

Hard-soft interfaces and the control of crystal growth

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e05-biomat-har

Biom mineralization is the process whereby organic molecules and scaffolds control the nucleation and growth of minerals. Understanding this therefore requires the understanding of a highly heterogeneous interface: soft organic matter on one side and hard mineral on the other. An important part of this process is the adhesion of large molecules to mineral surfaces. We shall discuss progress in simulating the binding of such molecules as ovocleidin and aspartic acid to calcium carbonate surfaces and DNA to fused silica using large-scale classical molecular dynamics simulations. We shall show the importance of local water structure and solution composition in determining the binding of molecules to surfaces for the cases we consider.

Blocking of Gas Diffusion in [NiFe]-hydrogenase Mutants: A Mechanistic Picture from Multiscale Simulation

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e05-biomat-blu

[NiFe]-hydrogenases are fascinating biological catalysts with potential application in biofuel cells. However, a severe problem in practical application is the strong sensitivity of hydrogenase to gaseous inhibitor molecules such as CO and O₂. Recently, a number of successful protein engineering studies have been reported that aimed at lowering the access of diatomic inhibitors to the active site pocket, but the molecular mechanism conferring increased resistance remained unclear. Here we use a multiscale simulation approach combining molecular dynamics with a master equation formalism to explain the steady drop in CO diffusion rate observed for the mutants V74M L122A, V74M L122M and V74M of *D. fructosovorans* [NiFe]-hydrogenase. We find that diffusion in these variants is controlled by two gates, one between residue 74 and 476 and the other between residue 74 and 122. The existence of two control points in different locations explains why the reduction in the experimental diffusion rate does not simply correlate with the width of the bottleneck of the main gas channel. We also find that in the more effective mutant (V74M) CO molecules are still able to reach the active site through transitions that are gated by the dihedral motions of the side chain of R476 and the thermal fluctuations of the width of the gas channel defined by M74 and L122. Reflecting on the molecular information gained from simulation, we discuss future mutation experiments that could further lower the diffusion rates of small ligands inhibiting the [NiFe]-hydrogenase.

Molecular dynamics study of phosphate-based bioglasses

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e05-biomat-lee

First principles (DFT-D) simulations have been carried out to calculate structural and mechanical properties of crystalline P_2O_5 . An interatomic forcefield for a ternary phosphate bioglass (PBG) system P_2O_5 -CaO- Na_2O , has been parameterized from the structural and mechanical properties of the crystalline phosphorus pentoxide α -(P_2O_5) $_{\infty}$ orthorhombic phase. The forcefield has been used to conduct melt-quench simulations of three molar compositions, $(P_2O_5)_{0.45}(CaO)_x(Na_2O)_{0.55-x}$ ($x = 0.30, 0.35$ and 0.40), relevant to a range biomedical applications. The implementation of the adiabatic shell-model, within the full charge formalism, has been shown to require frictional damping in order to control shell temperatures during the quench. The molecular dynamics simulations accurately reproduce available experimental and first principles short- and medium-range structural properties. A full structural characterization has been carried out along with a qualitative assessment of the relationship between composition and structure. The inclusion of modifier cations, Na and Ca, is noted to disrupt the pure Q^3 phosphate network connectivity found in α -(P_2O_5) and introduce varying amounts of $Q^{1,2}$ species, dependent on composition. The increased field strength of Ca^{2+} compared with Na^+ is shown to decrease the P-BO bond distance for compositions with increased Ca content, as found in experiment.

Towards a Multi-Scale Model for Nano-porous Membranes

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e05-enviro-mos

“Separations processes account for 40-70% of both the capital and operating costs in industry” [1]. Using nano-porous membranes can reduce this cost by as much as 90%. The membranes are a polymer sheet around 200 μ m thick. The filtration occurs in the top 80-200nm. Given that a typical polymer chain in these membranes is around 275nm long the entire region of interest may be considered to be on the surface of the membrane.

The formation mechanism behind the manufacture of these membranes is called phase inversion, and is a three phase thermodynamic process. The kinetics of this process, in particular the rate of diffusion of one solvent into another, determine the final membrane porosity [2].

