Talks

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Invited Talk

TBA

Capturing Complex Semiconductors from First Principles

Volker Blum[*]

[*] *Department of Mechanical Engineering and Materials Science & Department of Chemistry, Duke University, Durham, NC, USA*

Invited Talk

This talk focuses on software underpinings and application targets for complex semiconductors, addressing band structure and relativistic spin phenomena in chalcogenides and perovskites. The first part of the talk reviews large-scale hybrid density functional theory, spin-orbit coupling and developments towards four-component relativity in the FHI-aims code, as well as software for large-scale eigenvalue solutions supported in the open-source ELSI infrastructure. Accurate, all-electron hybrid density functional calculations including spin-orbit coupling for periodic systems including many thousands of atoms are possible in this framework. The second part of the talk outlines our work with experimental colleagues, especially the group of David Mitzi, on complex semiconductors materials. Multinary chalcogenides materials (four or more chemical elements I2-II-IV-VI4, where roman numerals indicate the formal valence of each constituent) on non-zincblende lattices form well-ordered structures away from the traditional zincblende lattice. Deliberately introduced size differences between the constituent elements I, II, IV, IV are expected to create resilience against formation of detrimental antisite defects in these materials. A size-dependent structure-tolerance factor is shown to discriminate between different space groups, which in turn are linked to specific band structure characteristics. The talk shows how substitution of II=Eu fits into this class of semiconductors, with Cu2EuSnSe4 emerging as a computationally predicted and experimentally validated compound with a band gap suitable for photovoltaics. The final part addresses design parameters for semiconductor materials with relativistic spin splitting, in both chalcogenide and hybrid perovskite semiconductors.

Machine learning and beyond DFT methods: quantitative materials modeling at your fingertips

Georg Kresse

University of Vienna, Faculty of Physics, Kolingasse 14, 1090
Wien and VASP Software GmbH

Invited Talk

I will present two closely intertwined key developments that we have pursued in recent years: machine-learned force fields (MLFF) – with an emphasis on Δ-learning – and the development of a quantum Monte-Carlo method (auxiliary-field QMC), both closely tied to VASP.

The talk will begin with an overview of density functional theory and its shortcomings, a brief introduction to the random-phase approximation and the MLFF approach implemented in VASP, and then highlight applications that rely on Δ-learning.

Δ-learning is an efficient approach to construct a machine learned force field for density functionals or correlated wavefunction methods that are expensive to evaluate. We have now used this approach for many materials, including zirconia [1], SrTiO3 [3] and CO adsorbed on Rh(111) [2], as well as liquid water. For the first three applications we have learned the difference between a semi-local functional and the random phase approximation. Typically, we find that the number of computations for the expensive method can be reduced by one to almost two orders of magnitude using Δ-learning. The final machine-learned force field has the same speed and convenience as any other force field and can be used to make finite temperature predictions or exhaustive searches of the configuration space as for any other MLFF. For water, we have learned the difference between expensive hybrid functionals and a semi-local functional. Remarkably as few as 20 hybrid functional calculations are sufficient to determine an MLFF that has comparable accuracy to conventional DFT-based MLFFs. This means that the difference between different approximations can be learned with very little training data. It also means that correlated wavefunction methods, often thought to be too expensive for routine computations, become a serious option for materials modeling. This has led us to develop and implement the auxiliary-field QMC [4], a method that is fully compatible with other quantum-chemistry methods but shows much more favorable scaling. First applications for small molecules and solids are presented [5-6].

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Utilisation of ionic liquids and catalysis for net zero applications

Chris Hardacre

University of Manchester ***Invited Talk***

The achievement of Net Zero requires a wide range of new chemical processes and approaches. This presentation will explore the use of four main aspects: • CO2 capture • CO2 conversion • Waste plastic conversion • Blue/Green hydrogen production

Capture of CO2 can be achieved has been studied widely using solid and liquid materials. We have utilised ionic liquids (ILs) to reversibly absorb over equimolar amounts of CO2. This high CO2 capacity, paired with a low vapor pressure and increased thermal stability, means that they have been proposed as a suitable alternative to the aqueous amine solvents (e.g. monoethanolamine) currently used in industrial CO2 capture plants. ILs have the potential to overcome the disadvantages of volatility, corrosion, and the high energy penalty associated with synthesizing and regenerating MEA. For a sorbent to be used in a separation process it must also be able to withstand poisoning from impurities within the feed stream such as SO2, NOx and water. In this talk, the use of superbase ILs for the capture and utilisation of CO2 will be presented especially in the presence of flue gas impurities. In addition, the ability of the superbase ionic liquids to activate the CO2 for electrochemical reduction will be shown. The presentation will also examine the utilisation of ILs for the decomposition of polymers. ILs have been shown to dechlorinate and separate the components of composite materials containing PVC. The IL process has been shown to reduce the temperature of dehydrochlorination and improving the product yield compared with conventional processing. For example, a multicomponent blisterpacks containing PVC/aluminium/oPA has been studied in detail correlating the reactivity and selectivity as function of the IL structure. Hybrid heterogeneous catalyst-plasma systems represent an important advance in catalytic reaction engineering as they combine the advantages of having fast and low temperature reactions from atmospheric non-thermal plasma and high product selectivity from the catalyst. They have been successfully applied in a large number of reactions, from VOC oxidations and automotive catalysis to reforming and hydrogenation reactions. Herein, we will examine their use in the conversion of CO2 to methanol and low temperature water gas shift. Both thermally activated reactions and those under non-thermal plasma control will be investigated and compared using in situ spectroscopic and structural methods. The sustainable production of hydrogen is a key step in the transition and accomplishment of Net Zero especially for the chemical industry. This presentation will focus on the photocatalytic production of hydrogen from sustainable sources, for example biomass. Biomass to hydrogen can be achieved using photocatalytic aqueous phase reforming where the biomass acts as a sacrificial electron donor (SED). SEDs can undergo irreversible photocatalytic oxidation and in doing facilitate the reduction of protons to H2. Interestingly the yield of hydrogen from biomass depends on the variety of feedstock, any pretreatment and the growing conditions.

Towards Exascale Smoothed Particle Hydrodynamics on Heterogeneous Supercomputers

Abouzied Nasar

University of Manchester

PAX-HPC Talk

With the advent of exa-scale supercomputers capable of more than 1018 floating-point operations per second (FLOPS), the race is on for scientific software developers to adapt their codes to leverage these new machines. Due to the greater energy efficiency of graphics processing units (GPUs) most new machines are heterogeneous, composed of central processing units (CPUs) and GPUs. The current state of the art in Smoothed Particle Hydrodynamics (SPH) computational acceleration is to host the simulation on CPUs but execute the computations fully on the GPU with the CPU only being used for extraneous activities such as I/O or inter-node communications.

