

Posters

The development of ab-initio and force-field models to analyze colorants in cultural heritage

Ian Shuttleworth

*School of Science and Technology
Nottingham Trent University*

e05-surfin-shu

Theoretical and computational investigations can productively contribute to the understanding of how the materials in cultural heritage age. Within this field, force-field and molecular dynamics techniques are set to establish themselves as powerful complementary approaches to the experimental analysis of the structure-property relationships of colorant materials i.e. dyes, lakes and pigments, where large computational unit cells are required to realistically describe the experimental system.

The current work uses a combination of first-principles and molecular dynamic approaches to formulate accurate, predictive models of these systems. The investigations have initially focused on developing a reliable and robust force-field description of key compounds including red lead (Pb_3O_4), mercury (II) sulphide $\alpha\text{-HgS}$ (vermillion) and arsenic sulphide $\alpha\text{-As}_4\text{S}_4$ (realgar). The predictions of the force field descriptions of these systems have then been benchmarked against ab-initio un-defected and the far more intricate - though much more realistic - defected trial sets.

The dilemma in this development is the trade-off between transferability and accuracy. Large-scale model screening is a powerful tool to analyse experimental data but can involve significant compromises or approximations. The doubt caused by these factors will be discussed together with strategies that have been developed to quantify and minimize this error. Some discussion of the predictive and interpretive power of these models and to explain the aging and wearing phenomena sadly seen in painted art will be presented.

Accurate modelling of defective TiO₂ surfaces

Amit Chaudhari *, Andrew Logsdail

*Department of Chemistry, Cardiff University

e05-surfin-log

As part of an EPSRC-funded Prosperity Partnership titled “Sustainable Catalysis for Clean Growth”, which focuses on catalytic solutions to reaching Net-Zero 2050, the properties of transition metal oxides (TMO) are important knowledge for applications as catalyst supports. TMOs, such as TiO₂, are widely used to support metal nanoparticles due to a range of metal-support interactions that can be tuned to optimise catalytic performance; examples include charge transfer, geometric reconstruction and defect formation ¹. The tunability creates a multifunctional catalyst with possible active sites on the support, at the metal-support interface and on the metal sites ². Consideration of all the active sites is crucial in the design of materials that will enable the transition to Net-Zero 2050, particularly in the conversion of CO₂ to useful products such as methanol, ethanol, formic acid and formaldehyde.

TMO catalysts have been widely studied using computational approaches, such as Hubbard-corrected Density Functional Theory (DFT+U), where the choice of the exchange correlation functional and the magnitude of Hubbard correction are crucial contributors in ensuring an accurate representation of the material’s geometry, electronic structure and energetics. However, a thorough justification of the DFT parameters is often overlooked and so calibration of relevant DFT parameters is presented here with respect to bulk rutile and anatase TiO₂, and surface anatase TiO₂ models with (101) and (001) crystallographic planes. After establishing the optimal parameters, defects, particularly oxygen vacancies, are considered in bulk and at surfaces to ascertain whether the DFT+U methodology is required and what magnitude of U value is suitable. Comparison of DFT-computed structural and electronic properties with experimental literature allows optimisation of the U parameter, which we discuss further. The results are a foundation for future computational work regarding the reactivity of TiO₂-supported catalysts.

References

1. X. Du, Y. Huang, X. Pan, B. Han, Y. Su, Q. Jiang, M. Li, H. Tang, G. Li and B. Qiao, *Nat. Commun*, 2020, 11, 5811.
2. S. Kattel, P. Liu and J. G. Chen, *J. Am. Chem. Soc.*, 2017, 139, 9739-9754.

A First Principles Study of the $\Sigma 3$ {111} Twin Boundary in BaTiO₃

Thomas Richards-Hlabangana*, Keith McKenna

*Department of Physics, University of York

e05-surfin-mck

Ferroelectric materials have become an essential part of the modern world, found in capacitors for microelectronics, actuators, ultrasonic medical devices, and power storage devices. The behaviours and properties of these materials however are impacted by complicated extended defects such as grain boundaries. Using the VASP code, as well as PBEsol and HSE06 functionals, we present a density functional theory investigation into the $\Sigma 3$ {111} twin boundary in cubic and tetragonal barium titanate (BaTiO₃). We model the stability of the pristine twin boundary as well as its effects on the electronic properties and polarisation of BaTiO₃. We also examine the interaction between the extended defect and both neutral and double positively charged oxygen vacancy point defects in the material. The pristine twin boundary has a low formation energy and is benign in terms of its impact on the electronic properties of BaTiO₃. Oxygen vacancies segregate favourably to the twin boundary.