Through the use of multi-scale modelling techniques it is hoped to build the first computational model for this system. This model will be used to better understand the processes involved and to aid in the development of new technologies and materials in nano-porous membranes

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Molecular Dynamics Simulations of High-energy Radiation Damage in Nuclear Power and Fusion Applications

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e05-enviro-kos

Molecular dynamics (MD) simulation is an important tool for gaining insights into radiation damage effects in a way which is often not possible in experiments. Systems of interest include materials used in nuclear and future fusion reactors as well as materials to be used for safe encapsulation of nuclear waste. High-energy radiation damage in these systems has not been studied so far, yet it is important to simulate¹. New energy and time scales will give a more realistic view of the phenomena that take place during the irradiation and possibly lead to observations of new effects.

DL_POLY MD code², in combination with the massive parallel computing facilities of HECToR, UK's National Supercomputer, set the stage for simulating systems with up to 1 billion atoms, and therefore open the possibility to model radiation damage due to high energy recoils in the range between 100 keV up to 1 MeV.

We study the effects of high-energy radiation damage in several interesting nuclear materials, including iron and zirconia. We simulate recoil energies in excess of 200 keV in systems with over 100 million of atoms using a recently developed many-body potential. We investigate the dependence of the damage creation, evolution and recovery on time as well as the nature of the defects in the system.

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Water Adsorption on Rutile TiO₂(110) for Applications in Solar Hydrogen Production

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e05-surfin-nic

In order to improve the solar-to-fuel efficiencies in water splitting for hydrogen production, enhancement of the fundamental understanding of the photocatalysis is required [1-3]. The TiO₂-water interface is where the photocatalytic processes occur, and the debated mechanism acts upon the state of adsorbates at these crystal surfaces [4, 5]. For this reason, the interactions of water are important to understand, and the modelling of the surface chemistry is of great interest.

In this study, highly-accurate periodic hybrid-exchange density functional theory calculations are used to predict the structure of water on the TiO₂(110) surface. A detailed model is described, which allows us to gain a better understanding of water-water and water-surface interactions. The interactions that occur at the surface, as well as their influence on the adsorption mode and energy, are explored.

The results show that the preferred adsorption mode, and the binding energy, is dependent on not only coverage, but also on the arrangement of, i.e. distance between, adsorbed species. These dependencies have a critical influence on the nature of the interactions involved in the H₂O-TiO₂ system. The importance of direct intermolecular and surface-mediated interactions is shown; it is emphasised that water interactions between molecules are as important as the interactions with the surface, and that to consider these interactions is vital for understanding how the first layer of water adsorbs.

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Modelling of BaTiO₃:SiO₂ core-shell particles interface

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e05-nanodef-pvs

One of the most promising energy storage technologies, which have recently found wide application in automotive industry, is based on using capacitors. Capacitor devices can undergo rapid and frequent charge and discharge cycles at high current. Employing electrodes with high surface areas makes it possible to construct devices with extremely high storage capacity, so-called supercapacitors. Increasing the permittivity of the dielectric material between the electrodes is an alternative way to increase the capacitance.

It has been recently found that core-shell particles (CSP) formed by nanoscale grains of ferroelectric BaTiO₃ (BTO) coated with amorphous silica (SiO₂), exhibits a permittivity of the order of 10⁵ in a broad range of temperatures [1]. Experiments showed that a secondary phase growing between BaTiO₃ core and silica shell is fresnoite, Ba₂TiSi₂O₈ [2, 3], which itself is a ferroelectric material with a permittivity of 10. However, the permittivity of BTO is of the order of 10³ (depending on a temperature interval) and that the permittivity of SiO₂ is only of 3.8. Therefore, the origin of high permittivity phenomenon in BTO:SiO₂ core-shell particles is unclear.

