASE: Current Status and Future Changes	Thomas Purcell
15:30 – 16:00	Atomic Simulation Interface (ASI)	Pavel Stishenko
16:00 – 16:15	Break	
16:15 – 17:30	Hands-on Discussion 2	
17:30 – 18:00	Hands-on Discussion Summary 2	
18:00	Joint Dinner	

<b>Friday, August 4, 2023</b>		
09:00 – 09:30	Simulation of Tip-enhanced Raman Spectroscopy	Yair Litman
09:30 – 10:00	Small Basis Set DFT	Elisabeth Keller
10:00 – 10:30	Coffee Break	
10:30 – 11:00	Interpreting Ultrafast Electron Transfer on Surfaces with a Converged First-Principles Newns-Anderson Chemisorption Function	Simiam Ghan
11:00 – 11:30	Electronic Transport	Christian Carbogno
11:30 – 12:00	Current Status of DFPT	Connor Box
12:00 – 13:30	Lunch Break	
13:30 – 14:00	Active machine learning workflows for nonadiabatic dynamics at surfaces	Wojciech Stark
14:00 – 14:30	Solvation Models	Jakob Filser
14:30 – 15:00	Improving the Description of Molecular Crystals via Multimer Embedding	Alexander List
15:00 – 15:30	Coffee Break and Final Discussions	

## 4 Poster Abstracts

### 4.1 List of posters

1. Implementation of Code to Calculate Crystal Orbital Overlap Population (COOP) and its Application to the Chemical-Bonding Analysis in Li-intercalated Layered Materials
2. Accurate Modelling of N-Type Doped TiO<sub>2</sub> Polymorphs Using DFT+U with Occupation Matrix Control
3. Scalable and Efficient Ab Initio X-Ray Spectroscopy Calculations with Numeric Atomic Orbitals
4. Active-Learning for Machine-Learned Interatomic Potentials; The Example of Thermal Conductivity Predictions
5. Realistic Description of Conductivity of Disordered LTO from Machine-Learned Model
6. Spin-Dependent Optical Response of Magnetic Metals from First Principles
7. Energy Barriers of Polymorphic Transitions via First-Principles Nudged Elastic Band Calculations
8. Improved Forces for the Exchange-Hole Dipole Moment Model
9. Performance-Portable Implementation of SISSO++ and The Application in Materials' Mobility Prediction
10. First-Principles Light-Driven Molecular Dynamics: Case Study on LiNbO<sub>3</sub>
11. Implementation of Molecular Orbital Localization Through Unitary Optimizations
12. Non-Perturbative Electronic Transport Theory for Strongly Anharmonic Materials
13. Elucidating the Role of Polymorphism for Thermal Conductivities in Ga<sub>2</sub>O<sub>3</sub> Using Fully Anharmonic Green-Kubo Calculations
14. GW Approach for Periodic Systems in FHI-aims: Current Status and Ongoing Works
15. Separable Resolution-of-Identity in an All-Electron Numeric Atom-Centered Basis Set Framework

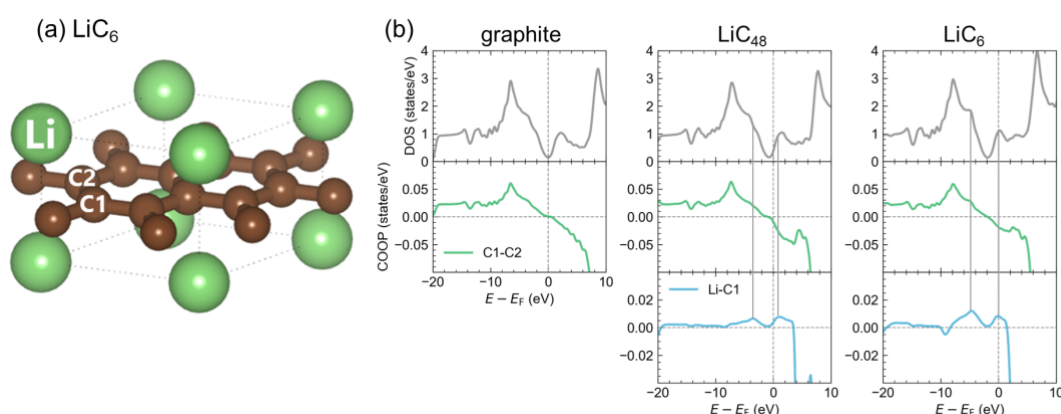
# Implementation of Code to Calculate Crystal Orbital Overlap Population (COOP) and its Application to the Chemical-Bonding Analysis in Li-intercalated Layered Materials