Simulating Hydrogenation in Magnesium through the Application of Machine Learning Models

Oliver M. Morrison*

* *Advanced Materials Research Group, University of Nottingham*

e05-surfin-lin

In this contribution, we simulate magnesium hydride systems through the application of machine learning (ML) models, with the goal of identifying the rate limiting steps of the hydrogenation process. If metal hydride systems are to reach their full potential, it is vital that we develop a detailed fundamental understanding of how these systems evolve. Experimentally, it is difficult to pinpoint the factors that contribute to the differences between metal hydride systems, e.g differences in the speed of hydrogenation. Accurate molecular dynamics simulations of metal hydride systems could shed light on the rate limiting steps of the hydrogenation and dehydrogenation reactions, but traditional approaches to approximating the potential energy surface, such as classical force fields and density functional theory (DFT), are either lacking in accuracy or computational efficiency. Large size, long-timescale simulations are therefore infeasible via these methods. ML has been applied to an abundance of problems, to assign simple functions to complicated patterns. A generic many-parameter model is designed, and parameter values are tuned to fit the model to specific examples. We apply the same concepts to produce a model that approximates the potential energy surface, mimicking the predictions of DFT with a less complicated, less computationally intensive model. This enables the simulation of large-scale atomic systems for longer time scales. The nature of ML incurs the risk of transferability issues; the model may extrapolate from our examples incorrectly when it encounters a particularly unfamiliar atomic structure. In such an event, we perform DFT on these structures and add them to set of examples used to train the model. Through repeated improvement of the ML model, we hope to identify the rate limiting steps of the hydrogenation process in magnesium, and consequently, potential improvements to the development of new catalysts to accelerate the reaction kinetics of metal hydride systems.

Combining Monte Carlo simulation and HPC to yield new insights into grain boundary structure and surface stability

Jay Zhou*, Tom L. Underwood*, Steve Parker*

*Department of Chemistry, University of Bath

e05-surfin-par

In Monte Carlo (MC) simulation the dynamics are *unphysical*, something which can be exploited to overcome certain issues which commonly bedevil atomistic simulation, e.g. the system getting trapped in a local free energy minimum. Here we showcase two novel applications of MC simulation which, in conjunction with state-of-the-art HPC resources and recent improvements to the community MC simulation program DL_MONTE, enable key properties of interfaces in crystalline materials to be calculated with improved accuracy:

Grain boundary structure and stability in doped metal oxides. Using a MC simulation method which involves *transforming* atoms' elements during the simulation (e.g. a Ce atom becomes a Zr atom), we calculated the equilibrium structures and formation energies of 6 different tilt-grain boundaries (GBs) in Zr-doped ceria, for a wide range of Zr concentrations. Interestingly, while varying Zr concentration we observed sudden transitions in GB structure akin to first-order bulk phase transitions. Moreover, we found that the doped-GB formation energies were often *negative*. Our methodology paves the way to a more accurate evaluation of the role of dopants on GB properties, e.g. microstructure and cation diffusivity, in metal oxide solid solutions.

Surface free energies of metal oxides and pharmaceutical crystals. While it is routine to calculate the *energy* associated with a given crystal surface, calculating the *free energy* is significantly more challenging. We have developed a MC method which involves transforming a slab system into a bulk system, in order to calculate the free energy of a given surface. We have applied the method to various surfaces of ceria and paracetamol. The method elucidates that with increasing temperature the *free energies* of the surfaces decrease, while the *energies* of the surfaces continue to increase. This reflects the fact that energy is increasingly inaccurate as a measure of surface stability as temperature is increased. Hence our method promises to provide an accurate measure of surface stability at high temperatures, something which should lead to an improved understanding of, e.g. wetting and reactivity, in many materials.

DFT + U study of UO_2 and PuO_2 with Occupation Matrix Control

Jiali Chen*, Nikolas Kaltsoyannis

**Department of Chemistry, University of Manchester*

e05-bulk-nik

In the actinide series of elements, many of the chemical and physical properties display a turning point at plutonium. The actinide dioxides, which are the subject of this work, change from Mott-Hubbard insulators to charge transfer insulators at PuO_2 .¹⁻² UO_2 and NpO_2 have antiferromagnetic (AFM) ground states,³⁻⁴ while a nonmagnetic (NM) ground state, which has been established by various experiments over a wide temperature range (4 - 1000K),⁵⁻⁸ is found for PuO_2 . However, previous DFT + U simulations have predicted an AFM ground state for PuO_2 .⁹ The inconsistency between experiment and DFT + U simulation over the correct magnetic ground state of PuO_2 needs to be clarified. As PuO_2 is a product of the recycling of spent UO_2 nuclear fuel, detailed understanding of PuO_2 is clearly essential not just at a fundamental level, but also to inform its safe current and long-term storage.

There are typically many different ways in which the actinide f orbitals may be populated, and use of the Hubbard U parameter in DFT calculations can lead to the location of meta-stable states arising from those electronic configurations.¹⁰ The occupation matrix control (OMC) method in VASP, developed by Allen and Watson, is able to impose initial occupation matrices (OMs) on the orbitals of interest.¹¹ By considering all possible occupations of the actinide $5f$ orbitals, the true ground state is the OM state with lowest energy. There are $C_7^2=21$ OMs for FM and 1k colinear AFM UO_2 , $C_7^1=7$ OMs for NM UO_2 , $C_7^4=35$ OMs for FM and 1k colinear AFM PuO_2 , and $C_7^2=21$ OMs for NM PuO_2 .