We aim to understand the origin of high permittivity phenomenon in CSP. For this purpose we have generated an atomistic model of a BTO:SiO₂ interface, characterized its atomistic and electronic structure. Our *ab initio* Molecular Dynamics simulations, performed with the SIESTA code [4], demonstrate that the Ti, Si, and O atoms diffuse across the BTO:SiO₂ interface forming a complex atomic structure. In particular, the interface is partially amorphous with a short-range order of the fresnoite crystal lattice. The analysis of the electronic structure of this interface suggests a significant band gap closure with respect to that of the crystalline fresnoite and BTO. This is attributed to formation of multiple gap states associated with oxygen vacancies and cation interstitial species in the vicinity of the interface. We suggest that these defects are responsible for

the enhanced dielectric constant of the SCP.

Acknowledgments

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Band gap control via tuning of inversion degree in CdIn_2S_4 spinel

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e05-nandef-cre

Based on theoretical arguments we propose a possible route for controlling the band-gap in the promising photovoltaic and photocatalytic material CdIn_2S_4 . Our ab initio calculations show that the experimental degree of inversion in this spinel, i.e. the fraction of tetrahedral sites occupied by In, corresponds approximately to the equilibrium value given by the minimum of the theoretical inversion free energy (including both configurational and vibrational contributions) at a typical synthesis temperature. Modification of this temperature, or of the cooling rate after synthesis, is then expected to change the inversion degree, which in turn sensitively tunes the electronic band-gap of the solid, as shown by our accurate screened hybrid functional calculations.

2D Polaronic Behavior in the Binary Oxides m-HfO₂ and m-ZrO₂

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e05-nandef-mck

Quasi-two-dimensional (2D) systems, including surfaces, heterointerfaces and layered materials, have become a rich playground for discovering exotic electronic effects such as high T_c -superconductivity and novel magnetic phases. The formation of polarons and the modification of their properties by reduced dimensionality have been implicated in many of these phenomena, but directly probing their properties experimentally remains extremely challenging.

In this study, we employ fully first principles methods that are free from the usual self interaction problems inherent to density functional theory to investigate the properties of hole polarons in the binary monoclinic oxides HfO₂ and ZrO₂. Although usually considered as 3D materials, our calculations show that they exhibit pronounced 2D polaronic properties. This unexpected effect is due to an asymmetry in the crystal structure of these materials, which induces small polaron formation in only one of its two oxygen sub-lattices, leading to highly anisotropic polaron conductivity. These results demonstrate how a small asymmetry in the lattice structure can determine the qualitative character of polaron localization and significantly broaden the realm of quasi-2D polaron systems.

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Theoretical Investigations of Clusters for Potential PEMFC Electrocatalysts

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e05-nandef-roy

One of the many issues with current PEMFC designs is their use of expensive platinum catalysts which have low availability and inherent durability issues. Our research focuses on improving catalytic properties investigating Pt-Ti clusters.

DFT has been used showing slightly weaker adsorption of OH and CO to the surface of bimetallic Ti-core Pt-shell clusters¹, weaker binding is advantageous to both ORR kinetics² and reducing poisoning effects³. This weaker binding was then explained studying electronic structure through changes in the Density of States (DOS) where shifts in *d*-centre were observed for bimetallic clusters.