Izumi Takahara, Kiyou Shibata, and Teruyasu Mizoguchi

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Crystal Orbital Overlap Population (COOP) is a powerful tool for analyzing chemical-bonding in molecules and solids [1]. If a single-particle wave function is expressed as a linear combination of atom-centered basis functions, Mulliken overlap population is defined as  $2c_{il}c_{jl}S_{ij}$ , where  $c_{il}$  represents the expansion coefficient for the  $l$ -th state and  $S_{ij}$  represents the matrix element of the overlap matrix. Positive overlap population indicates a bonding interaction between orbitals, whereas a negative value indicates an anti-bonding interaction. The density of states (DOS) weighted by overlap population is referred to as a COOP diagram, which allows us to obtain the nature of interactions between arbitrary orbitals and atomic pairs at specific energies. In this research, we have developed a code to calculate the COOP between desired orbitals or desired atoms based on the output by FHI-aims [2]. Our code is capable of MPI parallelization over k-points and supports output in both text and binary formats for flexible post-processing.

As an example of the application of the developed program, we have performed a chemical-bonding analysis in Li intercalated layered materials. Three representative layered compounds were selected and the changes in chemical bonding upon the Li intercalation were analyzed. Fig. 1 shows the result of the chemical-bonding analysis in Li-intercalated graphite, including graphite,  $\text{LiC}_{48}$ , and  $\text{LiC}_6$ . The DOS and COOP diagrams reveal that the Li-C bonding interactions increase with the increase in the Li content, while the C-C anti-bonding interactions increase around the Fermi level ( $E_F$ ). In the presentation, we will show the details of our COOP code implemented in FHI-aims.



**Figure 1:** (a) Crystal structure of  $\text{LiC}_6$ . (b) Total DOS and COOP diagrams in graphite,  $\text{LiC}_{48}$ , and  $\text{LiC}_6$ .

[1] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **26** (1987) 846-878.

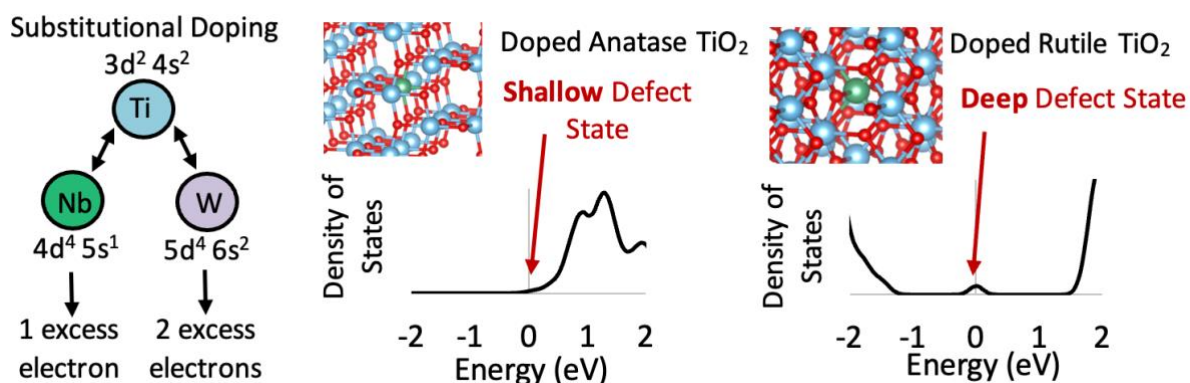
[2] V. Blum *et al.*, *Comput. Phys. Commun.* **180** (2009) 2175-2196.