We initially tested the OMC on UO_2 bulk, as UO_2 is much better studied than PuO_2 , with a wide range of U values (0.0 – 7.0 eV in 1.0 eV steps). When the U value not too small (> 2 eV), the [0000101], [00000101] and [0000200] OMs are always found to be the lowest energy state of AFM, FM and NM UO_2 , while the AFM ground state is found for UO_2 with $U \geq 3.0$ eV. After locating the ground state of UO_2 , various properties (lattice parameter, magnetic moment, band gap and densities of states) have been compared over a wide range of U . We conclude that $4.0 \text{ eV} \leq U \leq 5.0 \text{ eV}$, with $U = 4.0 \text{ eV}$ is the best, gives a good overall balance of agreement with experiments. Similar to UO_2 , when U is not too small (> 2.0 eV), the same OM states of PuO_2 are found to have the lowest energy for the AFM, FM and NM states, these are [1010101], [1010101] and [0000202],

respectively. The NM ground state is found for PuO₂ with $U > 2$ eV for the first time, in agreement with experimental results. $4.0 \text{ eV} \leq U \leq 4.5 \text{ eV}$, with $U = 4.5 \text{ eV}$ is the best, is a good compromise for the simulation of the studied NM PuO₂ bulk properties, i.e. lattice parameter, magnetic moment, band gap and densities of states.

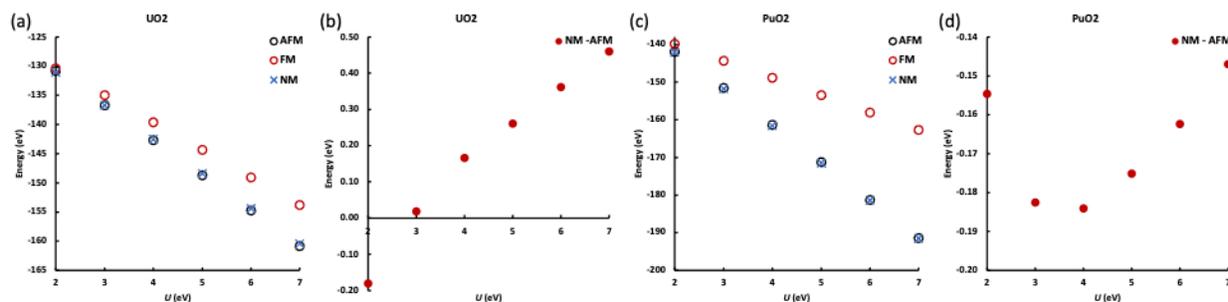


Figure 1 (a) energy of the most stable AFM, FM and NM OM state of UO₂ (b) energy difference between the most stable AFM and NM state of UO₂ (c) energy of the most stable AFM, FM and NM OM state of PuO₂ and (d) energy difference between the most stable AFM and NM state of PuO₂.

References

1. Chen, J.-L.; Kaltsoyannis, N. *The Journal of Physical Chemistry C* 2019, 123, 15540-15550.
2. Chen, J.-L.; Kaltsoyannis, N. *Journal of Nuclear Materials* 2022, 560, 153490.
3. Osborn, R.; Taylor, A. *Journal of Physics C: Solid State Physics* 1988, 21, L931.
4. Kern, S.; Morris, J. *Journal of Applied Physics* 1988, 63, 3598-3600.
5. Raphael, G.; Lallement, R. *Solid State Communications* 1968, 6, 383-385.
6. Kern, S.; Loong, C. K. *Journal of Physics: Condensed Matter* 1990, 2, 1933-1940.
7. Kern, S.; Robinson, R. *Physical Review B* 1999, 59, 104.
8. Yasuoka, H.; Koutroulakis, G. *Science* 2012, 336, 901-904.
9. Sun, B.; Zhang, P. *The Journal of chemical physics* 2008, 128, 084705.
10. Larson, P.; Lambrecht, W. R. *Physical Review B* 2007, 75, 045114.
11. Allen, J. P.; Watson, G. W. *Physical Chemistry Chemical Physics* 2014, 16, 21016-21031.

Incorporation and diffusion of krypton and xenon in uranium mononitride; a density functional theory study

Lin Yang*, Nikolas Kaltsoyannis

* *Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, Manchester M13 9PL*

e05-bulk-nik

Nitride fuels such as UN are considered as ideal candidates for Generation IV nuclear reactors, especially lead-cooled fast reactors, due to their high metal density and melting temperature, excellent thermal conductivity, and good compatibility with lead coolant. During irradiation of nuclear fuel, the fission of uranium generates a large number of fission noble gases (Ng). These Ng atoms have low solubility in the fuel matrix and may migrate in the fuel, form bubbles inside and on the boundary of the grains, or escape to the fuel-clad gap, leading to fuel swelling and reduction in the thermal conductivity of the fuel rods. Thus, for the safe and efficient use of nitride fuels, it is important to have a comprehensive understanding of the generation and migration of Ng atoms in the fuel matrix. Given the difficulty of experimentally studying radioactive materials, computational simulation is particularly valuable.

Based on the above considerations, we systemically studied the incorporation and diffusion behaviour of Kr and Xe in UN by density functional theory (DFT). We first calculated the solution energies of Kr and Xe in the UN interstitial site, U vacancy (V_U), N vacancy (V_N), and the bound Schottky defect (SD) sites, and found high stoichiometric dependence. Under U-rich and N-rich conditions, Kr and Xe have the lowest solution energy at SD and V_U , respectively, while under near-stoichiometric conditions, Kr and Xe behave differently with the former preferring a V_U and the latter preferring the SD.

