

Towards understanding biogenic magnetite

Amy Monnington*, David Cooke

**Depart. of Chemical & Biological Sci., University of Huddersfield*

e05-biomat-coo

There is an increasing number of new, exciting and dynamic uses for magnetic nanoparticles (MNPs), including many in the field of medicine (site-specific chemotherapy), technology (spintronics) and industry (ferrofluids). Magnetotactic bacteria produce chains of nanosized magnetite, Fe_3O_4 , particles that operate as internal magnets. This biosynthesis of magnetite is the earliest known example of biomineralisation, having first occurred some two billion years ago. Despite this, much of the detailed atomistic mechanism by which the process occurs is unknown. Therefore, we have begun to develop an atomistic model for the system, in an attempt to understand the processes involved. The magnetotactic bacteria that we are focused on are the strain *Magnetospirillum magneticum* AMB-1. Within this bacterium the Mms6 protein has been found to be linked to the control of the morphology and size of the magnetite crystal growth.

Developing an atomistic model for such a system is far from trivial, as the force field must accurately reproduce the inorganic magnetite crystal, the peptides to be attached to this crystal and their interactions with water, as well as the interface between the magnetite and the peptides. Additionally, as the complexity of the peptide increases so does the number of potential interactions with the surface and so it would be impossible to accurately describe the peptide/mineral interface using brute force dynamics alone and ways of characterising the likely interaction and scanning configuration space must be considered.

Having developed a force-field, based on ClayFF, for the magnetite [1] and AMBER's GAFF for the organics [2], and ff99SB for the amino acids and peptides [3] that correctly reproduces the interaction between simple organic functional groups and the surface. Here we report on two aspects of our current work with experimentalists who have identified the important section of the protein that are involved in iron binding. First we have taken the amino acids most prominent in these strands and performed constrained dynamics using an amended version of DL_POLY [4] to describe their interactions with the mineral surface and how they compare. Secondly we have used AMBERTOOLS to build solvated peptides based on the sequences considered

experimentally and have used molecular dynamics to study their behaviour both in pure water and in the presence of aqueous iron.

Future work will validate the interactions between the peptides, and related amino acids, and the magnetite {1 0 0} surface, enabling us to successfully fit the required organic/inorganic cross parameters to the system. This is in the aim of progressing to more complex protein attachment.

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Hard-soft interfaces and the understanding of biomineralisation

John Harding*, Steve Banwart¹, James Elliott², Tiffany Walsh⁴ and Mark Rodger⁴, Fiona Meldrum⁵, Roland Kroger⁶, Dorothy Duffy⁷, Susan Stipp⁸

*Dept. Materials Sci. and Eng., University of Sheffield

e05-biomat-har

The interface between minerals (hard) and organic molecules, arrays and scaffolds (soft) exemplifies problems in soft and hard matter science at several lengthscales. First, there are the issues of binding large molecules on surfaces. These include conformational folding induced by the surface and consequent effects on molecular function. Understanding this binding is in turn essential for understanding the attachment of cells and bacteria (and consequently biofilms) to surfaces. Equally, the presence of soft matter in the form of molecules, arrays or scaffolds can control the nucleation and growth of crystals. The resulting materials have complex structures, often with distinctive features at different lengthscales.

We present a number of examples from our recent work showing how a combination of theory and experiment can shed light on the fundamental mechanisms involved: from the atomic to the macroscopic level. We will consider interfaces between soft matter and calcium carbonate, calcium phosphate, titanium dioxide and fused silica. We demonstrate the important role that local water structure often shows at these interfaces. Also we show the importance of the flexibility of the soft interface in controlling crystal nucleation and growth.

- (1) Dept. Civil and Struct. Eng., University of Sheffield
- (2) Dept. of Mater. Sci. and Metallurgy, University of Cambridge
- (3) Dept. of Chem. and Sci. Computing, University of Warwick
- (4) School of Chemistry, University of Leeds
- (5) Dept. of Physics, University of York
- (6) Dept. of Physics and Astronomy, UCL
- (7) Nanoscience Center, University of Copenhagen, Denmark

Thermodynamics of electron conduction in the bacterial decaheme cytochrome MtrF

Marian Breuer*, Piotrek Zarzycki, Kevin M. Rosso, Jochen Blumberger

**Department of Physics and Astronomy, University College London* *e05-biomat-blu*

In this work we investigate electron conduction through the bacterial decaheme c-type cytochrome MtrF whose crystal structure has recently been resolved; *Shewanella oneidensis* and other metal-respiring bacteria use such biological “wire” proteins to shuttle electrons across the outer membrane on to extracellular solid metal oxides, e.g. Fe_2O_3 , which serve as terminal electron acceptors. The present work focuses on the investigation of the free energy surface for electron transfer along the ten heme cofactors in MtrF which form a “staggered cross” with four proposed electron entrance/exit sites. Reduction potentials have been computed for each cofactor using all-atom classical molecular dynamics (with the AMBER03 force field) and thermodynamic integration. Results are interpreted and analyzed with regard to protein structure and the contributions of individual residues, and a comparison with experimental data from protein film voltammetry is made.