# Accurate Modelling of N-Type Doped TiO<sub>2</sub> Polymorphs using DFT+U with Occupation Matrix Control

Amit Chaudhari, Andrea Folli, and Andrew Logsdail

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TiO<sub>2</sub> is a key component in enabling technologies for the transition to Net-Zero 2050. This includes catalysis, where TiO<sub>2</sub> acts as a non-inert catalyst support able to enhance the reactivity of supported metal nanoparticles; as well as electronics, where TiO<sub>2</sub>-based materials are promising transparent conducting oxide materials for photovoltaics [1]. To overcome limitations in the catalytic and electrical performance of TiO<sub>2</sub>, substitutional dopants such as Nb and W can be introduced in order to modify its physical and chemical properties (e.g. band gap and electrical conductivity) [2]. This is highly sensitive to the TiO<sub>2</sub> polymorph, as has been reported experimentally where Nb and W substitutionally doped anatase and rutile exhibit varying degrees of excess electron localisation resulting in the formation of deep defect states in rutile and shallow defect states in anatase [3]. There are conflicting theoretical rationalisations for this discrepancy, due to the well-known challenge of modelling charge localisation in strongly correlated metal oxides using density functional theory. This limits any atomic-level understanding of the nature of the defect states in both polymorphs and the ability to develop accurate structure-property models.



In this work, both Nb and W doped anatase and rutile TiO<sub>2</sub> are modelled using Hubbard corrected density functional theory (DFT+U) using the FHI-aims software. Control of the DFT+U occupation matrix allows accurate modelling of the formation of localised excess electron(s) and provides a theoretical rationalisation for experimentally observed differences in the defect states in anatase and rutile. These calculations also remain computationally inexpensive (compared to hybrid functionals) demonstrating their applicability for large systems with hundreds of atoms. This work is part of a Prosperity Partnership project funded by the UK Engineering and Physical Sciences Research Council (EPSRC), bp through the bp International Centre for Advanced Materials (bp-ICAM) and Johnson Matthey plc in collaboration with Cardiff University and The University of Manchester (EPSRC grant number EP/V056565/1).



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- [1] S. Sathasivam, D. S. Bhachu, Y. Lu, N. Chadwick, S. A. Althabaiti, A. O. Alyoubi, S. N. Basahel, C. J. Carmalt and I. P. Parkin, *Scientific Reports* **5**, 10952 (2015).
- [2] J. Z. Bloh, A. Folli and D. E. Macphee, *J. Phys. Chem. C* **118**, 21281-21292 (2014).
- [3] H.-Y. Lee and J. Robertson, *J. Appl. Phys.* **113** (2013).

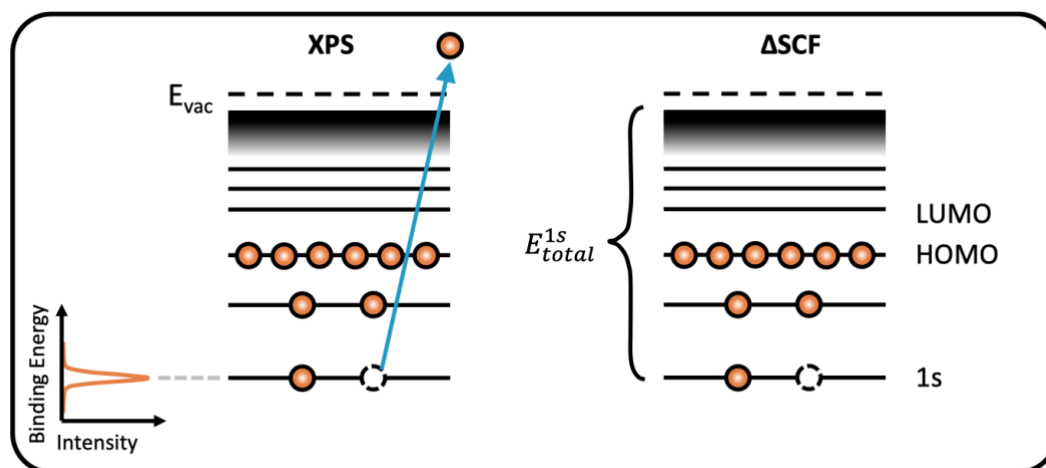
# Scalable and Efficient Ab Initio X-Ray Spectroscopy Calculations with Numeric Atomic Orbitals