Then, we calculated the diffusion coefficients of Kr and Xe in UN via the V_U -assisted and interstitial mechanisms. We found that the two mechanisms show opposite stoichiometric dependence, with the former increasing from U-rich to N-rich conditions and the latter decreasing. The reasonable agreement between our calculated V_U -assisted diffusion coefficient with experiment – similar or better than existing theoretical and empirical models – indicates that the V_U -assisted mechanism governs Xe diffusion in UN. We believe our work provides a good theoretical basis to predict the diffusivity of Ng in UN grains, and that it will contribute to fission gas release models in UN.

Efficient Extraction of Crystalline Force Constants via the Derivative of a Gaussian Process

Keerati Keeratikarn*, Jarvist Moore Frost

**Department of Physics, Imperial College London*

e05-bulk-fro

Machine learning (ML) a surrogate model is increasingly demonstrated as a useful tool for exploring potential energy surfaces (PESs). One of the ML models is a Gaussian process (GP) model [1, 2, 3], which is particularly well suited to Bayesian (probabilistic) model construction. To efficiently compute PESs with a minimal number of electronic structure calculations (i.e. DFT), the GP model can be differentiated [4, 5], and conditioned (trained) directly on the available forces (energy derivative) [6]. This exact transformation requires differentiating the GP kernel for the problem at hand. This could lead to the decrease in the number of data points (from expensive electronic structure calculations) required for a given accuracy (at the cost of an increasing complexity of a GP model). By obtaining a standard GP model, the second and the third force constants can be calculated by taking the derivatives (from the first until the sixth order) of the GP kernel and performing linear operation among the derivative kernels with arbitrary order. This construction can yield another GP model which links the information of energies and forces to the second and the third force constants. We apply this cutting-edge technique to deducing the anharmonic properties of crystals and compare them to the more standard approach such as a finite different approach.

[1] Sugisawa, T. Ida et al., *The Journal of Chemical Physics* 153 (2020) 114101.

[2] J. Dai et al, *Journal of Chemical Theory and Computation* 16 (2020) 1386.

[3] J. Broad et al, *The Journal of Chemical Physics* 155 (2021) 144106.

[4] E. Solak et al, *NIPS'02: Proceedings of the 15th International Conference on Neural Information Processing Systems* (2002) 8.

[5] A. McHutchon, *Differentiating Gaussian Processes*.

[6] E. Garijo del Río et al, *Physical Review B* 100 (2019) 104103.1

P-type impurities and doping in 4H-SiC

N. Smith*, A. Shluger

**Department of Physics and Astronomy, UCL*

e05-bulk-shl

To create a p-type 4H-SiC MOSFET device, 4H-SiC is generally bombarded with high energy ions of either Al⁺ or B⁺ during ion implantation. Out of these two dopant species, Al is most preferred. However, several recent experimental studies have discovered the occurrence of a drop in device channel mobility caused by the formation of a trap band of similar activation energy to Al's ionization energy ($E_v + 0.201$ eV). This appears to be a direct consequence of the implantation of high Al implantation dosages into 4H-SiC.

The most practical way forward for industry at present would be to use an alternative p-dopant species in the creation of p-type 4H-SiC MOSFET devices. However, no alternative dopants, which possess similar dopant levels to Al, are currently known.

We have conducted investigations, via the use of DFT calculations, into substitutional point defects produced as a result of insertion of trivalent (B, Ga, In, Tl, Sc) and divalent (Be, Mg, Ca, Ba, Zn, Cu) impurities, as well as F, in the aim to find a suitable p-dopant alternative. Substitutional defects, X_{Si} and X_C (where X=impurity), have been evaluated via calculation of incorporation energies and dopant levels to establish the favourability of formation and thermal activation of each. Given the shallowness of Al's dopant level, accurate doping levels have been verified via assessment of Kohn-Sham (KS) single electron eigenvalue defect levels and thermal ionization energies. Electronic structures have also been examined for confirmation that holes produced by insertion of these impurities are able to be fully mobilized. This has led to the widening of the KS defect level, in which the defect's VBM is taken to be the HOMO-1 state, for Al_{Si}, Ga_{Si}, and In_{Si}.

For trivalent impurities at X_{Si} sites, we find that incorporation energy is directly proportional to the impurity's atomic radius, except for Al, and that thermal ionization energy is affected by the impurity atom's position related to Si within the periodic table. Al is found to have both the smallest incorporation and ionization energies. Divalent X_{Si} defects do not appear to be more favourable than Al, but exploration of their energy landscapes is taking place due to the presence of their double hole states. Currently all investigated X_C defects are unfavourable. Therefore, our results so far indicate Al is the best and still the only industrially viable p-dopant for 4H-SiC.