SPH codes are excellent candidates for graphics processing unit (GPU) acceleration as has been demonstrated by numerous codes such as AQUAgpusph, DualSPHysics and GPUSPH. The afore-mentioned codes implement SPH such that the data and computations exist entirely on the GPU thereby minimising the requirement for time consuming CPU-GPU communication which could limit computational scalability. However, whilst these codes are able to efficiently leverage GPU power, leading to substantial speedups in comparison to execution on central processing units (CPUs), the CPUs hosting the GPU remain idle meaning a significant portion of the available compute power is untapped. SPH with Inter-dependent Fine-grained Tasking (SWIFT) [7] is an astrophysics SPH code with a plethora of physics features that are not entirely dependent on each other meaning that there is a great deal of flexibility in the choice of whether independent physics computations are executed on the CPU or offloaded to the GPU. For example, the hydrodynamics computations could be executed on GPUs whilst long-range gravitational interaction computations could be executed on CPUs for cosmology simulations requiring only resolution of hydrodynamics and gravity. In our branch of the Particles at Exa-scale on High-performance Computers (PAX-HPC) research project we focused on achieving this by developing a scalable GPU-accelerated implementation of SWIFT’s hydrodynamics. The talk will discuss the current state of code development where all the hydrodynamics SPH calculations are executed on the GPU demonstrating speedups of up to 11× in comparison to execution on 32 CPU cores

Atomistic Modeling of the Isotopic Enrichment via Ion Irradiation of Silicon-28 Layers for Quantum Architectures

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The lack of nuclear spin present in Silcon-28 makes it an ideal candidate for advancing silicon-based quantum computing architectures. Recent experiments have shown that ion beam implantation of silicon-28 can achieve purity levels suitable for applications in quantum computing. Optimisation of this enrichment process requires a detailed understanding of the atomic dynamics during the deposition process. Given the time and length scales of the deposition process it is difficult to probe experimentally and previous binary collision Monte Carlo simulations lack the mechanistic detail needed for process optimization. In this context, we employ molecular dynamics (MD) simulations, to examine the enrichment process by performing overlapping depositions of silicon-28 ions across a wide range of energies followed by a post-irradiation annealing, resulting in the overall enrichment of the sample with silicon-28, and reduced silicon-29 and silicon-30 isotopes. Our results show how the key variables, such as the deposition energy and angle of impact can influence factors including the enrichment depth and sputtering yield. By comparing with experimental outcomes, we aim to validate and enhance the understanding of the silicon-28 enrichment process for future quantum computing architectures.

The CAT and SOD Nanozymatic Activities of Nanoceria

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Reactive oxygen species (ROS) are produced via many cellular activities and play essential biological roles including cellular signaling. Naturally, the amount of ROS is kept balanced by biological enzymes, such as catalase (CAT), and superoxide dismutase (SOD), etc. Nanoceria has shown to be a promising nanoparticle that can be used as a nanozyme due to its multiple enzyme-mimicking activities, including CAT and SOD. However, the underlying mechanisms for these activities at the surfaces of nanoceria are unclear. Hence, the selective control of these nanozymatic activities is of great importance. Here, we study and compare the SOD and CAT reaction schemes of nanoceria on the three most stable {100}, {110}, and {111} surfaces of nanoceria. We cover different surface compositions including hydroxylation and oxygen deficient surfaces. We found that beside the Ce^{3+}/Ce^{4+} ratio that can influence shift between CAT and SOD activities, the complex hydrogen network as well as the oxygen vacancy are also fundamental factors influencing the expression of a specific activity.

Polarization control in nanoscale ferroelectrics

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The behaviour of nanoscale forms of matter, such as thin films or nanocrystal, is strongly influenced by the structure and behaviour of their surfaces and interfaces. In nanoscale ferroelectrics, a surface charge arises as a consequence of the ferroelectric polarization itself, and this surface charge leads to an electrostatic instability – the so-called "polar catastrophe" – if it is not compensated.

Here we show how the properties of ferroelectric materials at the nanoscale are linked to the compensation mechanism that takes place at their surface. We also demonstrate how the structural and electronic properties of $PbTiO_3$, $BiFeO_3$ and $KTaO_3$ lead to a different compensation mechanism in each case, and we discuss how to harness the properties of these nanoscale materials for applications in microelectronics and catalysis.

Polymeric nanoparticle strategy for improving passivation and stability of perovskite solar cells: insights from DFT and AIMD simulations

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Department of Materials, University of Oxford

*surfin-**isl***

Perovskite solar cells (PSCs) provide excellent potential for large-scale solar energy harvesting because of their high-power conversion efficiency (PCE) and facile preparation. However, long-term stability remains the Achilles heel for PSCs and the development of new methods to improve stability urgently. Film-forming polymer nanoparticles are widely used in the surface coatings industry to provide scalable, low-cost protection to surfaces. In recent years, there is growing interest in employing the polymeric particles, the “nanogel”, as additive to passivate surface defects, but atomistic nature of how they work on the perovskite surface remains unclear. Inspired by collaborative experimental research, our density functional theory (DFT) simulations show strong binding of the molecules that comprise the nanogels on the $FAPbI_3$ perovskite surface through Pb-O bonds. Further room-temperature ab-initio molecular dynamics (AIMD) simulations on defective surfaces confirm the strong binding strength and identify two binding scenarios where oxygen atom can stabilise near the facile iodine vacancy site. Our simulation results are in good agreement with the XPS and FTIR signals associated with the binding of the $C{=}O$ and $C{-}O$ groups to Pb. Through the combination of experimental and computational techniques, we show that nanogel coverage promotes enhanced surface stability.

Development of ReaxFF potential for phosphate-based bioglasses

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Phosphate-based bioglasses (PBGs) have diverse applications as biomaterials in hard and soft tissue engineering and investigation of their dissolution behaviour is very important to design the bioglasses for a specific application [1]. Over the past few years, considerable efforts have been devoted in our group to study the connections between the structure and dissolution of ternary phosphate glasses [2], [3].

In this talk, we present our work on the development of a ReaxFF potential [4], which allows formation and dissociation of chemical bonds during an MD trajectory, to model the dissolution of these glasses in the body. The potential was developed using the GarfFIELD code [5] to fit very large sets of *ab initio* structural and energetic data.

We did different short- and medium-range structural analysis on the bulk simulated PBGs with different compositions to validate the potential. Radial and angular distribution functions and coordination numbers of network formers and modifiers, as well as the network connectivity of the glass, are in agreement with experimental data and previous simulations, although the Q^n distribution of the simulated glasses is often broader than that seen experimentally. We also discuss our ongoing work on the simulation of these glasses interacting with water.

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Role of Lithium Entropy in the Polymorphism of Ion Conductor Li_3PS_4

Andrey Poletayev

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Ionic transport is a key ingredient of performance in batteries, and simultaneously a convenient dynamic phenomenon for testing machine-learned neural-network interatomic potentials. Of particular interest is the interplay between slow, rare, or stochastic lattice motions, ion conduction, and polymorphism. A mechanistic understanding of polymorph transitions assists in manufacturing the highest-performing phases of ion conductors for battery applications. Here we investigate the transport properties and polymorph transitions in the modern ion conductor Li_3PS_4 (LPS), where a paddle-wheel effect by flips of PS_4 anions has been proposed to benefit lithium transport. We focus on the transition between room-temperature insulating γ and high-temperature conductive β polymorphs of LPS. We use local equivariant graph neural network (GNN) potentials and enhanced sampling to simulate ion transport and continuous transitions between the two polymorphs.

First, we verify computational results versus experimental conductivity values without resorting to the Einstein relation. We find that PS_4 flips are too rare to drive ion transport in any polymorph at temperatures below 1000 K. Using well-tempered metadynamics enhanced sampling, we estimate the free-energy kinetic barriers for the polyhedral flips to be over 0.7 eV, which is more than double the activation energy of lithium-ion conduction. Notably, our estimate is not a zero-Kelvin extrapolation of any singular kinetic pathway, but a free-energy evaluation at practical temperatures.

Furthermore, PS_4 flips are collective and occur when one-dimensional strings of PS_4 tetrahedra rapidly change orientation together. This naturally mediates the polymorph transition via a sequence of one-dimensional string flips. Using the entropy of the Li-Li pairwise distance distribution as a reaction coordinate, we demonstrate that disorder among Li ions is necessary for the polymorph transition to take place and indeed drives the polymorph transition. In other words, the Li motion and disorder cause PS_4 flips, not the other way around. Our simulations reproduce the experimental temperature of the $\beta \rightarrow \gamma$ polymorph transition, quantify crystallite size effects, and allow the separation of the enthalpic and entropic contributions to its Gibbs free energy. Our insights contribute to a mechanistic understanding of transport and polymorphism in ionic materials.