Dylan B. Morgan<sup>1</sup>, Samuel J. Hall<sup>1</sup>, Benedikt P. Klein<sup>1,2</sup>, Matthew A. Stoodley<sup>1,2</sup>, and Reinhard J. Maurer<sup>1</sup>

<sup>1</sup> University of Warwick, Coventry, United Kingdom

<sup>2</sup> Diamond Light Source, Didcot, United Kingdom

First principles simulations of x-ray photoemission spectroscopy (XPS) and near-edge x-ray absorption fine-structure (NEXAFS) crucially support the assignment of surface spectra composed of many overlapping signatures. Core-level constrained Density Functional Theory calculations based on the  $\Delta$ -SCF method are commonly used to predict relative XPS binding energy (BE) shifts but often fail to predict absolute BEs due to basis set incompleteness or pseudopotential approximations. The all-electron numeric atomic orbital code FHI-aims enables an accurate prediction of absolute BEs. However, the existing code lacked computational scalability to address large systems and robustness concerning localisation of the core hole. In this contribution, I present the results of a recent code redesign. Code refactorization allowed us to remove over 3000 lines of redundant code. The new code shows massive improvements in the scaling whilst retaining the same functionality. We showcase the new capabilities by simulating core-level spectroscopic fingerprints of graphene moire superstructures. Future plans involve adsorbing single atoms and nanoclusters of Ni and Pt at the defect sites. The ultimate long-term goal for this project is to create an accurate and user-friendly black box simulation toolkit for ab initio XPS or NEXAFS simulations.



**Figure 1:** Visualisation of how the XPS simulation method  $\Delta$ -SCF compares to its experimental counterpart. In  $\Delta$ -SCF, two calculations are performed; 1 ground state and 1 with a core hole. The difference between the two is equivalent to the experimentally-derived binding energy.

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# Active-Learning for Machine-Learned Interatomic Potentials; The Example of Thermal Conductivity Predictions

Kisung Kang, Christian Carbogno, and Matthias Scheffler

*The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin, Berlin, Germany*

Reliable predictions of the thermal conductivity of strongly heat insulating materials are crucial for several applications, including the discovery of improved thermoelectrics that can convert otherwise wasted heat into useful electrical energy [1]. It has been established in recent years that heat insulators are highly anharmonic materials [2]. Therefore, the phonon picture is not necessarily a good starting point for the theoretical description but one needs to involve the full ab initio Green-Kubo approach [3, 4]. However, reaching convergence of the statistical mechanics with respect to supercell size and simulation time is challenging. It requires costly and long ab initio molecular dynamics (MD) simulations, even when coupled with physics-based separation and extrapolation methods [5]. In this regard, machine-learned interatomic potentials (MLIPs) promise to significantly accelerate such Green-Kubo calculations, while (hopefully) retaining ab initio accuracy. Still, training a MLIP requires utmost care and substantial electronic-structure theory data, especially for complex systems with involved interactions. One needs to ensure that the formation of all relevant defects and other causes of anharmonicities are described well, even if such defects occur very rarely in a MD simulation. To facilitate and speed up this involved training step, we present an active-learning scheme to train MLIPs that exploits subsampling and deep-ensemble based uncertainty estimation [6]. The approach is demonstrated for the message-passing neural network NequIP [7] and training data created by FHI-aims. As demonstrated for Si and  $\text{KCaF}_3$ , this allows for the iterative improvements of MLIPs in a data-efficient way, by avoiding redundant calculations already well-described by the MLIP. Furthermore, our approach enables one to granularly control the degree of accuracy of the MLIP, hence ensuring that those strongly anharmonic effects crucial for thermal conductivities are well captured, even when they are not particularly prominent in the thermodynamic sampling.

[1] G. J. Snyder and R. S. Toberer, *Nat. Mater.* **7**, 105 (2008).

[2] F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).

[3] C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).

[4] F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Lett.* **130**, 236301 (2023).

[5] F. Knoop, M. Scheffler, and C. Carbogno, *Phys. Rev. B* **107**, 224304 (2023).