Modelling the adsorption of organic compounds at clay mineral-water interfaces

Thomas V. Shapley*, Stephen C. Parker

* *Department of Chemistry, University of Bath*

e05-enviro-par

We present our recent research on the adsorption of organic compounds on clay mineral interfaces to investigate pollutant remediation. The clay mineral bentonite has been shown experimentally to be a viable adsorbent for organic pollutants. Here we model the adsorption of a range of organic compounds, focusing on polyhalogenated compounds (PHCs), on the clay minerals montmorillonite and pyrophyllite. Montmorillonite, a dioctahedral smectite, is the principal constituent of bentonite, while pyrophyllite is the template for all dioctahedral smectites. We considered both sodium montmorillonite and organo montmorillonite.

The CLAYFF and GAFF force fields are applied to the clay surface and organic molecules, respectively. Interatomic potentials are derived using simple mixing rules and flexible TIP3P water is used in solvated systems. DFT-D2 and vdW-DF2 calculations using the VASP code are carried out to validate the potential model. PMF free energy calculations were undertaken using the DL_POLY_2.0 code.

Our results indicate that the simple model is in good agreement with DFT calculations. When the organic cations are adsorbed on montmorillonite the PHCs show improved adsorption energies compared with sodium, but less favourable than pyrophyllite. Furthermore, for similarly structured PHCs the adsorption energy increased with the number of chlorine substituents, which is in line with previous studies.

***Ab initio* study of Anatase TiO₂ surfaces for nanoparticle modelling in solar hydrogen production**

F. Sanches*, L. Liborio G. Mallia, and N. Harrison

**Department of Chemistry, Imperial College London*

e05-enviro-nic

Photolytic water splitting as a method of hydrogen production has attracted a lot of attention since Honda et al first demonstrated this concept with TiO₂ in 1972 [1]. TiO₂ has since been used as a reference material in numerous experimental as well as theoretical studies in the field of solar hydrogen production[2][3][4]. The aim of this work is to study anatase TiO₂ surfaces with the aim of creating a reliable model of a TiO₂ nanoparticle. To achieve this, we use hybrid density functional theory. We study low-index and vicinal surfaces to gain an insight into the energetics and electronic properties at the nanoscale. The results presented here show the presence of some of these vicinal surfaces in Wulff constructions of the anatase phase. This could be significant to improve the understanding of the composition of (anatase) TiO₂ nanocrystals. Understanding the atomistic structure of a nanocrystal could provide knowledge fundamental to the comprehension of the interactions between TiO₂ and water during water photolysis.

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Excited state chemistry of TiO₂ clusters; a computational perspective

Enrico Berardo*, Scott Woodley, Martijn Zwijnenburg

* *Department of Chemistry, UCL, 20 Gordon Street, London*

e05-nandef-zwi

In this poster we will discuss the geometry and the electronic structure of a selection of different (TiO₂)_n clusters, where $n = 1-13$, obtained by means of time-dependent density functional theory (TD-DFT) calculations. The initial (TiO₂)_n cluster geometries are taken from previous works on TiO₂, or derived by similarity with others stable clusters of different size. We predict the optical absorption and photoluminescence spectra of these structures and simulate the relaxation process of the excited state. The results of several exchange-correlation potentials for their ability to recover the correlated wave function description of the excited state are also presented in this work

Understanding the excited state properties of MgO nanoparticles

Milena Wobbe* and Martijn Zwijnenburg

*Department of Chemistry, UCL, 20 Gordon Street, London

e05-nandef-zwi

It is well known that inorganic nanoparticles interact strongly with light. The difference between absorption and luminescence energies in such particles (the Stokes shift) is much larger than that in the bulk. As a result magnesium oxide nanoparticles, for example, can be used for down conversion; converting short wavelength ultraviolet photons into longer wavelength photons in the visible spectrum. The physical microscopic processes underlying the absorption and emission of photons in these structures are still poorly understood and hence tuning of the optical properties (e.g. by doping) is currently a trial and error procedure. Therefore, we study these processes using computational chemistry methods.

Our approach of using density functional theory (DFT) and time-dependent density functional theory (TDDFT) is to first optimise the ground state structure before then performing an excited state calculation and following the excited state energy surface until an excited state minimum is reached. This minimum is the likely structure from which luminescence is likely to take place. We are interested to see how the electron density changes and where the excited electron(s) and hole(s) are localised both after the initial absorption of a photon and at the excited state minimum.

A Theoretical Study of Ru-loaded Nanoporous Oxide $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$

Navaratnarajah Kuganathan* and Peter V. Sushko

*Depart. of Physics and Astronomy, UCL, London, WC1E 6BT

e05-nandef-pvs

Cement $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) has an unusual crystalline structure, which gives rise to its unexpected physical and chemical properties, such as the coexistence of the optical transparency and electrical conductivity. Its lattice is formed by a positively charged framework of cages, compensated by negative extra-framework species. Significant progress has been made in the experimental and theoretical studies of the C12A7 bulk and, recently, research focus has shifted on the surface properties of this material.^{1,2}

In particular, it is expected that the ability of oxygen-deficient C12A7 (C12A7:e⁻) to accept and release electrons and atomic species can make it promising for applications in chemical catalysis and in electronics. To optimise the material's performance, it is necessary to establish how the Fermi energy of C12A7:e⁻ could be controlled by judiciously selecting extra-framework species.