Ab Initio Design of Molecular Qubits with Electric Field Control

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Current commercial quantum computers have large footprints and complex interconnections due to the design of superconducting qubits. Molecules offer a promising alternative due to their atomic scale and the ability to tune their properties through chemical design of their ligands. The use of electric fields to manipulate molecular spins offers a level of precision and selectivity required for individual qubit control that is not possible using current methods that employ magnetic fields. For instance, electron paramagnetic resonance (EPR) spectroscopy has been widely adopted for molecular spin manipulation. However, microwave frequency radiation has wavelengths of the order of centimeters and hence measurements are always performed on ensembles of molecules, defeating the inherent benefits of molecule-based quantum information. Several recent studies have shown molecular spin manipulation using applied electric fields, however the mechanism of the spin-electric coupling is not well understood.

In this work we have elucidated a set of design criteria to build molecular qubits with enhanced electric field control. We investigate how structural perturbations give rise to off diagonal matrix elements in the crystal field Hamiltonian, where the time reversal conjugate symmetry of degenerate Kramers doublet states is broken using a weak static magnetic field. Furthermore, we use molecular point group symmetries to decompose molecular distortions into their irreducible representations of the point group to investigate the role that symmetry and coordination geometry has on the spin-electric coupling. We use perturbation theory to rationalize the electric and magnetic field orientation dependence of the spin-electric coupling. Finally, we present a fast and accurate analytical model using a single shot *ab initio* calculation to predict spin-electric coupling, which provides large savings in computational cost.

Polaron Induced Degradation of a-Ta_2O_5 ReRAM devices for Neuromorphic Computing

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Resistive random-access memory (ReRAM), characterized by a simple metal–insulator–metal (MIM) device structure, holds promise for diverse applications, including non-volatile data storage [1], in-memory logic [2], and neuromorphic devices [3]. Among potential memristor candidates, Ta2O5 stands out as the most favourable material. It is widely accepted that applying a sufficiently high voltage initiates the formation of a conduction path, driven by mechanisms such as vacancy migration. [4] Once established, this conduction path can be reset (broken, resulting in high resistance) or set (re-formed, resulting in lower resistance) by applying another lower voltage.

Using density functional theory, we investigate the role polarons have on oxygen vacancy formation as a plausible mechanism for filament formation. The atomistic mechanisms of these processes remain partially unexplained with the initial generation of oxygen vacancies within Ta2O5 remains unclear. Vacancy formation may produce different charged species depending on the charge being trapped by the defect. When hole trapping is involved, a positively charged vacancy and a neutral interstitial oxygen atom is formed. Conversely, when electrons are trapped a neutral oxygen vacancy and negatively charged oxygen interstitial ions are produced instead. The charged species in either mechanism is responsible for filament formation. We propose electron/hole trapping in crystalline and amorphous Ta2O5 followed by bipolaron trapping in amorphous Ta2O5 for oxygen vacancy formation. Under zero bias we report a high energy barrier for Frenkel pair formation but a reduced energy barrier for bipolaron assisted Frenkel pair formation as a more feasible mechanism for filament formation.

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Accurate and Efficient Spin–Phonon Coupling and Spin Dynamics Calculations for Molecular Solids

Nicholas F. Chilton,* Rizwan Nabi, Jakob K. Staab, Andrea Mattioni, Jon G. C. Kragskow, Daniel Reta and Jonathan Skelton

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Molecular materials are poised to play a significant role in the development of future optoelectronic and quantum technologies. A crucial aspect of these areas is the role of spin–phonon coupling and how it facilitates energy transfer processes such as intersystem crossing, quantum decoherence, and magnetic relaxation. Here, we demonstrate the maturity of *ab initio* methods for calculating spin–phonon coupling by performing a case study on a rare-earth-based single-molecule magnet (Figure 1, left) and showing quantitative agreement with experimental magnetic relaxation rates (Figure 1, right), allowing us to explore the underlying origins of its spin dynamics. This feat is achieved by leveraging our recent developments in analytic spin–phonon coupling calculations in conjunction with a new method for including the infinite electrostatic potential in the calculations. Calculations using this approach are facilitated by the open-source packages we have developed, enabling cost-effective and accurate spin–phonon coupling calculations on molecular solids.

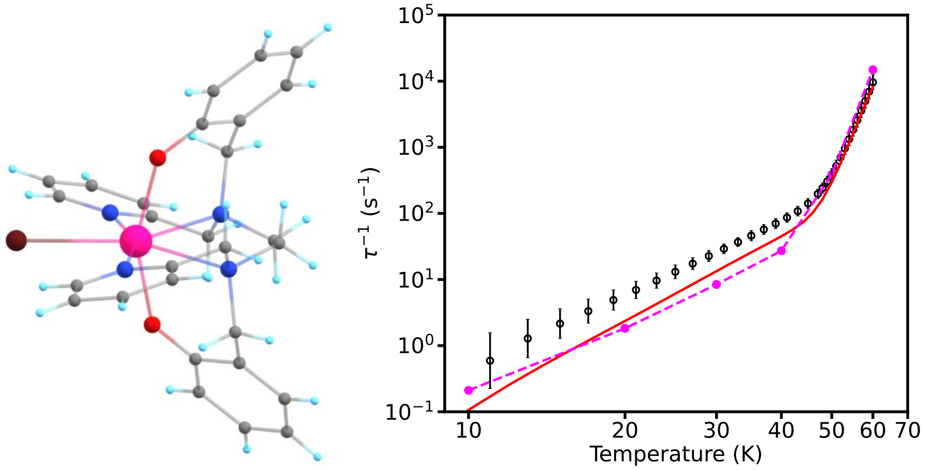

Figure 1. Molecular structure (left), and magnetic relaxation rates (right; black = experimental, calculated = red/pink).

Selective Catalytic Reduction of Nitrogen Oxides with Ammonia over Cu-CHA and Fe-BEA Zeolite

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*Department of Chemistry, University College London react-sok

In these two new studies, first, we made a comparison between water- and ammonia-solvated and bare Cu species [1]. Our results show the promoting effect of solvent on the oxidation component of the NH_3-SCR cycle since the formation of important nitrate species is found to be energetically more favourable on the solvated Cu. Conversely, both solvent molecules are predicted to inhibit the reduction component of the NH_3-SCR cycle. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) experiments exploiting (concentration) modulation excitation spectroscopy (MES) and phase-sensitive detection (PSD) identified spectroscopic signatures of Cu-nitrate and Cu-nitrosamine (H_2NNO), important species which is further supported by the QM/MM-calculated harmonic vibrational analysis. Further, we made a significant addition to the just-published work and now extended the study to Fe Beta-zeolite. We examine framework substituted and extra-framework exchanged transition metal zeolite catalysts, in the extensively studied Fe – zeolite Beta focusing on the influence of the transition metal cation on the NH_3-SCR reaction, and aiming to unravel the underlying mechanisms and their impact on catalytic performance. The new results are significantly promising since we found the formation of key intermediates in a system containing Fe-framework is highly exothermic as compared to Al-framework zeolite.