[6] L. Kahle and F. Zipoli, *Phys. Rev. E* **105**, 015311 (2022).

[7] S. Batzner, A. Musaelian, L. Sun, M. Geiger *et al.*, *Nat. Commun.* **13**, 2453 (2022).

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# Realistic Description of Conductivity of Disordered LTO from Machine-Learned Model

**Tavinder Singh and Harald Oberhofer**

*Theoretical Physics VII and Bavarian Center for Battery Technology (BayBatt), University of Bayreuth, 95447 Bayreuth, Germany*

Lithium Ion Batteries are of great importance to our daily lives. We incorporate them into small gadgets and tools and, moreover, likely need to introduce them into heavy machinery and cars for a sustainable future. Yet, especially with a view on the latter, reliability and energy density of batteries hampers their adoption. This drives the search for new materials exhibiting favourable properties like high transport efficiencies, wider ranges of electrochemical stability, and at least for the emerging class of all-solid-state batteries-zero strain on ion insertion for anode materials.

In this respect, Lithium Titanium Oxide is a potential candidate exhibiting such properties. In the past, we have shown that in this material the electronic conductivity is due to the formation of polarons, which in turn might influence the movement of ions. Yet, a full study of the possibly correlated motion of both types of carriers is still lacking due to the combinatorial explosion of possible polaron and ion sites making it hard to compute necessary energies and barriers from first principles. Thus, we will use a compressed sensing model based on Density Functional Theory energetics to increase the efficiency of our sampling and obtain a full description of conductivity and correlated motion in  $\text{TiO}_2$ .

[1] Kick, M., Grosu, C., Schuderer, M., Scheurer, C. and Oberhofer, H., *J. Phys. Chem. Lett.* **11**, 2535–2540 (2020).

[2] Kick, M., Scheurer, C. and Oberhofer, H., *ACS Appl. Energy Mater.* **4**, 8583–8591 (2021).

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# Spin-Dependent Optical Response of Magnetic Metals from First Principles

**Maria K. Pogodaeva, Sergey V. Levchenko, and Vladimir P. Drachev**

*Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30/1, Moscow 121205, Russia*

We present a real-space implementation of analytic electron velocities  $\partial\varepsilon_{n\mathbf{k}}/\partial\mathbf{k}$  in FHI-aims. The electron velocities are necessary for the description of elementary excitations near the Fermi level in metals, which determine transport and optical properties of metals. The analytic derivatives allow us to avoid problems of finite-difference schemes with the discontinuity of bands due to crossings. They are also faster and more accurate than finite differences. Using this implementation, we also implemented calculation of plasma frequency of metals, including spin-orbit coupling effects. We demonstrate that our all-electron implementation is accurate by comparing with experimental measurements for a series of metals. We also analyze contributions of different spin channels to the plasma frequency in magnetic metals, and show that the differences contribute to the dependence of the optical response on magnetization. Spin-orbit coupling is found to strongly affect plasma frequency of some metals.

We also present a real-space implementation of transition dipole moments, which is applicable to both finite and periodic systems. The transition dipole moments are necessary for the calculation of interband contributions to optical transitions in metals in the random-phase approximation. We discuss the differences between our implementation and the one widely used in literature, where the transition dipole moments are calculated via matrix elements of the momentum operator.

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# Energy Barriers of Polymorphic Transitions via First-Principles Nudged Elastic Band Calculations

Natalia Goncharova, Johannes Hoja, and A. Daniel Boese

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Accurate knowledge of polymorphic energy landscapes of molecular crystals are vital for drug design. In terms of thermodynamic stability rankings of polymorphs, remarkable results could be achieved via molecular crystal structure predictions [1,2]. However, kinetic properties of transitions between polymorphs remain much less understood. Until now, energy barriers of transitions between molecular crystals polymorphs have been mostly assessed with the help of force-field molecular dynamics simulations [3,4]. Herein, we present an alternative approach, based on the combination of first principles methods with nudged elastic band (NEB) calculations. Specifically, we utilize here a solid-state nudged elastic band (NEB) approach [5], which allows fully periodic NEB calculations with varying unit-cell parameters. We examine the feasibility of this method by applying it first to simple test cases using molecular crystals made out of small rigid molecules with similar unit cells. Hence, we illustrate this approach for energy barriers of one polymorphic transition for 1,4-diodobenzene and oxalic acid dihydrate, respectively. The underlying first-principle calculations were performed at the PBE+MBD and PBE0+MBD level utilizing FHI-aims. Eventually, such calculations could help to reduce the overprediction problem of thermodynamic crystal structure predictions.