To this end, we investigate the effect of Ru species, incorporated into C12A7 lattice cages, on the electronic structure of this material. More specifically, we use the density functional theory and the VASP code to determine the charge state of incorporated Ru species and the nature of the gap states induced by them. Our results show that Ru introduces occupied and unoccupied states in the band gap of the stoichiometric insulating C12A7, thus, converting to a semiconductor with the band gap of ~1 eV. Importantly, these unoccupied states are below the so-called cage conduction band of C12A7, which implies that extra-framework Ru in C12A7 (C12A7:e⁻) may become negatively charged and provide novel chemical functionality.

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Modelling Oxygen Defects at the Pt/ HfO₂ Interface for Resistive Switching Applications.

Samuel R. Bradley*

*Department of Chemistry, UCL, London, WC1E 6BT

e05-nandef-shl

The platinum/ hafnia (HfO₂) interface is technologically relevant for both high-k MOSFET transistors and new resistive switching (RRAM) devices. These HfO₂/ Pt based RRAM devices are of particular interest as they may be used in new generations of non-volatile memory storage devices but also because the exact switching mechanism within the materials is unknown. It has been proposed that oxygen vacancies at and across the interface are a key component to this switching mechanism however experimentally it is difficult to resolve the exact details of such devices so theory is needed to tackle the problem [1,2].

HPC resources and periodic density functional theory have been used to develop an optimal Pt/HfO₂ interface model. The electronic structure of this model has been extracted and analysed across the interface layers. This model has then been extended and oxygen defects introduced to investigate the stability of oxygen vacancies, interstitial ions and Frenkel pairs at and across the Pt/HfO₂ interface. Our results suggest a stabilisation of both defects at the interface as well as the stabilisation of Frenkel pairs in which the interstitial oxygen ion is absorbed into the Pt layer. Using this interface as a test case it is shown that a large, complex, metal/ oxide system can be modelled to a reasonable level of accuracy using the VASP code on the current HECToR system.

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Simulation of Structure and Dynamic Properties of Binary Oxides

Nicholas R. Williams*, Nicholas A. Brincat, Stephen R. Yeandel, Marco Molinari, Stephen C. Parker

**Department of Chemistry, University of Bath*

e05-nandef-par

We present current work using computer simulation techniques on a range of binary oxides, uraninite, thoria, ceria and zincite which find widespread usage as low carbon energy sources for energy conversion devices.

UO₂ and ThO₂ represent current and potential candidates for nuclear fuels. The build-up of defect clusters and extended defect structures (such as grain boundaries) alter oxygen distribution within the materials and affect thermo-chemical properties. A combination of static lattice and DFT calculations are used to investigate the experimental defect structures, such as the Willis cluster, while MD simulations are employed to evaluate oxygen transport. The latter indicate the existence of three regions of diffusion: superionic immediately below the melting point, lattice in intermediate range temperature and oxygen vacancy diffusion at low temperature.

We also consider other energy materials. CeO₂ is a solid electrolyte for SOFC in which the oxygen diffusion needs to be enhanced. Static lattice simulations show that the presence of grain boundaries reduces the migration of oxygen ions across the boundary due to the presence of a high positive potential at the core of the boundary.

Other binary oxides, most prominently Zincite, have great potential as next generation thermoelectric materials. Thermal conductivity data is currently being calculated for different structures comprising various structural features, including bulk, point defects, grain boundaries and self-assembled nanostructures.

Thermodynamics of surfaces and dopants in rutile-structured VO₂

Thomas A. Mellan*, Anna L. Gould, Ricardo Grau-Crespo

* *Department of Chemistry, University College London*

e05-nandef-cre

Vanadium oxide VO₂ is a thermochromic material with potential applications in smart windows coatings and in sensor devices. We present here a density functional theory investigation of the surface properties and the stability of dopants for the high-temperature metallic phase, which has a tetragonal, rutile-like structure. We find that the (110) surface is the most stable one with a surface energy of only 0.29 J/m². The (011) surface also appears in the equilibrium Wulff morphology. For the most stable surface, we investigate the stability of different degrees of oxidation/reduction as a function of temperature and oxygen chemical potential, and we find that under most conditions, the (110) surface will be fully oxidized. We also discuss here the solubility of dopants in the bulk structure. We find that Ti and Ge are the most soluble in VO₂ among all the tetravalent cations considered in this study. We also discuss the solubility of tungsten (W) cations assuming different charge compensation mechanisms.

Controlling the localisation of d - and f - electrons using DFT+ U with occupation matrices

Jeremy P. Allen* and Graeme W. Watson

*Sch. of Chem. & CRANN, Trinity College Dublin, Dublin 2, Ireland e05-nandef-wat

The correct modelling of localized electrons in d - and f -element systems has been a widely discussed topic in materials chemistry, particularly for defective systems. One of the most common methodologies used for such systems is that of DFT+ U , which contains a correction that penalises delocalisation. However, despite its numerous successes, recent studies have criticized this approach for not finding the correct electronic ground state. One approach to correct this, suggested by Dorado *et al.*¹ for simulating UO_2 , has been through the use of occupation matrices to trial different orbital localizations. However, the work of Dorado *et al.* does not fully account for the cubic set of f -orbitals, nor does it allow for any control of d -element systems.