Modeling of Intrinsic Hole Trapping in Crystalline and Amorphous Ga₂O₃

Chaiyawat Kaewmeechai, Jack Strand, Alexander L. Shluger*

Department of Physics and Astronomy, UCL

e05-bulk-shl

Ga₂O₃ is a transparent semiconductor possessing ultrawide bandgap (~5 eV), a high breakdown electric field, which is a potential candidate for the power electronics. It has been found that holes can be trapped spontaneously in crystalline Ga₂O₃, however there are no clear evidence about holes trapping in amorphous Ga₂O₃. In this work, we studied geometry relaxation and hole trapping in crystalline and amorphous Ga₂O₃ using the density functional theory (DFT) with optimized PBE0-TC-LRC nonlocal functional satisfying the Koopmans' theorem. Twenty structures were produced initially using ab initio molecular dynamics (MD) melt and quench (MQ) methods, then initial amorphous Ga₂O₃ were calculated using DFT. We found that the average bandgap of amorphous Ga₂O₃ is 4.2 eV, which decrease from crystalline structure. The dominant coordination number of Oxygen (90%) is three, which is same as β -crystalline β -Ga₂O₃ containing ~60%. The self-trapped hole energy in amorphous structure is deeper than that of crystalline structure ~0.7 eV. We found that holes trend to localize around lower (two or three) coordinated Oxygen in amorphous structure, which is the same as found in crystalline structure, where holes can be trapped only three coordinated Oxygen.

A QM/MM Study of Native Point Defects in AlN: Donor-acceptor Behaviour, and Optical Transitions

Lei Zhu, C Richard A Catlow, John Buckeridge, Xingfan Zhang, Qing Hou, Thomas W Keal, You Lu, and Alexey A Sokol

**Department of Chemistry, University College London*

e05-bulk-sok

Understanding the donor and acceptor behaviour of aluminium nitride is still a challenging task for both experimentalist and computational scientists. For the first-principle research of charge defects in AlN, one of the key challenges is that the electron ionisation process is not well described in the periodic boundary condition based DFT techniques. Here we present an embedded cluster method, which is able to describe the ionization process without any ambiguity from the origin of the problem to the vacuum level. By using the Chemshell code, embedded defective AlN clusters in the QM/MM environment are treated with DFT methods with the PBE0, B97-2 and BB1K hybrid exchange functionals to obtain the formation energies of native vacancy, interstitial, and anti-site point defects. We are able to present a full picture of the donor and acceptor behaviour of all defects. These new results allow us to draw the coordinate-configuration diagrams to show many possible optical transitions related to the intrinsic defects, which gives new insight to the experimental observations and other previous calculations.

Investigating structurally distortive Néel transitions in 3d transition metal monoxides using atomistic approaches

Isa T. Lough, Scott M. Woodley, Alexey Sokol

**Department of Chemistry, University College London*

e05-bulk-smw

The 3d transition metal monoxides (TMOs), despite their structural simplicity, have complex ground state magnetic properties which today still pose a challenge to model. MnO is a classic example of this class of material, in the paramagnetic (PM) phase it has the cubic NaCl structure. Below the Néel temperature (118° K) the antiferromagnetic (AFM) phase is stable and the onset of magnetic order is coupled with a rhombohedral lattice distortion ($\Delta a = 0.62^\circ$, $\Delta a = 0.08 \text{ \AA}$) [1]. Spins on the Mn^{2+} ions are coupled antiferromagnetically between every Mn-O-Mn 180° bridge via super-exchange (next nearest neighbour, J_2), a competing, weaker AFM super-exchange also acts between nearest neighbour Mn^{2+} cations (J_1), mediated via Mn-O-Mn 90° bridges. The stronger J_2 interaction drives the observed long-range AFM ordering but also results in FM ordered planes stacked along the [111] axis, which opposes the spin orientation favoured by the J_1 exchange, resulting in frustrated interactions in the (111) planes. Below the ordering temperature, the rhombohedral distortion is believed to alleviate the magnetic frustration [2].

In this work we propose an approach to model the cooperative lattice distortion in MnO by including parametrizable interatomic potentials to model spin-spin super-exchange interactions within the lattice. We aim to model the rhombohedral lattice distortion by including the effects of super-exchange in the vibrational dynamics of the MnO lattice, utilising functionality from the simulation codes VAMPIRE [3] and GULP [4]. Quantitative predictions will be made by averaging ensembles of states over a temperature range, crossing T_N .

[1] A.J. Logsdail, C.A. Downing, C.R.A. Catlow, A. A. Sokol, Chem. Phys Lett. 690 (2017) 47-53.

[2] J.A.M. Paddison, M.J. Gutmann, J.R. Stewart, M.G. Tucker, M.T. Dove, D.A. Keen, A.L. Goodwin, Phys. Rev. B 97 (2018) 1–5.

[3] R. Evans, W. Fan, P. Chureemart et al., J. Phys. Cond. Mat., 26 (2014)

Weak anisotropy of band gap modulation using uniaxial strain in MoS₂

Alex Armstrong*, Keith P Mckenna, Yue Wang

**Department of Physics, University of York*

e05-nano-mck

Strain in nanomaterials is often a useful parameter to examine, especially for light emitting materials due to its potential to modify band gap and photoluminescence efficiency. Although strain is known to reduce the band gap in monolayer transition metal dichalcogenides such as MoS₂, the effect of strain direction has not yet been fully investigated. The variation of band gap with strain in few-layer systems is also yet to be systematically studied. Here, density functional theory is used to investigate the effects of uniaxial strain on monolayer MoS₂ as well as the effect of biaxial strain in monolayer and few-layer systems. For monolayer MoS₂ the linear band gap variation is found to only weakly depend on the direction of applied strain. The direct band gap gradient with respect to strain varies by only 4.6 meV/% (from -52.7 ± 0.6 meV/% to -57.3 ± 0.1 meV/%) for strain applied along the armchair and zigzag directions respectively. These gradients are also shown to decrease when biaxial strain is applied to an increasing number of layers. These findings should be directly applicable to the other hexagonal-shaped Van der Waals-bonded transition metal dichalcogenides