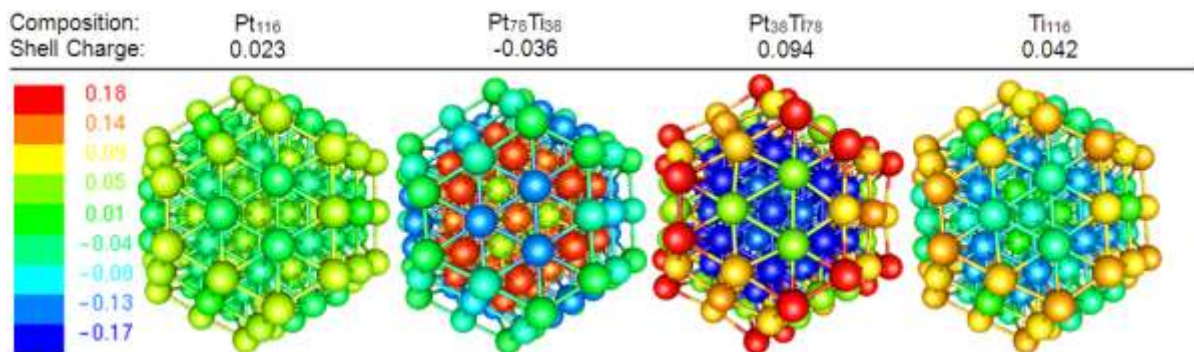


Fig. 1: Lowdin charge analysis of 116 atom mono- and bimetallic clusters

The combination of weaker adsorption energies explained through changes in electronic structure suggests that, whilst significant cost reductions can be made, Pt-Ti electrocatalysts can improve ORR kinetics as well as reduce susceptibility to CO poisoning.

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First Principles Approaches to Understanding the NMR Parameters of Energy Materials

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e05-power-gre

Achieving a detailed atomic level understanding of the key processes and phase transformations involved in the electrochemical activity of advanced battery cathode phases is a key task underpinning the future development of the field. Progress is complicated by the fact that many such materials exhibit structural disorder and complex phase diagrams, particularly in intermediate states of charge and in the presence of dopant species, the latter often intended to confer some desirable *in operando* property. Solid state NMR is a key technique for the characterisation of such complex materials, but is complicated by the fact that most cathode phases bear open shell transition metal (TM) cations and are paramagnetic at battery operational temperatures, leading to chemical shifts lying well beyond their normal diamagnetic ranges. However, recent work has shown that this apparent disadvantage can, in fact, yield detailed insight into the processes occurring in such materials, given that the paramagnetic shift is very sensitive to the disposition and oxidation state of neighbouring TM cations. The assignment of experimental spectra remains challenging, but has been greatly assisted by hybrid DFT calculations of relevant electron–nuclear hyperfine parameters for a range of model environments. Applications of this combined experimental and theoretical approach to a range of cathode phases will be outlined, including:

- i. ^{67}Li and ^{29}Si NMR of structurally complex $\text{Li}_{2-x}\text{FeSiO}_4$ phases,
- ii. ^{67}Li NMR of layered– and spinel–type oxides,
- iii. ^{67}Li and ^{31}P NMR of mixed metal $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$, $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ and corresponding delithiated phases.

Utilizing theory in the search for new layered perovskite materials for SOFC cathodes

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e05-power-dar

In the search for new Solid Oxide Fuel Cell (SOFC) cathode materials we have focussed our attention on complex layered perovskites as potential candidates [1,2]. As the number of elements and unit cell sizes increase it is becoming harder to find new materials solely using chemical intuition. Brute force exploration of the phase diagram is also problematic when the stoichiometries of many components can be varied. In this work we examine how the integration of theory based on chemically intuitive models of local layer structure, coupled closely with experimental synthesis can assist the isolation of new layered perovskite materials, with structures characterised using Powder Neutron diffraction (PND) and Mossbauer spectroscopy, and in the investigation of suitable dopants that might modify the conductivities of these materials.

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Lithium-ion batteries from rust and sand

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e05-power-isl

Polyoxyanion compounds are receiving considerable attention as alternative cathodes to the current LiCoO₂ material for the next generation of rechargeable lithium batteries. The importance of exploring new low cost and safe cathodes for larger scale lithium batteries for hybrid electric vehicles has led to increasing interest in Li₂FeSiO₄ [1,2]. Indeed, iron and silicon are among the most abundant and lowest cost elements, and hence offer the tantalising prospect of preparing cheap and safe cathodes from rust and sand! However, the structure of Li₂FeSiO₄ undergoes significant change on cycling, which results in a change in the cell voltage and the lithium-ion diffusion pathways [2]. Here we report recent atomistic modelling and DFT studies on the Li₂FeSiO₄ material focusing on the different structural polymorphs, and atomic-scale insights into the changes in cell voltages and lithium transport pathways. The effect of changing the stoichiometry of the silicate especially Li-rich phases is also examined, and extends related work on non-stoichiometry of oxide anodes [3].