This study details a comprehensive approach of occupation matrix control of d - and f -element systems, with both cubic and general f -orbitals included. To demonstrate this we consider the orbital (and site) of the d and f electrons with the following systems;

- d^1 systems: a $[\text{Ti}(\text{CO})_6]^{3+}$ cluster and a neutral oxygen vacancy in a 2x2x1 anatase TiO_2 supercell.
- f^1 systems: a $[\text{CeF}_4]^{3+}$ cluster and a neutral oxygen vacancy in a 2x2x2 CeO_2 supercell.

For d electrons the accessibility of high energy electronic configurations is difficult, with systems relaxing to a lower energy state when the occupation matrix control is switched off. The method is successful in investigating where the location of the excess electrons are on oxygen vacancy formation, finding the split vacancy to be the lowest energy configuration in agreement with previous studies.² For f electrons, once localised within a specific orbital the electronic structure is maintained when the occupation matrix control is turned off allowing different orbital and site occupations to be compared. From a practical viewpoint, this ease of accessing the different local minima highlights the importance of fully assessing f -electron localisations. Overall, this method represents a viable approach to the modelling of a range of different electron localisations.

¹Dorado *et al.*: *PRB* **79** 235125 (2009); *PRB* **82** 035114 (2010); *PRB* **83** 035126 (2011);

²Morgan and Watson: *JPCCC* **114** 2321 (2010).

Coupled atomistic-continuum radiation damage simulations of band-gap materials

S.L.Daraszewicz*, D.M.Duffy

**Department of Physics and Astronomy, University College London (UCL)*

e05-power-duf

Classical molecular dynamics (MD) simulation methods are limited in their application to radiation damage problems due to their neglect of the effects of excited electrons. Radiation deposits energy in a material by interacting with both the atomic nuclei (elastic collisions) and the electrons (inelastic collisions). The relative amount of energy deposited in each subsystem depends strongly on the type of radiation. For example, for the most energetic ions, of energies of several MeV/u, the electronic energy loss is dominant.

Thus far, the electronic effects were incorporated in MD by linking this method with the inelastic thermal spike model (ITSM), which was based on a two-temperature (TTM) approach. This model was previously employed to describe, for instance, swift heavy ion interaction with metals. However, we argue that the application of the TTM model to band-gap materials is limited, since it does not treat the evolution of carriers explicitly. We discuss the extended thermal spike model, which incorporates an additional conservation equation for carrier density and may therefore be applied to band-gap materials.

We describe the coupling of the extended inelastic thermal spike model to molecular dynamics. This hybrid simulation method developed for band-gap materials is applied to study the swift heavy ion radiation, which deposit the energy mainly through inelastic collisions with electrons. We discuss a modified (scaled to the local electronic temperature) Langevin thermostat – a mechanism for the electronic energy transfer to the atomistic lattice. We compare and contrast the results obtained using the extended model with those obtained using the standard TTM+MD technique developed for metals. Exemplar results for swift heavy ion irradiation of silicon allow us to determine the transient phononic and electronic systems temperatures and to describe the phase change processes, thereby elucidating the radiation damage mechanisms.

Design and Optimisation of Electronic Energy Materials

L. A. Burton, C. H. Hendon, A. Jackson, D. Tiana and A. Walsh*

* *Department of Chemistry, University of Bath*

e05-power-wal

This poster will give an overview of our group's growing efforts towards the development and application of electronic structure methods for:

- Overcoming efficiency bottlenecks in thin film solar cells: assessing the physicochemical properties, phase stability and defect chemistry of sustainable absorber materials including $\text{Cu}_2\text{ZnSnS}_4$ and its parent compounds including Cu_2S and ZnS .
- Developing low cost routes to the fabrication of III-V materials, including the thermodynamics and kinetics, as well as the electronic effects, of material oxidation due to environmental oxygen.
- Tuning the conductivity of metal organic frameworks, including pseudo-1D polymers and hybrid quantum well structures.

These studies employ a range of electronic structure, analytical forcefield, and multi-scale techniques and are heavily reliant on the HECToR system.

Recent publications:

"Kesterite Thin-Film Solar Cells: Advances in Materials Modelling of $\text{Cu}_2\text{ZnSnS}_4$ " A. Walsh, S. Chen, S.-H. Wei and X. G. Gong, *Advanced Energy Materials* (2012).

"Nature of the Band Gap and Origin of the Conductivity of PbO_2 Revealed by Theory and Experiment" D. O. Scanlon, A. B. Kehoe, G. W. Watson, M. O. Jones, W. I. F. David, D. J. Payne, R. G. Egdell, P. P. Edwards, and A. Walsh, *Physical Review Letters* 84, 233301 (2011).

"Effects of reduced dimensionality on the electronic structure and defect chemistry of semiconducting hybrid organic-inorganic PbS solids" A. Walsh, *Proceedings of the Royal Society A* 467, 1970 (2011).

"Surface oxygen vacancy origin of electron accumulation in In_2O_3 " A. Walsh, *Applied Physics Letters* 98, 261910 (2011).

The Investigation of Small Pt-Cr clusters using a GA-DFT Approach

Paul C. Jennings*, Bruno G. Pollet, Roy L. Johnston

* *Department of Chemical Engineering, University of Birmingham*

e05-power-roy

A Genetic Algorithm coupled with Density Functional Theory (GA-DFT) approach has been employed to investigate small Pt-Cr clusters. Global Minimum structures are obtained for various compositions.