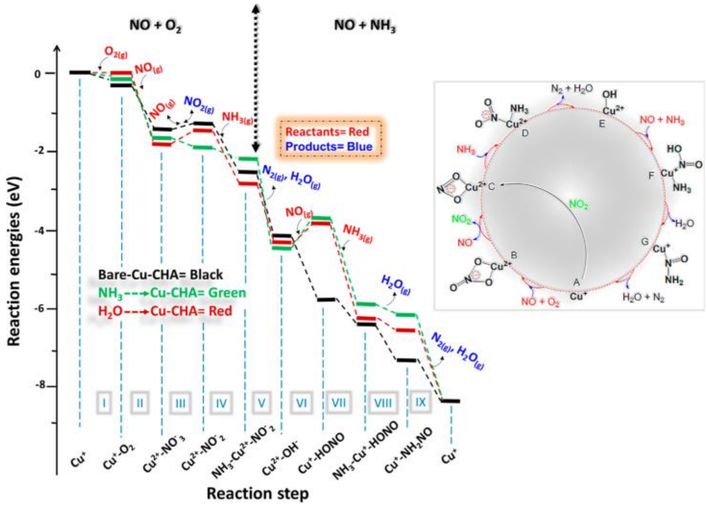

Figure 1. Potential reaction-energy landscape for NH_3-SCR on the activated Cu-CHA site and (black) on the bare site, (green) with physisorbed ammonia and (red) with physisorbed water. Inset right: NO-activated NH_3-SCR of the NOx catalytic cycle.

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Computational Insights into the Stability and Phase Transition of Cobalt Oxide Nanoparticles for Fischer-Tropsch Catalysis

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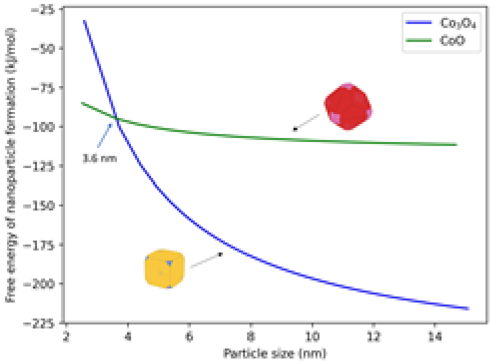
The Fischer-Tropsch (FT) reaction, involving the conversion of syngas (CO and H_2 mixture) to liquid hydrocarbons, is important in producing sustainable hydrocarbon fuels. The energy barrier for CO hydrogenation in FT reaction necessitates the use of transition metal catalysts to make the process feasible.[1] Cobalt-containing metal oxides, dispersed on TiO_2 support, have emerged as a precursor of metallic catalysts for Fischer-Tropsch synthesis, along with Mn promoters to improve the selectivity.[2] In the Mn-promoted Co/TiO_2 FT catalyst, an increase in Mn^{2+} loading enhances the selectivity towards alcohols (oxygenates) and olefinic products.[2] Mn was found to reduce the size of nanoparticles, enhancing the dispersion of cobalt oxide over the support and inducing a phase transition from spinel Co_3O_4 to rocksalt (RS) CoO, indicating transition metal (Co, Mn and Ti) interactions. The enhanced dispersion is then manifested into metallic Co leading to better selectivity. However, nature of the interactions that drive the phase transition of cobalt oxide in the catalytic precursor, remains elusive.

Density functional theory has been used in this work to investigate the stability of Co_3O_4 and CoO nanoparticles as a function of particle size to rationalize the cobalt oxide phase transition observed in experiments for smaller particle sizes. Slab calculations of RS CoO reveal that the high miller index facets are more stable than the low miller index facets. In the case of Co_3O_4, the (001) facet was found to be the most stable. The relative stabilities of the surface facets were used to predict the equilibrium nanoparticle morphology via Wulff constructions. Subsequent analysis with the Barnard[3] model reveals that the phase transition between RS CoO and Co_3O_4 occurs at a critical size of ~3.6 nm (shown in figure below). Notably, CoO proves to be more stable for particle sizes less than 3.6 nm. These findings concretize the experimental observation of phase transition of cobalt oxide nanoparticles by offering insights about nanoparticle stability over a range of particle sizes and widens the opportunity of using DFT to further understand the Co-Mn-TiO_2 interaction in the FT catalysts.



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Mechanism of photocatalytic water splitting on the pristine $CuWO_4$ (010) surface

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Photocatalysis has gained significant attention and interest as an environmentally friendly and sustainable approach for the production of hydrogen through water splitting. Copper tungstate ($CuWO_4$) is a highly promising candidate for these applications, owing to its appropriate band gap and superior stability under different conditions. In this study, we have employed density functional theory calculations to investigate water adsorption and splitting on the $CuWO_4$ pristine (010) surfaces. The electronic properties of Bader atomic charge, charge transfer, adsorption energy, surface free energy, work function, and band gap of each coverage of H_2O were calculated. The surface phase diagrams as a function of the temperature and partial pressure of H_2O were also constructed to determine coverage of water under particular environmental conditions. Two mechanistic pathways have been considered to explain the formation of H_2. Our study provides a comprehensive understanding of the adsorption and reactivity of water on the major $CuWO_4$ surface, which can catalyse the formation of H_2 under favourable conditions.

Multiscale investigation of the mechanism and selectivity of CO_2 hydrogenation over Rh (111)

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react-***cat***

CO_2 hydrogenation comprises multiple reaction pathways, presenting a wide range of possible intermediates and end products. Rh catalysts show selectivity towards either CO or methane being of particular interest. We investigate in detail the reaction mechanism of CO_2 hydrogenation to the single-carbon products on the Rh(111) facet by performing periodic density functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations, which account for the adsorbate interactions through a cluster expansion approach. We observe that Rh readily facilitates the dissociation of hydrogen, thus contributing to the subsequent hydrogenation processes. The reverse water-gas shift (RWGS) reaction occurs via three different reaction pathways, with CO hydrogenation to the COH intermediate being a key step for CO_2 methanation. Temperature plays a pivotal role in determining the surface coverage and adsorbate composition, with competitive adsorption between CO and H species influencing the product distribution. The observed adlayer configurations indicate that the adsorbed CO species are separated by adsorbed H atoms, with a high ratio of H to CO coverage on the Rh(111) surface being essential to promote CO_2 methanation. The present work also illustrates the value in combining different computational techniques to provide a multiscale analysis of reaction mechanisms. Whilst DFT simulations can provide valuable insights from reaction profiles with static energies, kMC simulations can provide a deeper insight into the exploration of the reaction mechanism with a statistical and dynamical method under the realistic conditions based on the DFT calculated reaction profile.

Single-atom catalysis for carbon dioxide dissociation using greigite-supported M_1/Fe_3S_4(111) (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) under electrostatic fields

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Single transition metal adatoms (M) supported on a solid surface, such as the reactive greigite Fe_3S_4(111) surface, combine the best properties of homogeneous and heterogeneous catalytic systems and are highly selective materials capable of altering the pathway of difficult reactions. In this talk, we will discuss the development of realistic computational models to describe the process of carbon dioxide (CO_2) dissociation on the single-atom catalyst (SAC) M_1/Fe_3S_4(111) using state-of-the-art first-principles simulations.[1] We will discuss how reconstructions of the symmetrical stacking sequence of charged atomic planes determines the possible stable non-polar terminations of the Fe_3S_4(111) surface. We will show the impact of external electrostatic fields on both the thermodynamic stability and the work function, which are used as descriptors for the most stable termination of the pristine Fe_3S_4(111) surface as well as the M_1/Fe_3S_4(111) catalysts. We will also present the electron density plots for the M_1/Fe_3S_4(111) surfaces, to rationalise the covalent metal-support interactions (CMSI) that the M adatom forms. We will also illustrate the effect of external electrostatic fields on the adsorption properties and reactivity of the M_1/Fe_3S_4(111) catalysts towards the CO_2 molecule. Finally, we will illustrate our energy profiles for the dissociation of the CO_2 molecule to explain how carefully selected transition metal adatoms, such as V, Cr and Co, and positive external electrostatic fields can be used to tune the catalytic properties of SACs.