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Electrochemical and Surface Properties of β -MnO₂ and α -MnO₂

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e05-power-isl

The oxide materials α -MnO₂ and β -MnO₂ are of current interest to energy storage systems based on multiple technologies. They have been experimentally shown to have promising performance as Li-ion battery cathodes, Li-air redox catalysts and supercapacitor electrodes. Furthermore, they offer the possibility to produce these useful systems based on comparatively inexpensive starting materials. We have investigated α -MnO₂ and β -MnO₂ using density functional theory with Hubbard U corrections (DFT+U) and hybrid functional HSE06. The value of U employed is self-consistently calculated and we find good agreement with measured experimental voltages obtaining 3.0 V in α -MnO₂ and 3.2 V in β -MnO₂. We consider the pathways for lithium migration and find a small barrier of 0.2 eV for β -MnO₂ in the dilute limit, however large Li-Li interactions are found away from this dilute limit and are likely to contribute to the need to produce a mesoporous form to obtain good intercalation properties¹. The thermodynamics of lithium intercalation at very deep discharge and charge states are considered. The results indicate that full discharge is thermodynamically inhibited in β -MnO₂ and may contribute to limited battery capacity. Finally, the electronic density of states in α -MnO₂ with the incorporation of Li₂O into its structure is shown to give rise to metallic behaviour which may be critical to its good performance as a catalyst in Li-air batteries. The surface energies and crystal morphologies have also been examined in both polymorphs. The (110) surface is the lowest energy surface in both polymorphs. However, in α -MnO₂, high index surfaces such as the (310) that has been observed experimentally², also contribute to the morphology. It is found that the thermodynamic equilibrium morphology of α -MnO₂ favours more elongated structure, which is consistent with the large set of needle-like nanostructures it forms experimentally. We consider potential active catalytic sites for the Li-air redox reactions.

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A Hybrid-exchange Density Functional Study of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as a candidate material for Magnetic Refrigeration

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e05-qmdev-nic

The Magnetocaloric Effect (MCE) [1, 2] is described as the change in temperature of a magnetic material upon the application and removal of an external field, under adiabatic conditions. At the present time, the main application of the MCE is in room-temperature magnetic refrigeration technology. Manganites are a new class of magnetocaloric materials that have attracted much attention due to their rich phase diagrams [3]. These specific materials exhibit a variety of crystallographic, electronic and magnetic properties manifested in ferromagnetic-, antiferromagnetic (collinear and canted)-, metallic-, insulating-, charge- and orbital-ordered states. An insight into the competition and coupling between various degrees of freedom in doped manganites is of interest for the optimisation of the magnetocaloric effect in such materials. In this work, hybrid-exchange density functional theory (DFT) calculations have been carried out to determine the effects of Ca doping on the structural and electronic properties of perovskite-type manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. A stability plot is compiled with respect to the ferromagnetic (F), antiferromagnetic A-type (A-AF), G-type (G-AF) and C-type (C-AF) configurations. At this level of theory, the structural, magnetic and electronic states for the compositions studied are compared to available experimental data. This provides a basis for a first principles description of the magnetocaloric effect in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ systems.

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Point defects and the origin of p -type behaviour of GaN

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e05-qmdev-sok

A thermodynamic analysis of relative stability of “free” charge carriers in the valence (or conduction) band vs. intrinsic point defects in GaN shows that electron holes are marginally stable in this material. This is in agreement with a long established difficulty in reliable production of p -type GaN: so far the only synthetic route found and used industrially is by heavy magnesium doping followed by high-temperature annealing. The behaviour of Mg impurities in GaN, however, is unusual for a semiconductor material as Mg ions tend to aggregate on the surface of tetrahedral clusters with an inverse wurtzite structure. Moreover, accurate hybrid QM/MM embedded cluster calculations on intrinsic point defects and group 2 impurities in GaN show unambiguously that none of these species could be responsible for shallow hole states in GaN. Shallow electron donor states instead are characteristic of the neutral and negatively charged nitrogen vacancy. These observations provide a good rationale for optical absorption and photoluminescence peaks appearing in Mg doped GaN, with the 3.25 eV line assigned to the $\text{Mg}_{\text{Ga}}^{\times}$ and 3.45 eV line to V_{N} , respectively

In this presentation we will show a summary of our studies on point defects in GaN and will address the problem of the Mg clusters formation in Mg:GaN.