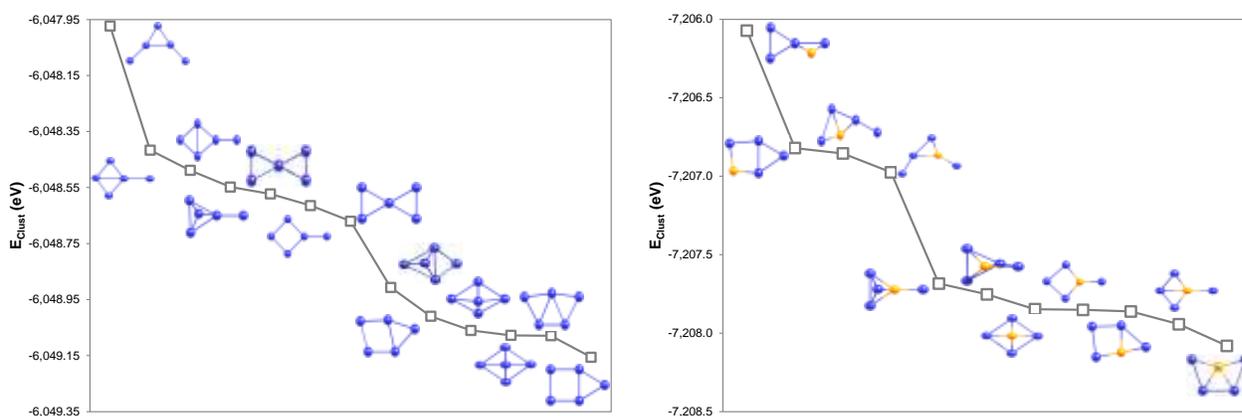


Fig 1: Structures obtained showing 2D GM for Pt₅ and 3D GM for Pt₄Cr₁ clusters.

Various spin constrained searches have been performed revealing changes in energetic ordering. Spin un-constrained optimizations have also been run on select structures obtained from the spin constrained searches for comparative purposes. Electronic properties of the clusters have been investigated to provide a possible explanation of structural and energetic changes when accounting for spin.

Theoretical study of charge transfer in organic semi-conductors

Fruzsina Gajdos*, Harald Oberhofer, Jochen Blumberger

*Department of Physics & Astronomy, University College London

e05-power-**blu**

Organic solar cells are a promising alternative to present day inorganic solar cells. They are inexpensive to produce and operate at ambient temperature. In addition, their light weight, tunable and wide absorption spectra, and the fact that these organic semi-conductors are flexible plastic substrates make them even more appealing to the industry. However, in terms of light to current efficiencies organic solar cells cannot compete (yet) with inorganic solar cells [1]. While the mechanisms of charge photogeneration and charge transfer in inorganic semi-conductors are rather well-known and can be described by material parameters and the nature of the junction, in the case of the organic molecular crystals these mechanisms are less understood and require the development of new theoretical models and simulation.

To reach this goal the electron mobility of a promising and widely used organic electron acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) has been studied using HPC resources and *ab initio* methods to model the charge transfer in the molecular crystal using the Marcus theory. The molecular crystals were obtained from crystallographical data of spin-coated [2] thin films and were optimized using dispersion corrected DFT. Electronic coupling calculations were performed using the fragment orbital density functional theory (FO-DFT) implemented in the CPMD code [3]. These parameter are then used to compute analytically the electron mobility in PCBM crystals.

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DFT Simulation of CO₂ Adsorption onto Magnetite.

David Santos*, Dr. Alberto Roldan, Prof Nora de Leeuw

**Department of Chemistry, University College London*

e05-react-lee

The reduction of the current level of carbon dioxide in the atmosphere has been considered an essential effort for trying to mitigate the global warming and therefore to reduce its consequences. Among all the options to reduce carbon dioxide, enhancing the capacity of carbon sinks to absorb carbon dioxide from the atmosphere is the most promising initiative which targets the root cause of global warming. Basically, it involves the use of some compounds that have the ability to capture, store or convert the carbon dioxide from the air. However, most of the work reported in the literature so far in developing carbon sinks has been focused on exploring classic catalysts such as Cu, Ni, and TiO₂. In this poster, we present the preliminary results of a computational study based on DFT calculations of the carbon dioxide adsorption on magnetite using the computer code VASP.

The bulk properties of magnetite were calculated, such as lattice parameter, first neighbor distance, the charge on the ions as well as spin density of each ion in the unit cell. We also compared them with the previously reported values in order to validate our methodology. For the different non-dipolar terminations of the low Miller index surfaces, we calculated the surface energy before and after relaxation as well as various surface properties. We focus on the most stable cut of the {111} surface to study the carbon dioxide adsorption as there is evidence it is one of the most important surfaces in magnetite. We present the adsorption energy of all interaction modes found. In every case, the carbon dioxide molecule has changed its linear geometry for a bent one, which is the active form while the carbon atom is interacting directly with a surface oxygen atom.