Predicting and Modelling Clusters

Scott M Woodley, Woongkyu Jee, Alexey, Sokol, and Tonggih Kang

**Department of Chemistry, University College London*

e05-nano-smw

We are interested in modelling clusters isolated in vacuum¹⁻³ and on surfaces, ^{4,5} and one of the developers of a cluster database of predicted nanoclusters: <http://hive.chem.ucl.ac.uk>. Our focus in this area is that of predicting the atomic structures of clusters, using a global optimization scheme, as implemented as part of the KLMC code⁶, that first searches for local minima (LM) on the energy landscape defined using interatomic potentials (IP), which are subsequently refined using a DFT approach*. To calculate the IP and DFT energies and perform the local optimizations, we use the GULP and FHI-aims software, respectively. This approach relies on the success of the global optimization procedure for finding LM and the availability and quality of the interatomic potentials to reproduce both the DFT LM and the DFT energy ranking of the LM. Thus, we develop and test the suitability of interatomic potentials for this approach to structure prediction. Here we will present results from our investigation of different functions employed as IPs, show the match between IP and DFT landscapes for example inorganic clusters, including a metal fluoride, oxide, and nitride, and present analysis of a selection of the predicted atomic structures. * We acknowledge the support of EPSRC, The MMM Hub and the MCC for computer resources (grant references EP/R029431 and EP/T022213).

References: [1] Structure and properties of nanosilicates with Olivine (Mg_2SiO_4)_N and Pyroxene (MgSiO_3)_N compositions; DOI: 10.1021/acsearthspacechem.9b00139 [2] Are octahedral clusters missing on the carbon energy landscape? DOI: 10.1039/C8NA00013A [3] Synthesis target structures for alkaline earth oxide clusters DOI: 10.3390/inorganics6010029 [4] Development of interatomic potentials for supported nanoparticles: The Cu/ZnO case; DOI: 10.1021/acs.jpcc.7b04502 [5] Morphology of Cu clusters supported on reconstructed polar ZnO (0001) and (000 $\bar{1}$) surfaces; DOI: 10.1039/D0TA08351H [6] An efficient genetic algorithm for structure prediction at the nanoscale; DOI:10.1039/c6nr09072

Growth and reactivity of Hexagonal Boron Nitride

Anthony J.R. Payne*, Marco Sacchi*

**Department of Chemistry, University of Surrey*

e05-react-msa

The properties of epitaxially grown 2D materials such as hexagonal boron nitride (hBN) and graphene are highly dependent on the growth mechanism and on the presence of defects in the epitaxial layer. In our study we employ density functional theory (DFT) to investigate the epitaxial growth of hBN on a Ru(0001) surface and develop a detailed understanding of the formation of hBN from borazine ($B_3H_6N_3$). Our results predict the formation of a (3×3) meta-stable structure, consistent with results from helium atom scattering experiments. Our findings may have implications for CVD processes, the creation of defect sites and the design of new nanomaterials based on exploiting the growth phases of hBN.

We have also investigated the effect of defects on the catalytic activities of hBN. hBN has many advantages for heterogeneous catalysis, including high surface area, high thermal stability, and high durability whilst being more sustainable than the ubiquitously employed precious and transition metal-based catalysts. Through DFT simulations, we have explored metal-free hBN as a valid alternative to precious metal catalysts for producing H_2 via the reaction of ammonia with a hBN divacancy (VBN). Ammonia decomposition proceeds with an activation barrier of 0.52 eV. Furthermore, the reaction of ammonia with epitaxially grown hBN on a Ru(0001) substrate was investigated, and we observed similar NH_3 decomposition energy barriers (0.61 eV), but a much more facile H_2 desorption barrier (0.69 eV vs 5.89 eV).

Computational investigation of CO₂ hydrogenation over low index Rh surfaces

Shijia Sun*, Michael D. Higham, Richard A. Catlow

*Department of Chemistry, University College London

e05-react-cat

The alleviation of CO₂ emissions has become an urgent issue, requiring the development of technology for carbon dioxide capture, utilization and storage. Particularly, attractive is the energy-efficient catalytic CO₂ conversion using renewable energy, which has attracted great attention worldwide and which could potentially mitigate CO₂ emissions and produce commodity fuels and chemicals. It is thermodynamically feasible to convert CO₂ conversion by introducing H₂ to produce oxygenates (alcohols and dimethyl ether) and hydrocarbons (olefins, liquid hydrocarbons, and aromatics). However, the mechanistic routes of CO₂ hydrogenation even to C1 molecules (CO, CH₃OH and CH₄) are multiple and complex. A powerful tool for exploring the reaction mechanisms under realistic conditions is provided by the combination of Density Functional Theory (DFT) and dynamics simulations which can complement *operando* experimental techniques and identify descriptors of activity and selectivity for CO₂ hydrogenation.