[1] A. M. Reilly *et al.*, *Acta Cryst. B* **72**, 439-459 (2016).

[2] J. Hoja, H.-Y. Ko, M. A. Neumann, R. Car, R. A. DiStasio Jr., and A. Tkatchenko, *Sci. Adv.* **5**, aau3338 (2019).

[3] P. Lucaioli, E. Nauha, I. Gimondi, L.S. Price, R. Guo, L. Iuzzolino, I. Singh, M. Salvalaglio, S.L. Price, and N. Blagden, *CrystEngComm* **20**, 3971-3977 (2018).

[4] M. Salvalaglio, C. Perego, F. Giberti, M. Mazzotti, and M. Parrinello, *PNAS, Proc. Natl. Acad. Sci. USA* **112**, E6-E14 (2014).

[5] D. Sheppard, P. Xiao, W. Chemelewski, D. Johnson, and G. Henkelman, *J. Chem. Phys.* **136**, 074103 (2012).

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# Improved Forces for the Exchange-Hole Dipole Moment Model

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London dispersion is a weak, attractive, intermolecular force that determines adhesion, friction, crystal structure packing, and the properties of layered materials. Most commonly-used DFT functionals do not account for dispersion, so a correction such as the exchange-hole dipole moment (XDM) model must be added. XDM has been successfully implemented in numerous electronic-structure codes, most recently FHI-aims and, when paired with hybrid functionals, has demonstrated unprecedented accuracy for molecular crystals. However, the current implementations of forces within most dispersion corrections, including XDM, erroneously assume that the dispersion coefficients are constant with respect to changing atomic positions and lattice vectors. While this assumption holds well for molecular crystals, it fails to accurately describe inorganic solids, such as bulk metals. This can introduce energy errors when performing geometry optimizations compared to manual scans of geometry and can also cause a cascading force error in molecular dynamics simulations. To address these issues, we are currently developing an improved version of XDM.

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# Performance-Portable Implementation of SISO++ and The Application in Materials' Mobility Prediction

Yi Yao<sup>1</sup>, Sebastian Eibl<sup>2</sup>, Markus Rampp<sup>2</sup>, Luca M. Ghiringhelli<sup>1,3</sup>, Thomas A.R. Purcell<sup>1</sup>, and Matthias Scheffler<sup>1</sup>

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<sup>2</sup> *Max Planck Computing & Data Facility, Garching, Germany*

<sup>3</sup> *Physics Department and IRIS-Adlershof of HU, Berlin, Germany*

Sure-independence screening and sparsifying operator (SISO) is a powerful, artificial intelligence tool for identifying symbolic descriptors and predictive models [1]. It has been successfully used to discover new optimal materials in a number of applications, e.g., thermal conductivity [2]. Recently, we have developed SISO++, a new implementation of SISO that uses both OpenMP and MPI and achieves scalable parallel performance on CPU clusters [3]. Here, we present an updated implementation that uses the C++ performance-portability framework Kokkos [4] to offload the performance-critical regions of the algorithm to accelerators, such as Nvidia or AMD GPUs. With the SISO++ code, we trained models for the experimentally measured charge carrier mobility of bulk materials. All primary features were calculated using FHI-aims [5] and represent the structural and electronic properties of a material. Subsequently, we trained a preliminary SISO model, which exhibited promising initial results.

[1] R. Ouyang et al., *Phys. Rev. Mater.* **2**, 083802 (2018).

[2] T. Purcell et al., *npj Comput. Mater.* **9**, 112 (2023).

[3] T. Purcell et al., *Journal of Open Source Software* **7**, 3960 (2022).