Computational Study of Microporous-aided Oxidation of Alkanes

Filippo Marozzelli*, David J. Willock

* School of Chemistry, Cardiff University

e05-react-wil

It has been experimentally¹ shown that reaction rate and regioselectivity of Mn(II)-catalysed oxidation of *n*-hexane occurring inside zeolites, i.e. MFI (ZSM-5), MFS (ZSM-57), MOR (Mordenite) and DDR (Deca-Dodecasil-3R or ZSM-58)², are affected by structural features of the supporting material. In the gas phase a methyl group C-H (terminal) bond is less reactive than a methylene C-H (secondary) bond, and therefore more difficult to oxidise. Instead, inside zeolites the restricted access to catalytic centres forces the reaction to favour the production of terminal rather than secondary alcohols.

Our study aims to computationally investigate alkane oxidation in zeolites studying both the shape selectivity and reaction at the metal centre separately. Calculations using Monte Carlo to investigate shape selectivity will compare 6 (hexane)-, 8 (octane)- and 10 (decane)-term linear alkanes as adsorbates inside MFI (ZSM-5), MFS (ZSM-57) and MOR (Mordenite) frameworks.

For the reaction centre we aim to employ ChemShell so that the ion exchanged Mn²⁺ cations oxidation and reduction processes can be accurately modeled. Initial results with ChemShell have looked at methanol adsorption at a Bronsted acid site to test the methodology. In the oxidation catalyst model Mn²⁺ cations interact with the oxidant (i.e. ROOH) during its decomposition. By simulating the different possible cation positions a clear definition of Mn²⁺ role will be provided, together with a clear understanding of the influence of the combination zeolite structure and alkane chain length over the rate and regioselectivity of the reaction.

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Mn – Doped nanoporous aluminophosphate catalysts for the aerobic oxidation of hydrocarbons – A DFT study using hybrid functionals and GGA methods

Panagiota Pelekanaki*

* *Department of Chemistry, University College London*

e05-react-cat

This project employs state of the art electronic structure techniques based on different functionals in DFT and periodic boundary conditions to study the catalytic oxidation of hydrocarbons by Mn-doped AlPOs. Particularly, this research will use ethane and Mn-AlPO₅ as models for hydrocarbon and solid catalyst; we compare the results obtained with four hybrid-exchange (B3LYP, BLYP25, PBE25 and PBE50) and with two GGA functionals (BLYP and PBE), and show that DFT results are strongly dependent upon the functional employed, in particular on the amount of HF exchange employed. Previous work based on elucidating the mechanisms of the regio-selective oxidation of hydrocarbons in microporous transition metal-doped catalysts was limited to the B3LYP functional. In this work, computational studies are focused on two elementary steps of the overall mechanism. The first is part of the preactivation mechanism, and consists in the activation of ethane through hydrogen transfer to the active site, yielding a change of the Mn oxidation state in Mn from III to II. The second step is part of the propagation mechanism, which involves a H-transfer from an ethane molecule to an ethoxy radical RO• coordinated to MnIII, to form an ethanol molecule ROH and an ethyl radical R•. In the latter step Mn does not change its oxidation state. Fully optimized configurations for reactants and products were used to find the reaction enthalpies of these two steps and further computational analysis has been performed to find the reaction pathway. Clear trends arise in the structural and electronic properties with the increase of HF exchange. In the first step, the transition state becomes lower in energy and closer to the reactants upon increasing the fraction of Hartree-Fock exchange in the functionals. In the second step, instead, the transition state becomes higher in energy upon increasing the fraction of Hartree-Fock exchange. Both trends can be rationalised as a consequence of the self-interaction error that affects pure DFT functionals.

Electronic structure of Mo / GaAs (100) interfaces

Steven P. Hepplestone* and Peter V. Sushko

*Department of Physics and Astronomy, UCL

e05-surfin-pvs

The continued scaling of transistors requires using new techniques and materials. Growing thin layers of III-V semiconductors upon silicon substrates, utilising the high mobility of the III-V layer (when compared with silicon) is a promising method currently being explored [1]. However, developing ultra-low resistance metal-semiconductor contacts to these devices remains challenging. Recently, the junction of Mo and $\text{In}_{0.53}\text{Ga}_{0.43}\text{As}$ has been shown to have a nearly Ohmic contact with a contact resistance of $(1.6 \pm 0.9) \times 10^{-8} \Omega \text{ cm}^2$ [2]. Motivated by this, we construct a model of an Mo/GaAs(100) interface and investigate its electronic properties using the density functional theory and several density functionals implemented in the Vienna Ab initio Simulation Package. Understanding the effects of the lattice orientation and lattice strain induced by In impurities may help us to develop generic rules for optimising metal-semiconductor contacts.

First, we construct several models of Mo/GaAs interfaces, in which the Mo layer bonds to the Ga- or As-terminated GaAs (100) surface. Then, the positions of the GaAs band edges with respect to the Mo Fermi energy are calculated by analysing both the layer projected density of the states and behaviour of the average electrostatic potential across the junction. These data are used to estimate the interface Schottky Barrier Heights (SBH). The effects of In impurities and cross-interface intermixing on the SBH and other properties are then investigated in a similar manner.

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[2] Baraskar, A. K., Wistey, M. a., Jain, V., Singiseti, U., Burek, G., Thibeault, B. J., Lee, Y. J., et al. (2009). Ultralow resistance, nonalloyed Ohmic contacts to n-InGaAs. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 27(4), 2036.