It has been noted that metal Rh catalyst can perform with better selectivity for CO, CH₄ or CH₃OH when interacting with various oxide supports. First of all, the reaction mechanisms of Rh catalyst which shows high CH₄ selectivity need to be studied and compared with the later calculations. When calculating the initial steps of CO₂ hydrogenation over Rh(111), (100), and (110) surfaces, it has been found that CO₂ dissociation is more favorable when compared with the formation of HCOO* and COOH*. Bidentate HCOO* adsorbed with both O atoms located between two surface Rh atoms transforms into the most stable state (with both O atoms positioned on top of surface Rh atoms) by barrierless rotation. In addition, H₂ adsorption at the top site results in considerable H₂ bond elongation, suggesting that Rh readily facilitates H₂ dissociation. With the electronic analysis by the means of density of states (DOS) and crystal orbital Hamilton population (COHP), H₂ adsorption at the top site is more stable when compared with the physical adsorption – corresponds to s-s and s-d interactions between Rh and H atoms. Meanwhile, the s-s interaction contributes more to the Rh-H bond strength when elongated H₂ adsorbed at the Rh top site.

Photocatalytic Degradation of Organic Pollutants in Wastewater: the Effect of Dissolved Chloride Anions over TiO₂ Activity

Maicon Delarmelina*, C. Richard A. Catlow

*School of Chemistry, Cardiff University, United Kingdom

e05-react-cat

Dissolved organic compounds are one of the main responsible for environment pollution caused by wastewater.¹ Despite the promising performance of TiO₂ towards the photodegradation of such pollutants, its activity can decrease drastically in the presence of dissolved anions.^{2,3} Recently, experimental investigation at Cardiff University has observed that phenol degradation catalysed by TiO₂ is drastically modified in brine. Anatase presented a drop of activity in brine, whilst enhancement of rutile activity was observed under the same reaction conditions. In this work, the effect of chlorides over the photocatalytic degradation of phenol by titania polymorphs (anatase and rutile) is investigated by periodic DFT methods. After the generation of charge separation in the modelled titania systems, adsorbed chlorides were the preferential site for partial hole localisation, although small energy differences are computed between partially localised hole densities over adsorbed chloride or hydroxyl. Moreover, chlorides can reduce or inhibit the ability of r-TiO₂ (110) and a-TiO₂ (101) systems to localise polarons in the slab structure. These results indicate that both mechanisms – hole scavenging and the inhibition of hole localisation - can be the origin of the effect of chlorides on photocatalytic activity of both titania polymorphs. Interestingly, whilst such effects result in a depletion of hydroxyl radical formation over anatase, an increase of rutile activity in brine is observed due to high energy barriers for formation of hydroxyl radicals over this system, more facile formation of chlorine radicals, and potential phenol degradation by chlorine radicals. Despite the slight endothermicity of the reaction between chlorine radicals and phenol, such an energy cost can be surmounted by the exothermicity of the overall phenol degradation process. These results provide fundamental insight into the photocatalytic properties of titania polymorphs and elucidate the effect of adsorbed anions over radical formation and oxidative decomposition of organic pollutants.

¹Q. Guo *et al.*, Chem. Rev., **2019**, 119, 11020. ²E. Bouleghimat *et al.*, Chemosphere, **2020**, 251, 126469. ³M. Krivec *et al.*, Phys. Chem. Chem. Phys., **2014**, 16, 14867.

The hydrogen and water interactions with the pristine surfaces of monoclinic and orthorhombic FeNbO₄

Xingyu Wang, David Santos-Carballal, and Nora de Leeuw

**Department of Chemistry, University of Leeds*

e05-react-abc

The FeNbO₄ materials has shown the potential of being used as the catalytic electrode to the hydrogen evolution/oxidation reaction. Unlike other Fe-based materials, such as the FeVO₄ and LaFeO₃ material, the orthorhombic FeNbO₄ shows a unique structure where the Fe³⁺ and Nb⁵⁺ cations distribute randomly in the 4f site of the structure. In this way, it was believed to reduce the loss of oxygen and reduction of Fe³⁺ under the hydrogen atmosphere.

In this study, we have employed the Density Functional Theory (DFT) to study the pristine surfaces and the related dissociation reactions of H₂ and H₂O respectively. The simulation results show that there are three pristine surfaces, namely (010), (110), and (111), and those three surfaces in both the monoclinic and orthorhombic FeNbO₄ showed a similar configuration, even if the distribution of the cations are totally different. We have also found that the oxygen within the water molecule prefers to get coordinated with the surface cations, forming the chemisorption, while the adsorption reaction between the H₂ and surface atoms is so weak that only physisorption was formed here. In addition, out of those three surfaces, we have studied the hydrogen dissociation at the (010) surfaces and found that in the heterolytic dissociation pathway (Fe-O site), there exit a low energy barrier around 0.46 eV, which we thinks is worth of doing further research.