[4] Ch. Trott et al., *IEEE Transactions on Parallel and Distributed Systems* **33**, 805 (2022).

[5] V. Blum, R. Gehrke, F. Hanke, P. Havu, et al., *Comp. Phys. Comm.* **180**, 2175 (2009).



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# Chirality and Molecular Dynamics: Performance of FHI-aims on Chiral PdGa Systems

Raymond C. Amador<sup>1,2</sup>, Nestor Merino-Diez<sup>1</sup>, Samuel Stolz<sup>3</sup>, Roland Widmer<sup>1</sup>, Oliver Gröning<sup>1</sup>, and Daniele Passerone<sup>1,2</sup>

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<sup>3</sup> Dept. of Physics, University of California Berkeley, Berkeley, CA, United States

Van der Waals (vdW) interactions play a central role in the structure, stability, and function of a wide variety of systems, ranging from microscopic, few-molecule systems such as the benzene dimer, to mesoscopic scales as seen in surfaces and clusters. They are responsible for many natural processes, and thus, an accurate description of vdW forces is essential for improving our understanding of various biological, chemical, and physical phenomena [1]. In this poster, we present our findings on the role of non-local vdW interactions on the enantioselective adsorption and debromination of the graphene nanoribbon precursor molecule, 10,10'-dibromo-9,9'-bianthracene (DBBA) [2], as catalyzed by chiral surfaces of the palladium-gallium (PdGa) intermetallic compound [3,4]. We employ density-functional theory (DFT) [5] with a variety of dispersion corrections [6,7] throughout this work. We then present several figures of interest – adsorption configurations after geometry optimizations; an analysis of the molecule-substrate dispersion interaction according to the Tkatchenko-Scheffler scheme; the experimentally observed regioselective mono-debromination – and finally explore effects of both vdW interactions and the nonlocal exchange term via the inclusion of these various methods. We find a consistent disagreement in the results of simulation and those of the experiment in the adsorption configurations, while finding agreement in the regioselective dehalogenation. We show tests of computational performance of these PdGa slabs using GGA and hybrid functionals using many-body dispersion using the FHI-aims simulation package. In doing so, we provide the foundations for further study of non-local electronic correlation in enantioselective adsorption.

[1] A. Tkatchenko and M. Scheffler., *PRL* **102**, 073005 (2009).

[2] Y. Shen et. al., *Langmuir* **33**, 2993–2999 (2017).

[3] A. V. Yakutovich et. al., *J. Am. Chem. Soc.* **140**, 4, 1401–1408 (2018).

[4] S. Stolz et. al., *Adv. Mater.* **34**, 2104481 (2022).

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# First-Principles Light-Driven Molecular Dynamics: Case Study on LiNbO<sub>3</sub>

Elia Stocco<sup>2</sup>, Christian Carbogno<sup>1</sup>, and Mariana Rossi<sup>2</sup>

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This project aims to develop a first-principles approach to perform molecular dynamics when an external time-dependent THz field is applied. In these cases, the adiabatic and weak-field approximations can be safely assumed, leading to a coupling of the external field with the vibrational modes only. Focusing on the crystalline ferroelectric LiNbO<sub>3</sub> as a first benchmark for the method requires the adoption of the Modern Theory of Polarization to properly describe these dynamics.

We have implemented a molecular dynamics protocol that allows for time-dependent Born-Effective-Charges and coupling to the field in the i-PI code [1]. Preliminary results show the key role played by the anharmonic couplings between the phonon modes when the system is driven out of equilibrium, and that the main bottleneck of the simulations is the calculation of Born-Effective-Charges at each time step. Therefore, an automatic-differentiable E(3)-equivariant Neural Network targeting the polarization emerges as the most adequate tool to construct a reliable method suitable to study larger systems and perform longer-time simulations. We show initial benchmarks of such an implementation.

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# Implementation of Molecular Orbital Localization Through Unitary Optimizations

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Localized molecular orbitals provide many advantages over the delocalized canonical representation; they allow a more intuitive interpretation of electronic structure and separation of a large structure into subsets of electron density, which is required for many embedding schemes. Although a Foster-Boys localization scheme is implemented in FHI-aims, the unitary rotation scheme utilises a Jacobi sweep method, which suffers from slow convergence for larger systems.