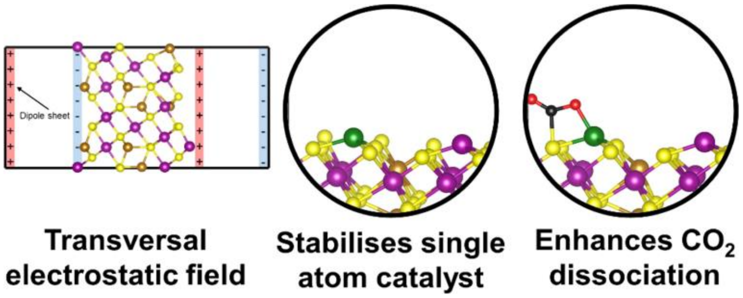

Figure 1. Transversal electrostatic fields stabilise the single atom catalyst and enhances CO_2 adsorption and dissociation on the greigite-supported M_1/Fe_3S_4(111) (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn).

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Machine learning the DFT+U projectors to model polarons in energy materials

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Strong correlation between electrons occupying localised *d* and *f* orbitals is widely known to govern the performance of transition metal oxides (*e.g.* TiO_2) and rare-earth oxides (*e.g.* CeO_2) for applications in energy materials for the transition to Net-Zero 2050 (especially in heterogeneous catalysis but more generally in batteries, photovoltaics and solid-oxide fuel cells). In particular, understanding the tuneable formation of electron polarons (*i.e.* trapped electrons at lattice defects) is essential to model the mobility of charge carriers including electrons and ions. However, these electronic correlations cannot be modelled accurately using standalone density functional theory (DFT), therefore we need beyond-DFT methods with superior accuracy but with minimal additional computational cost. Hubbard-corrected DFT+U can achieve this by adding a tuneable on-site Coulomb repulsion (given by the Hubbard U value) to the correlated orbital electrons. However, reproducing the experimentally observed localisation of polarons trapped at point defects remains challenging- due to errors in the predicted stoichiometric ground state character as well as failures in identifying accurate, self-consistent and numerically stable ground states of point defects. In this work, we trace the origin of the aforementioned DFT+U challenges to the default Hubbard projector function used in the FHI-aims software [1]; which is used to filter out a correlated subspace to which the on-site correction is applied. We further show the application of supervised machine learning methods, specifically symbolic classification using support vector machines and symbolic regression using the SISSO algorithm [2], to optimise Hubbard U values and projector functions for Ti *3d* and Ce *4f* orbitals, enabling the reproduction of experimentally observed polaron localisation at bulk oxygen vacancies in TiO_2 and CeO_2. Our work establishes a transferable workflow for DFT+U parameter optimisation, enabling the development of more quantitatively accurate structure-property models for complex catalytic reaction environments involving strongly correlated metal oxides containing point defects.

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Acknowledgments

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Machine Learning Optimisation and Structural Dynamics of Hybrid Halide Perovskites

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Our research aims to advance the efficiency and stability of perovskite photovoltaic (PV) devices through an in-depth exploration of the structural effects of their constituent components and the underlying phase transition processes.

Molecular dynamics (MD) simulations stand out as a suitable method for probing these behaviours at the atomic level, while density functional theory (DFT) provides a high-accuracy approach for modelling the atomic structure of materials. However, the computational demands of DFT calculations impose limitations, particularly for largescale and long-term simulations, especially in systems with slow rotational dynamics of organic molecular cations.

To overcome these challenges, one promising avenue involves leveraging machine learning potentials (MLP). These MLPs offer a means to approximate the energy landscape, enabling more efficient simulations without sacrificing accuracy. A significant aspect of this research lies in the development and implementation of a real-space structural analysis method. This method offers a direct and intuitive means to comprehend the dynamic structure of perovskites, aiding in the interpretation of simulation results and real-space experimental measurements. Central to this analysis framework is an octahedral structure matching kernel, which effectively dissects the effects of octahedral tilting and distortion, providing a compact and exact descriptor of their status within the dynamic structure. This is implemented in an open-source package https://github.com/WMD-group/PDynA. The method includes the quantification of organic molecule orientations, lattice spacing, and a series of correlation functions to assess their temporal and spatial correlations. Initial simulations focus on single-composition and mixed halide perovskite structures, successfully replicating experimentally identified phases. These simulations reveal additional symmetry-breaking effects near phase transitions, particularly in the octahedral tilting of halide perovskites with organic A sites1,2. Looking ahead, the aim is to extend this workflow to more complex perovskite material systems featuring mixed chemical species in both A and X sites.

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Developing Standardised Modelling Workflows for QM/MM Simulations of Metal Oxides

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Modelling plays a key role in advancing our understanding of materials, thus, our models need to be both accurate and efficient, yet there is often a compromise between accuracy and computational cost. QM/MM (Quantum Mechanical/Molecular Mechanical) simulations achieve high accuracy with good computational efficiency by limiting the full quantum mechanical calculation to a small region of interest where preserving physicality is critical; the interactions with the quantum region are then modelled though coupling to an environment of classical charges.[1] QM/MM has advantages over periodic density functional theory (DFT) simulations; the latter method can be resource inefficient, scale poorly with increasing sizes of cells and require corrections for nonphysical interactions, such as defect interactions, due to limitations in cell size.[2] The advantages of QM/MM methods for modelling point defects come from eliminating the simulation cell altogether, fully isolating defects as we would expect to find them in nature.

We have performed calculations on neutral and charged point defects in bulk MgO, employing QM/MM simulations (validating these against periodic DFT calculations) to develop a full workflow for producing accurate and realistic simulations. Our initial methodology is based on the simple system of bulk magnesium oxide to facilitate accurate model development, allowing us to design heuristics for easily setting up embedding simulations.[3-6] Currently, we have been exploring how to best define an optimal size/shape of the QM and MM regions for accurate and efficient simulation, building on previous work in this area that suggests a unit cell based partitioning approach is superior to the simpler radial partitioning method.[7, 8] A study by Shushko, Shluger and Catlow explored MgO surfaces with a similar but distinct embedding method, and we hope to be able to replicate their results using our newer models.[9] Our investigation into MgO is now being extended into surface models to achieve this goal, utilising the same methodologies as seen in the bulk studiesThe outcomes of both these studies will show if the best method of partitioning can be rigorously identified from chemical observables of the periodic bulk or surface systems.

In the future, we hope to use this work to investigate species that are more challenging to model for their applications in catalysis such as rocksalt structure MnO and CoO as well as expanding the scope to materials for photocatalytic hydrogen production such as TiO_2.

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RAFFLE: Structure prediction for material interfaces

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Much of materials discovery has been centred around random structure search methods tailored for bulk materials. However, Nobel laureate Herbert Kroemer's assertion that "the interface is the device" highlights the critical role of interfaces in device functionality. Interfaces dictate device performance and operational limits, making their accurate prediction essential. However, predicting the structure of interfaces at the atomic scale is a significant challenge. In response, we introduce RAFFLE (pseudoRandom Approach For Finding Local Energetic minima) [1], a novel open-source software package designed specifically for interface structural prediction.

RAFFLE employs a methodology that combines genetic algorithms with physical insights derived from morphological characteristics observed in analogous systems. Additionally, it incorporates void-filling and pseudorandom-walk filling techniques, mirroring experimental growth processes. RAFFLE integrates seamlessly with first principles methods, facilitating a thorough exploration of interface configurations. Moreover, it can leverage internally embedded machine-learned potentials models, to broaden the scope of structural testing. The combined utilisation of first-principles calculations and machine learning potentials enables RAFFLE to efficiently navigation through vast configuration spaces.