First-principles calculations on AB_2 alloy for hydrogen storage

Siow Mean Loh, David M. Grant, Gavin S. Walker and Sanliang Ling

*Advanced Materials Research Group, Faculty of Engineering,
University of Nottingham*

e05-discov-lin

AB_2 Laves phase alloys as promising materials for solid state hydrogen storage have been studied in this work by ab initio density functional theory calculations. The formation energies of AB_2 alloys and the hydrogenation enthalpies (differences between total energies of the hydride and alloy/ H_2) of AB_2 hydrides were shown to relate to the electronegativity, atomic and covalent radii of atoms in the unit cell. In an $Ti_{1-x}A'_xB_2$ alloy with fixed B atom, the formation energy of the alloy generally increases as the atomic radius of A' atom increases or decreases as the electronegativity of A' atom increases. The enthalpy of an $Ti_{1-x}A'_xB_2$ hydride (where $0.125 \leq x \leq 0.375$) generally decreases as the average atomic/covalent radius of atoms in the unit cell increases or increases as the average electronegativity of atoms in the unit cell increases. The effects of electronegativity and atomic/covalent radius in formation energies of $Ti_{1-x}A'_xB_2$ alloys and enthalpies of $Ti_{1-x}A'_xB_2$ hydrides are in reverse. In general, the stabilities of AB_2 alloys or AB_2 hydrides after hydrogenation are inversely proportional to the volume change of the unit cell. If an atomic substitution leads to the increase of formation energy, the alloy becomes less stable when the substitution concentration increases, and vice versa. The relation between enthalpy of an $Ti_{1-x}A'_xB_2$ hydride and average covalent radius or volume change of unit cell is nearly linear ($R^2 > 0.9$) when the substitution concentration x is smaller than 0.13. This study will benefit experimentalists when choosing an appropriate AB_2 alloy composition for hydrogen storage at specified conditions (e.g. temperature and plateau pressure of hydrogen absorption/desorption).

A Computational Re-evaluation of Se as a Solar Absorber

Alp E. Samli*, Seán R. Kavanagh, David O. Scanlon

*Department of Chemistry, University College London

e05-power-dos

Trigonal selenium (c-Se) was the first material to display the photovoltaic (PV) effect and has recently regained interest due to its suitable direct band gap, high earth abundance, non-toxicity, simple composition and low melting point.¹ It was used by Charles Fritts to make the world's first PV solar cell but the cell's low power conversion efficiency (PCE) of <1% made it commercially unfeasible. Starting with silicon in 1954, many other materials and technologies reached much higher PCEs and effectively rendered c-Se obsolete.^{2,3} However, c-Se solar cells have improved considerably in the last 40 years with a current record PCE of 6.5%.⁴

In this work, the Vienna Ab initio Simulation Package (VASP) was used to perform hybrid density functional theory calculations on crystalline selenium's 5 known polymorphs (c-Se, rhombohedral, β -monoclinic, γ -monoclinic, δ -monoclinic) to determine the ideal phase for solar cell operation. Band structure calculations revealed that all polymorphs except γ -monoclinic have an indirect fundamental band gap with a slightly higher direct band gap. C-Se was found to have the lowest direct band gap (1.904 eV with spin-orbit coupling) and highest charge carrier mobilities, allowing it to reach the highest efficiencies in single junction cells. The band gap is still quite high which allows tandem applications with low band gap absorbers like silicon.⁵ Analysis of the material's optical response showed that it can reach PCEs up to 23% with a thickness of 2 μm , making it a promising cheap alternative to commonly used high efficiency solar absorbers.

References:

- 1 M. Zhu, G. Niu and J. Tang, *J. Mater. Chem. C*, 2019, **7**, 2199–2206.
- 2 D. M. Chapin, C. S. Fuller and G. L. Pearson, *J. Appl. Phys.*, 1954, **25**, 676–677.
- 3 A. Goetzberger, J. Luther and G. Willeke, *Sol. Energy Mater.*, 2002, 11.
- 4 T. K. Todorov, S. Singh, D. M. Bishop, O. Gunawan, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez and R. Haight, *Nat. Commun.*, 2017, **8**, 682.
- 5 T. H. Youngman, R. Nielsen, A. Crovetto, B. Seger, O. Hansen, I. Chorkendorff and P. C. K. Vesborg, *Sol. RRL*, 2021, **5**, 2100111.

Lithium manganese oxide Nb⁵⁺ surface doping and the effect of ethylene carbonate and hydrogen fluoride adsorptions

Brian Ramogayana*, David Santos-Carballal, Khomotso P. Maenetja, Kemeridge T. Malatji, Nora H. de Leeuw and Phuti E. Ngoepe

*Materials Modelling Centre, University of Limpopo, South Africa
School of Chemistry, University of Leeds, United Kingdom

e05-react-lee

Cation doping is recommended as an effective method of reducing trivalent manganese (Mn³⁺) ions which undergo disproportionation reaction in lithium manganese oxide-based (LiMn₂O₄) lithium-ion batteries. Despite the intense studies on LiMn₂O₄ doping, the surface interaction between the modified spinel and the electrolyte components is not fully understood. Here, we discuss the adsorption of ethylene carbonate (EC) and hydrogen fluoride (HF) onto the major pure and Nb-doped LiMn₂O₄ surfaces using the density functional theory. The constructed morphologies of the pristine surfaces indicated the dominance of the (001) surface, which was in agreement with the reported literature. However, upon Nb doping on the second layers, the (111) surface stability improved, resulting in an enhanced (111) plane on the morphology. Moreover, the adsorption of EC further improves the dominance of the (111) surface, while a minimal charge transfer was recorded which was mainly due to the electronic rearrangement within the molecule. Similarly, the HF adsorptions further enhanced the (111) surface plane, where the molecule dissociates to form Mn/Nb-F and O-F bonds. These are interesting findings, since exposing the (111) surface plane on the particle morphologies promotes the formation of a stable solid electrolyte interface (SEI), which significantly reduces Mn dissolution.