As part of a larger development project for QM-in-QM embedding, this project seeks to implement the iterative unitary optimization scheme of Lehtola et al. using the Pipek-Mizey scheme. We will demonstrate the advantages of this scheme compared to the existing Foster-Boys implementation and provide an overview of potential use cases. Finally, we will discuss future developments of this project, such as parallelisation, the use of alternative cost functions and the extension to periodic systems.

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# Non-Perturbative Electronic Transport Theory for Strongly Anharmonic Materials

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First-principle approaches for phonon-limited electronic transport are typically based on many-body perturbation theory, which can be questionable in strong anharmonic systems. Combining ab initio molecular dynamics (aiMD) and Kubo-Greenwood (KG) formalism, we implement and investigate a non-perturbative stochastic method to calculate carrier mobility, which can account for all orders of anharmonic and vibronic couplings. We exploit several numerical strategies to speed up the KG calculation in ab initio material simulation package FHI-aims, including Fourier interpolation to denser k-grids for the Brillouin zone integration, efficient k-grid parallelisation, and methods to extrapolate to the direct current limit. Our method is capable to reproduce the temperature-dependent electron mobility of strongly anharmonic SrTiO<sub>3</sub>, but is still numerically challenging for more harmonic material like Silicon. In this regard, we discuss convergence challenges and possible solutions to overcome this hurdle.

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# Elucidating the Role of Polymorphism for Thermal Conductivities in Ga<sub>2</sub>O<sub>3</sub> Using Fully Anharmonic Green-Kubo Calculations

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Polymorphism in semiconductors has significant influence on several material properties, including thermal conductivities. We illustrate the implications for both theoretical understanding and practical application using three different Ga<sub>2</sub>O<sub>3</sub> polymorphs, namely the  $\alpha$ -,  $\beta$ -, and  $\kappa$ -phases. For this purpose, we employ the ab initio Green-Kubo (aiGK) method, which accounts for all anharmonic effects through aiMD [1-3]. We demonstrate the workflow for assessing anisotropic thermal conductivities using FHI-aims and FHI-vibes [4,5], and discuss its peculiarities. Eventually, we relate our results to structural properties and analyze the application potential of the different polymorphs for electronic applications.

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# GW Approach for Periodic Systems in FHI-aims: Current Status and Ongoing Works

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Many-body perturbation GW approach has been recognized as state-of-the-art practice to predict accurate electronic structure of weakly correlated extended systems [1]. In the framework of numeric atomic-centered orbitals (NAO), the all-electron one-shot  $G_0W_0$  method for periodic systems has been recently implemented in FHI-aims [2], based on frequency/reciprocal-space representation [3] and the localized resolution of identity (LRI) [4]. In this contribution, we will discuss the current performance of periodic GW functionality of FHI-aims in terms of accuracy as well as time/memory scaling for small and large systems. We will also briefly mention the recent development and current ongoing efforts to make the conventional  $G_0W_0$  approach in FHI-aims feasible for unit cells containing hundreds of atoms.

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# Separable Resolution-of-Identity in an All-Electron Numeric Atom-Centered Basis Set Framework

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The resolution-of-identity (RI) is a common way in quantum chemistry and computational materials science to reduce the computational cost of two-electron Coulomb integrals, another central entity in computational quantum mechanics. In 2019, Duchemin and Blase proposed the separable-RI approach [1], which preserves the accuracy of the standard, global RI method with the Coulomb metric (RI-V) and permits the formulation of cubic-scaling random-phase approximation (RPA) and Green's function-based GW approaches.

In this work, we present the first implementation of the separable-RI in an all-electron numeric atom-centered orbital framework. Separable-RI is implemented in the FHI-aims code [2] and optimized for massively parallel execution. We extend the separable-RI framework beyond the original Hartree-Fock and MP2 implementations of Duchemin and Blase to canonical RPA, SOSEX, rSE, CCSD and canonical GW. Our separable-RI energies and GW quasiparticle energies for the Thiel test set of small organic molecules reproduce the exact calculations of the two-electron Coulomb integral in the meV range.

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