Towards the *in silico* design of porous molecular crystals

Edward O. Pyzer-Knapp*, Graeme M. Day

*Department of Chemistry, University of Cambridge

e05-surfin-day

Most molecules tend to crystallise in such a way as to most effectively fill space, minimizing the empty (“void”) space into which guests can be adsorbed. This can be somewhat negated by the use of molecules with a macrocyclic or cage structure which can encapsulate cavities of molecular dimensions.

We are applying methods of crystal structure prediction developed within the group to the problem of rationally designing a porous molecular crystal with a good degree of success. Recent publications have documented the application of our methods in the successful prediction of large cage molecules and their co-crystals.¹

We have studied the series of tetrahedral imine cages developed by Cooper *et al.*² which have an intrinsic ‘pore’ of molecular dimensions, enclosed by arene units, but accessible through open windows in the structure. The porous character of the material (isolated voids vs connected channels) is therefore determined by the arrangement of these cages in the solid state. The challenge of rationally designing the porosity of the solid – by predicting which packing arrangement is most stable - is dependent on an accurate ranking of the energies of generated hypothetical polymorphs.

One issue that can affect the accuracy of the ranking is the existence of packing forces in the crystal that can distort the molecular geometry away from the idealized structure of the isolated molecule, which is used for structure generation. To take account of this we are allowing a relaxation of the low energy crystal structures through the use of dispersion-corrected periodic DFT, which we expect to provide a very accurate energy ranking of the final structures.

We show the prediction process, discuss the promise of the methods, as well as challenges that must be addressed in developing methods that will guide future development of materials.

1. Jones et al Nature 474, 367 (2011)
2. Tozawa et al Nature Mater. 8, 973(2009)

Molecular Adsorption at Mineral Interfaces

Luiza N. Woronycz^{*}, Jennifer C. Crabtree, Thomas V. Shapley, Stephen C. Parker

^{*}*Department of Chemistry, University of Bath*

e05-surfin-par

The structure, stability and reactivity of solids and their interfaces at an atomic level is an important area of research. Our work investigates surface phenomena for several different applications.

The interaction of corundum-structured chromia, $\alpha\text{-Cr}_2\text{O}_3$, with water and amino acids is important for medical applications. Chromia is a major component of the protective passive layer of stainless steels and, therefore, is frequently exposed to organic compounds and water. The interactions between biomolecules and inorganic surfaces play an important role in fouling and bio-corrosion and it is essential to understand the nature of these chemical interactions. A combination of computational techniques was used to simulate both the Cr and O terminated (00.1) surface and the (01.2) surface, their interaction with water, and the adsorption of amino acids.

The adsorption of molecules at interfaces is also important in environmental applications such as the reduction of CO_2 emissions. Silicate materials such as zeolites have been shown to be good adsorbents for CO_2 . Current work is focussed on Grand Canonical Monte Carlo (GCMC) simulations, using the DL_MONTE code, for the generation of adsorption isotherms. The work is also being extended to other materials such as Zeolitic Imidazolate Frameworks (ZIFs) as they have been shown to be promising new materials for selective CO_2 adsorption.

The mechanism of templating in zeolite growth is not fully understood, so this presents a further area for atomistic modelling. Organic cations or templates determine the eventual form of a zeolite's framework. By modelling the adsorption of the template tetrapropylammonium on various cuts of the low index surfaces of silicalite (siliceous ZSM-5), we aim to gain a better understanding of the experimental crystal morphology.

The Si/SiO₂ interface and its defects

Al-Moatasem El-Sayed*, Francisco Lopez

*Department of Physics, University College London

e05-surfin-shl

Advances in device performance have been brought about by scaling technologies which has led to oxide layers approaching 1nm. Consequently leakage currents are becoming an unavoidable problem as they lead to power dissipation and are known to generate electrically active defects. These defects are implicated in many reliability issues such as the percolation theory of oxide breakdown and the negative bias temperature instability (NBTI). To continue developing reliable devices it is essential to understand how these defects are formed and how they can interact and what part they play in reliability issues.

The Si/SiO₂ interface was modeled using ReaxFF, an empirical force-field which allows charge states to vary and also allows bond breaking/formation. Molecular dynamics melt and quench procedures are investigated in the formation of amorphous silica and the Si/SiO₂ interface and validated against experimental data. The structures are optimized at the DFT level and the electronic structure is extracted and compared to previous results. The P_b defect is investigated and its structure is calculated in this model using DFT implemented in the CP2K code. The validity of this model is discussed as well as some of the methods used. Defects which are implicated in reliability issues are also investigated in bulk silica. The structures of the neutral oxygen vacancy, E' centre and Ge electron centre are calculated and analyzed in quartz and the self-trapping of an electron in amorphous silica is investigated using the HSE functional in CP2K. The hyperfine interactions are calculated for the E' centre and Ge electron centre in quartz, and for the trapping of an electron in amorphous silica.