In summary, RAFFLE represents a powerful tool for interface prediction, offering researchers a robust framework to explore and understand interface phenomena crucial for advancing materials science and technology.

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Data distribution aware models for high throughput materials discovery

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In the dynamic field of materials design, machine learning is driving remarkable progress[1]. However, the challenge of handling unevenly distributed and often scarce data persists. Machine learning models typically require significant amounts of data to achieve good prediction accuracy. For regression tasks that map feature space to target material properties, this necessitates even data distribution across the possible range of values. In reality, the distributions of most material properties are naturally imbalanced. Our research aims to develop machine learning models that are aware of and less sensitive to the imbalanced distribution of datasets, achieving better accuracy at the extremes where materials discovery is focused. We first assess the distribution imbalance level (DIL) of the dataset and incorporate this information into model training. We employ two key techniques, Label Distribution Smoothing (LDS)[1] and Feature Distribution Smoothing (FDS)[1], to enhance the models' awareness of data imbalances. The data distribution imbalance awareness of the machine learning models was then quantitatively evaluated using the Pearson correlation coefficient (PCC) between local test data counts and test error. Typically, calculated PCCs are negative and have a high absolute value (between 0.5 and 1), indicating a strong dependence of model accuracy on available data counts. By using LDS and FDS, we observed a decrease in the PCC between local test error and test data counts in all models, indicating better generalizability and performance of our DIL-aware models. We demonstrate the efficacy of our method by training DIL-aware models to accelerate the design and discovery of next-generation intermetallic alloys for hydrogen storage and hydrogen compression applications. Our data imbalance-aware models identified potential intermetallic alloys with high hydrogen storage capacity, showing good agreement between predictions and experimental measurements.

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Unbiased Monte-Carlo Approach to Study Discharging of a Cathode

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bulk-***smw***

Manganese oxides stand out as a widely utilised environmentally friendly and cost-effective option whose significance has surged recently, driven by the escalating demand for mid- and large-range batteries in electric vehicles. Among the various polymorphs of manganese oxides, we focused on the ramsdellite phase, which shows the most electroactive properties. Despite its potential, this material as a cathode has been relatively underexplored in previous research. For this work, we developed a grand canonical stochastic approach to the study of charging/discharging behaviour of ion-intercalating batteries. We employ an atomistic level of theory, exploiting the capability of modern High-Performance Computing (HPC) platforms in order to sample the vast search space and construct our partition functions.

Key findings of our study include successful modelling of the charging/discharging voltage profile and X-ray diffraction patterns of the ramsdellite manganese oxide across the full range of lithium concentrations, showing excellent agreement with recent experimental results. Our calculated volt-age profile shows a qualitative improvement in comparison to ab initio computational studies. This advancement is attributed to the use of an appropriate number of configurations and accurately evaluate the effect of configurational entropy, which is unattainable using ab initio level of theory with available HPC resources. Moreover, we employed complementary embedded-cluster techniques to model the limit of infinite dilution that correctly describes fully charged regime of the cathode (adding a single lithium to the entire cathode material). We identify a two-stage phase transformation, highlighting distinct ordered or semi-ordered phases of this material, which is closely related to the observed voltage profile. We also provide for the first time grand canonical ensemble averaged radial distribution functions for key lithium concentrations, giving mechanistic details of ordering/disordering of lithium ions, and this result is further supported by the calculated entropy profile for the full range of lithium concentration. Our approach allows systematic exploration of configurational space of lithium manganese oxide, which is important to obtain accurate thermodynamic potentials of this material and is applicable to the study of other intercalating type ion-batteries.

Automated Strategies for Potential Development: Investigating Tetrahedrite Diffusion

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Materials with ultralow thermal conductivity are crucial for many technological applications, including thermoelectric energy conversion, thermal barrier coatings, and optoelectronics. Liquid-like mobile ions disrupt phonon propagation, suppressing thermal conduction. However, their high mobility can degrade liquid-like thermoelectric materials due to ion migration and metal deposition at the cathode, hindering practical application. Here, a new type of behavior, incipient ionic conduction, is identified, and demonstrated in tetrahedrite, an established thermoelectric. Through simulation and experiment we show that while Cu atoms are mobile above 200 K they are largely confined to crystallographic cages, mitigating undesirable migration of cations to the cathode. Simulations are the result of the new 'Automated Potential Development (APD) workflow'[1], which calculates necessary density functional theory training data, optimizes potentials, and runs molecular dynamics simulations. Theoretical results are presented alongside neutron spectroscopic measurements, performed at the ISIS pulsed neutron and muon source at the Science and Technology Facilities Council (STFC)[2].

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Unforeseen Phononic Crystal In Li Electrodes

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ZrS_2 is a potential electrode material for Li, Na and other batteries [1] with capacities of 300 mAhr/g, better than current industry standards. However, to understand its viability as an electrode material, one needs to understand the electronic and phonon properties. We utilise first principles techniques, Density Functional Theory, to investigate the thermodynamic characteristics of ZrS_2 electrodes during ion intercalation processes. In addition to a notable capacity, we also show that intercalated ZrS_2 (nominally $LiZrS_2$) is an unusual phononic crystal, possessing a band gap of approximately 1THz, one of the largest observed in a solid phononic crystal. We demonstrate both the transverse and longitudinal modes possess this gap in the same energy range which is highly unusual. We then indicate how the overall system geometry affects the macroscale heat performance of the electrode.

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Temperature-dependent dynamic disproportionation in $LiNiO_2$

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Lithium nickel oxide $LiNiO_2$ (LNO) is a model for industry-leading lithium-ion battery cathodes, $Li(NiMnCo)O_2$. Much of the degradation of such cathodes is attributed to its properties. There remains an opportunity to improve cathode energy density by extending the operating voltage window. However, correlated electron physics of LNO slows progress in the battery context. For example, a comprehensive model for LNO does not yet exist. Here we propose a unified model for nickel speciation in LNO and verify it using three soft x-ray spectroscopies, with $NaNiO_2$ (NNO) as a control.

Unlike in NNO, in LNO three nickel environments, distinguished by spins S = 1, ½, and 0, and reminiscent of formal charge states of +2, +3, and +4, interconvert dynamically. Our ab initio molecular dynamics showcase temperature-dependent spin dynamics and inform synchrotron-based experiments. We model the Ni $L_{2,3}$ edge absorption spectra with a charge-transfer multiplet model (Figure 1) and verify consistency with density-functional theory simulations. We additionally detect the S = 1 species with x-ray magnetic circular dichroism (XMCD), and the S = 0 species using resonant inelastic x-ray scattering (RIXS).

The three-state dynamic disproportionation model explains many unusual physical properties of LNO, including (1) heat-activated electronic conductivity with a variable activation energy, (2) magnetic moments too high for a 3+ formal oxidation state, and (3) the presence of ubiquitous antisite defects. We further predict Ni speciation at all states of charge using a DFT-based decorated cluster expansion model and charge-neutral Monte-Carlo sampling and verify that with bulk-sensitive x-ray spectroscopy.

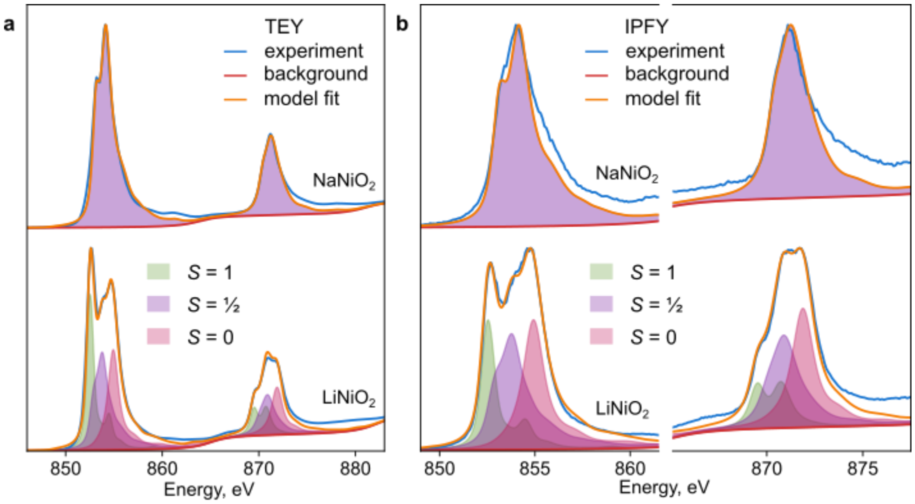

Figure 1: Ni $L_{2,3}$ edge spectra of $NaNiO_2$ and $LiNiO_2$. (a) surface-sensitive TEY spectra, (b) bulk-sensitive IPFY spectra. The L_2 edge in IPFY has been rescaled due to saturation.

Ab initio workflow for predicting the figure of merit of thermoelectric materials

Jonathan M. Skelton*, Joseph M. Flitcroft, Ioanna Pallikara, Sophie K. Guillemot, Alveena Z. Khan, Min Zhang, Adel Althubiani

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60-70% of the energy used globally is currently wasted as heat, and strategies to improve the efficiency of energy-intensive processes are therefore vital to addressing global warming. Thermoelectric recovery, which exploits the Seebeck effect in a TE material to extract electrical energy from a temperature gradient, is a leading technology, with proven applications in the aerospace industry and potential applications at scales from low-power IoT devices to transport and industry.

The thermoelectric figure of merit $ZT = S^2\sigma T / (\kappa_{\mathrm{el}} + \kappa_{\mathrm{latt}})$ requires a balance of a large Seebeck coefficient S and electrical conductivity σ with low electronic and lattice thermal conductivity $\kappa_{\mathrm{el}}/\kappa_{\mathrm{latt}}$. S, σ and κ_{el} are linked through the carrier concentration n, while the κ_{latt} depends on the structure and chemical bonding and can often be optimized by nanostructuring. Optimising ZT is therefore a multidimensional problem, made more challenging by the fact that experiments can typically only access a limited part of the design space.

We have developed fully *ab initio* modelling workflow to predict the four properties S, σ, κ_{el} and κ_{latt} and the ZT as a function of temperature and n. The electrical properties are determined using semi-classical Boltzmann transport theory with an approximate model for the electron relaxation times, implemented in the AMSET code, and the structural dynamics and κ_{latt} are calculated using the Phonopy and Phono3py codes. Benchmarking against several well-known families of TEs, including chalcogenides, oxides and oxychalcogenides, suggests that the model is capable of close to experimental accuracy. For example, a study of the bismuth oxychalcogenides Bi_2ChO_2 (Ch = S, Se, Te) that suggests experiments on n-type Bi_2SeO_2 have achieved close to the best ZT possible, whereas the ZT of Bi_2TeO_2 could be improved sixfold with a modest increase in doping level.

This talk will present examples drawn from a number of our recent studies, showcasing the predictive power of the modelling workflow, and will highlight some best practices for performing the calculations.

Unusual properties: A study of oxide interfaces

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Oxide interfaces, whether naturally occurring or intentionally engineered, hold immense promise across various disciplines, from superconductivity to ferroelectricity and magnetism [1]. Their properties are pivotal to the efficiency and functionality of devices, with interfaces often serving as fertile grounds for the emergence of novel phenomena.

Here, we present a comprehensive suite of studies focused on elucidating the distinctive properties attributed to oxide interfaces. Our exploration covers a diverse range of systems, from identifying the mechanism behind colossal permittivity in copper oxide-based grain systems through the formation of dilute metal layers, to highlighting the drastic change in band alignment from type 1 to type 2 of mixed-dimensional (2D|3D) heterostructures based on relative crystal orientations.

These unique properties offer great potential across a range of applications, from capacitors to solar cells and catalytic water splitters. Identifying phenomena present in oxide interface will drive innovation and advance in device efficiency.

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https://doi.org/10.1038/nmat3223

Radiation damage in $YBa_2Cu_3O_7$ high-temperature superconductors: an ab initio molecular dynamics study

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High-temperature superconductors (HTS) are a potentially game changing technology for magnetic confinement fusion, owing to their remarkable field strengths and high critical temperatures. It is crucial to assess the performance of these materials in operando, where broad spectrum neutron and gamma-ray irradiation may damage the HTS and compromise the magnetic field. Understanding the extent of this damage is pivotal to estimating material lifespan and determining the requisite shielding within the reactor, minimising the overall reactor cost.

Reproducing the conditions that the HTS tapes will be exposed to during operation poses a significant challenge. Therefore, the successful development of fusion will rely on modelling and simulation. Theoretical approaches to predicting levels of defect creation during irradiation typically require the threshold displacement (Td) energies for the different species in the host matrix. Previous work employed classical molecular dynamics to determine Td for YBa2Cu3O7 and highlighted how the anisotropy of the crystal structure imparts significant directional dependence on the values obtained [1]. Use of an empirical potential is accompanied by all the typical uncertainties, therefore, in this work we use ab initio MD to determine Td for oxygen in YBa2Cu3O7. A further advantage of using ab initio MD is that it allows us to examine how the electronic structure evolves during the displacement event, enabling investigation of the performance of HTS in operando. Observation of the electronic structure in operational conditions is crucial to understanding the effect of incident radiation on current flow in the material, and, consequently, how the HTS magnets will perform during fusion magnet operation [2].

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Understanding the structural and electronic properties of a complex defect-bearing heteroepitaxial binary copper oxides interface

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Oxides of copper are abundant, low cost, non-toxic, and easy to fabricate p-type semiconducting materials whose electronic band gap energies are making them potential photovoltaic powercells as well as possible transparent conducting oxides [1,2]. However, poor chemical stability in aqueous conditions combined with fast electron-hole recombination due to trap states present in the band gap hinder photocurrent commence and limit practical utilization.

Here we present our study on the $Cu_2O/Cu_4O_3/CuO$ heterointerface and insights we obtained into the atomic structure in the contact region when intrinsic defects are present. We shed light on the influence impurities have on the electronic densities of state, charge density, and orbital hybridization; which are otherwise very intricate or inaccessible in experimental studies [3]. Furthermore, we elucidate impurity-like states present at a non-defective interface which are a result of the coordination mismatch present at the interface and discuss potential routes of bypassing this fundamental integral geometrical contact limit of the heterostructure itself [4].

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Variable Band Edge Positions in Metal Oxides: Bulk, Surface, and Environmental Effects

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The absolute band edge positions and work function (*Φ*) are key electronic properties of metal oxides that determine their performance in electronic devices and photocatalysis. However, experimental measurements of these properties often show notable variations, and the mechanisms underlying these discrepancies remain inadequately understood.

We employed a combination of theoretical approaches, including shell-model interatomic potentials,[1] density functional theory (DFT), and hybrid quantum mechanics/molecular mechanics (QM/MM) embedded-cluster approach, to shed light on the origins of variable electronic energies in CeO_2 and other metal oxides. We determined a theoretical bulk ionisation potential (*IP*) of 5.38 eV for CeO_2 using the hybrid QM/MM model that excludes any surface effects, while changing surface terminations can modify the *IP*s from 4.2 eV to 8.2 eV.[2] Similar conclusions were also seen in other MO_2-type oxides with high dielectric constants (TiO_2, ZrO_2, and HfO_2).