MgO surface defects and their interactions with CO₂

Chris Downing

**Department of Chemistry, UCL*

e05-surfin-cat

One of the most critical challenges in the near future is the development of new catalysts for use in the conversion of CO₂ to useful products such as methanol. The presented work involves QM/MM calculations using Chemshell, which have been used to investigate the (100) surface of MgO and its vacant oxygen sites (F₀, F₊ and F₂₊), along with their interactions with CO₂. These findings will later be compared with those for other metal oxide surface sites, such as the F₀ center on the (0001) surface of ZnO which has previously been suggested as a catalytic active site.[1]

Early work on the MgO (100) surface has mostly involved the determination of the optimum cluster configuration within Chemshell by varying the size of the QM and MM regions. These findings suggest that having a sufficiently large MM region is crucial to improving the accuracy of calculated defect formation energies. Also, geometry optimization calculations on a CO₂ molecule over the QM region of a perfect (100) surface suggest that the formation of a surface carbonate species is favourable.

[1] French, S. A. et. al, (2001) *Angew. Chem. Int. Ed.* 40, 4027-4437

Structure and dynamics of water nano-droplets on graphene and diamond surfaces

Ming Ma, Angelos Michaelides*, Gabriel Aeppli

* London Centre for Nanotechnology, University College London

e05-surfin-mic

The wettability of graphene and diamond and the diffusion of water droplets across their surfaces is of central importance to many emerging applications in nanofluidics. Here we report an extensive set of molecular dynamics simulations for water nanoclusters on graphene and diamond surfaces. Ab initio quantum Monte Carlo [J. Ma, A. Michaelides, D. Alfe, L. Schimka, G. Kresse, and E. G. Wang, Phys. Rev. B 84, 033402 (2011)] and van der Waals density functional data has been used to carefully parameterize the water-carbon interaction, enabling long timescale molecular dynamics simulations of the diffusion of water droplets containing up to 2,000 water molecules. The structures and contact angles of the droplets against each surface have been established, as have the diffusion rates and internal hydrogen bond dynamics. A strong size dependence in the lateral diffusion coefficient of the water droplets has been observed as has a marked difference in the diffusive behaviour on diamond and graphene. The general understanding this study provides to surface transportation in carbon based nanofluidics will also be discussed.

Ice Formation on Kaolinite by Direct MD Simulation

Stephen J Cox*, Shawn M. Kathmann, Angelos Michaelides

*Department of Chemistry, University College London

e05-surfin-mic

Ice formation is a familiar everyday process, yet the underlying molecular details are only poorly understood. At temperatures close to the melting point, ice formation almost exclusively occurs heterogeneously i.e. the presence of a foreign body catalyses the liquid-to-ice phase transition. This process is important in atmospheric science, as up to 3000 Tg of mineral dust can be injected into the atmosphere every year [1], influencing cirrus and mixed-phase cloud formation in the upper troposphere [2-4]. Kaolinite, one of the main constituents of atmospheric mineral dust, has been observed experimentally to be an effective ice nucleating agent [5] and we therefore use this as a model system to study heterogeneous ice formation in molecular detail, probing the nucleation mechanism directly using molecular dynamics simulation.

We find that there are a number of differences between nucleation that proceeds homogeneously and nucleation that proceeds on the kaolinite surface. In the homogeneous case, a mixture of cubic and hexagonal ice forms whereas only hexagonal ice forms on the kaolinite surface. Furthermore, ice formation on kaolinite proceeds through growth on the (10-10) prism face as opposed to the (0001) basal face, as in homogeneous nucleation. We attribute this to the corrugation of the prism face allowing more water molecules to bind favourably, in non-icelike positions, to the kaolinite face during the nucleation process.

- [1] IPCC Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge, UK, 2001
- [2] P. DeMott, *et al.*, *J. Geophys. Res-Atmos* **102**, 19575 (1997)
- [3] D. Rogers, *et al.*, *Geophys. Res. Lett.* **25**, 1383 (1998)
- [4] R. W. Saunders, *et al.*, *Atmos. Chem. Phys.* **10**, 1227 (2010)
- [5] M. L. Eastwood, *et al.*, *J. Geophys. Res.* **113**, D22203 (2008)

Quantum diffusion of hydrogen on Ru(0001)

Thor Wikfeldt*, Angelos Michaelides

*London Centre for Nanotechnology, Department of Chemistry,
University College London

e05-surfin-mic

Hydrogen (H) interacting with transition metal surfaces is an important topic from a practical perspective, for instance for heterogeneous catalysis, electrochemistry and hydrogen fuel cells. There is also a large interest in this topic from the perspective of fundamental low-temperature chemical dynamics, because for certain surfaces at low temperatures the dynamics of H changes from normal Arrhenius-like activated hopping to quantum tunneling-dominated under-barrier motion, and this dynamical crossover poses a challenge to various rate theories that attempt to include quantum effects at different levels of approximation. Different dynamical behaviour is seen for H on different surfaces as temperature is reduced, where variables such as surface friction (mainly coupling to surface phonons), shape of the potential energy surface and adsorbate-adsorbate interactions play a key role. Accounting for all these effects in theoretical simulations is challenging and simplified schemes are commonly used. With the computational resources available through HECToR, we have undertaken an ab initio path-integral MD simulation study at the DFT level to investigate the quantum behaviour of hydrogen and deuterium on the Ru(0001) surface, for which direct comparisons to accurate experimental ^3He spin-echo data can be made. We find that the crossover temperature to tunneling-dominated diffusion is well reproduced by the simulations, and we are able to characterise the effect of adsorbate-adsorbate interactions. Moreover, our results shed light on the role of surface phonon coupling as well as the extent of tunneling from excited vibrational states.