Furthermore, we examined the intricate interplay between environmental conditions and surface potentials of reduced ceria (CeO_{2-x}).[3] Under O-deficient conditions, reduced ceria exhibits a decreased *IP* and *Φ* with significant sensitivity to defect distributions. In contrast, the *IP* and *Φ* are elevated in O-rich conditions due to the formation of surface peroxide species. Surface adsorbates and impurities can further augment these variabilities under realistic conditions. The consistency between theoretical predictions and experimental measurements provides a systematic understanding of the factors that govern the electronic properties of metal oxides, thereby paving the way for the rational design and engineering of oxide materials with tailored functionalities for catalytic and energy conversion applications.

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Standby Talks

Modelling of magnetochiral dichroism for lanthanide(III) complex

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Since the pioneering work of van Vleck[1] it has been well established that crystal field splitting is at the origin of both magnetic and luminescent properties in lanthanide based complexes. Magneto-chiral dichroism (MChD) corresponds to the difference in absorption when the orientation of the magnetic field and the light beam are parallel and antiparallel [2]. This phenomenon could be responsible for the homochirality of life[3] and is envisaged for the optical reading of magnetic state of compounds with light[4].

The first MChD spectrum for a lanthanide-based complex has recently been reported for an ytterbium(III) ion (Figure 1a)[5]. The MChD phenomenon is described by the Barron and Vrbancich theory[6], while the electronic structure of lanthanide complexes requires multiconfigurational methods and the consideration of spin-orbit coupling for evaluating it. Based on CASPT2 calculations and self-made post-processing programs, the MChD spectrum of this complex has been successfully simulated (Figure 1b).

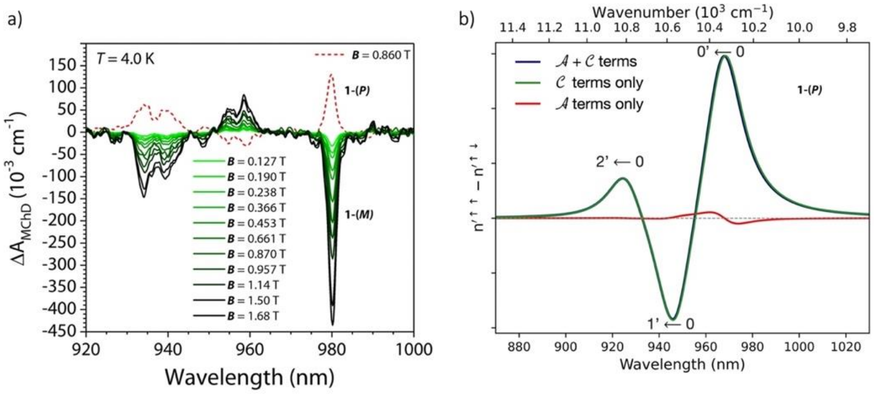

Figure 1. a) *Field dependence of the MChD signal for [Yb(hfac)$_3$(M−H6bpy)] (green curves) and at B = 0.860 T for [Yb(hfac)$_3$(P−H6bpy)] at 4 K (red dashes); reprinted from [5]. b) Simulated MChD signal of [Yb(hfac)$_3$(P−H6bpy)] at 4 K (blue curve) with decompositions of the Faraday terms.*

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Thermal transport in TMDC heterostructures

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A critical factor influencing the vast majority of devices is heat management. This is largely dictated by the thermal conductivity of the host material. 2D materials continue to yield promising results and have shown huge potential in this field [1,2]. Transition metal dichalcogenides (TMDCs) represent an exciting category of 2D materials known for the large variety in their unique electronic properties [3]. However, unexplored areas still exist, such as the thermal properties of heterostructures and superlattices formed by stacking different TMDC layers.

We investigate the thermal properties of TMDC heterostructures from fundamental features of phonons and electrons, via ab initio calculations. We have investigated thermal transport in TMDC heterostructures in two ways. When using a constant coupling rate between all phonon modes and conservative parameter fitting, we show that the possible conductivity values are typically reduced below both the constituent materials. We however go further and perform 3-phonon calculations a variety of TMDC heterostructures. By perusing this higher level of theory, we provide a clear understanding of how the thermal transport varies in TMDC heterostructures. This study not only enhances our understanding of thermal behaviour in layered materials but also suggests practical pathways for optimizing thermoelectric performance by manipulating material properties.

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Exploring formate adsorption on diluted Cu alloys

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CO_2 reduction to alcohols, such as methanol and ethanol, is a crucial part of CO_2 utilization. Some Cu-based catalysts show high alcohol selectivity via CO_2 thermal reduction, but their alcohol yields are too low for commercial viability.[1] Cu-based alloy catalysts couples copper's ability of nondissociative activation of C-O bond with C-O scission or C-C coupling ability from other metals, allowing better alcohol yield. In search of promising Cu alloy catalysts, the single atom alloy (SAAs) of Cu[2] is employed as a simple model for the diluted Cu-based alloy. Formate adsorption is investigated on M-Cu (M: substituent atom) SAA surfaces as a descriptor for catalytic performance since formate is a pivotal intermediate defining alcohol selectivity [3].

Two major binding configurations for monodentate formate were studied, both with and without a H⋯Cu/M bond (Figure 1). The latter configuration is more stable whose charge accumulation primarily localise on the O atoms. Os-, Ru-, and, Rh-Cu SAAs are most favourable for formate adsorption (Figure 2), and all have similar thermochemical electronegativity (*X*)[4] (2.65-2.72) and stronger oxophilicity (*Θ*)[5] (0.3-0.4) compared to Cu (*X*: 2.86, *Θ*: 0.2). Pt and Pd, with similar *X* (2.70-2.98) and low *Θ* (0.0-0.1), struggle to stabilize formate (Figure 2). These results suggest the dopant oxophilicity is crucial for formate adsorption. A metal with a moderate to strong *Θ* and a *X* comparable to Cu is likely to form a M-Cu diluted alloy to facilitate formate adsorption. This study indicates Os-, Ru-, and Rh-Cu alloy as potential catalysts for CO_2 reduction to alcohol.

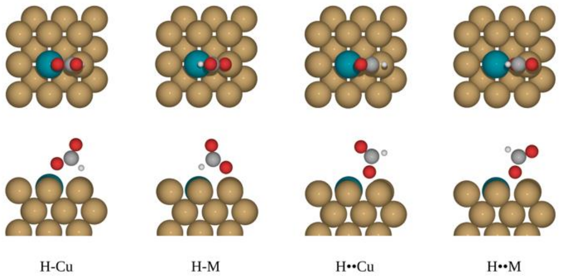

Figure 1. Binding configurations for monodentate formate on a PdCu SAA (100) surface. Brown, cyan, red, grey and white spheres refer to Cu, Pd, O, C and H atoms respectively.

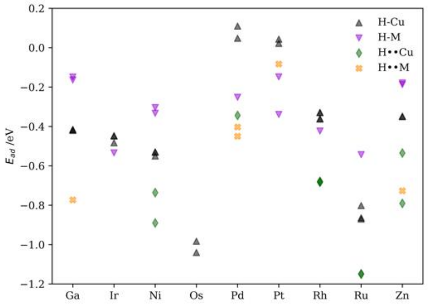

Figure 2. Adsorption energies of different monodentate formate configurations on various Cu SAA (110) surfaces. The x-axis is the metal atom substituent in the SAA model.

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