Electronic transport in conjugated polymers

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e05-qmdev-nic

The fields of molecular electronics and charge transport through nanojunctions has been deeply investigated in the past fifteen years. At the experimental level many different techniques have been developed, including those based on break junctions, nanostructured and scanning probe layouts, or self-assembled monolayers. Measurements have been performed on a number of systems ranging from saturated olephins (alkanes) to biological molecules} (such as DNA). Theoretically, the mechanism underlying these experiments can be understood by separating the effect of the electronic structure of the insulating layer (I) through the calculation of the complex band structure (CBS), or evanescent states, in the limit of an infinitely long insulating region. The CBS approach is also particularly interesting for an ab initio evaluation of beta, where the calculations can be performed either using waveunfnction- or green's function-base approaches.

We have numerically investigated four polymers, namely poly-ethylene (PE), poly-acetylene (PA), poly-para-phenylene-vinylene (PPV), and poly-phenylene-imide (PPI). In this work, DFT and hybrid-DFT calculations have been performed using the CRYSTAL package. The code implements all-electron electronic structure methods within periodic boundary conditions and adopts an atomic basis set expanded in gaussian functions. Once the Hamiltonian matrix elements are obtained, the real and complex band structures are interpolated using the WanT package. Differently, GW results have been obtained using the plane-waves and pseudopotentials implementation of SaX, which is interfaced to Quantum-ESPRESSO for what concerns DFT calculations. In this case, once the Kohn-Sham electronic structure is evaluated, we first compute maximally-localized Wannier functions using WanT and then apply the CBS technique.

Environmental Catalysis : Towards Multi-scale Computational Catalysis

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e05-react-jon

Computation Methods have progressed to the point where it is feasible to simulate the surface chemistry of catalytic process over a series of materials. This technology has opened up the possibility of predicative screening for materials that can optimise the chemistry for a given reaction. Despite a number of successes there remain a number of challenges in this field. One such example is obtaining a description of the support material in a given process and how this modifies the surface chemistry or perturbs the supported metal catalyst. A second example is to answer what influence the reaction environment has on the chemistry, for instance, how does diffusion through the porous catalyst layer influence the overall catalytic process. Many of these effects are highly dependent on the reaction of interest and the specific conditions under which the catalysis is being carried out. Nevertheless by choosing one class of catalysts to focus on (in this case NO_x & SO_x abatement catalysts) general principles can be established which will allow a wide range of important reactions to be understood.

The first part of the talk will present data from studies conducted on the reactivity and electronic structure of isolated nanoparticles used in the selective catalytic reduction of NO_x, following which preliminary results of CeO₂ being used as an oxidation catalyst for SO_x will be discussed. This will culminate in a discussion of our experience to date with the ONETEP code for modelling a combined oxide/nanoparticulate system. The second part of the talk will present kinetic results from 3D reconstructed porous structures, which have been carried out in conjunction with experimental studies of CO oxidation in catalytic layers for automotive exhaust catalysts.

H₂ formation on graphene: the combined role of dispersion and quantum tunnelling

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It is becoming increasingly recognised that quantum nuclear effects and dispersion forces can play an important role in processes at surfaces. Here we use a combination of state of the art techniques, namely vdW-DF and path-integral molecular dynamics, to show that these effects work together cooperatively to alter the chemisorption barrier for H at graphene. The vdW-DF includes long-range dispersion forces, which are normally missing in traditional DFT calculations. We show that dispersion lowers the barrier to chemisorption from the PBE value of 0.2 eV to 0.1 eV. Furthermore including quantum nuclear effects reduces this to just 0.02 eV. This makes the chemisorption of H atoms at graphene much easier than previously thought, potentially enabling the formation of H₂ between physisorbed (or gas phase) hydrogens and more stable chemisorbed states. Our findings have clear implications for the formation of H₂ at graphitic surfaces and if shown to lower barriers for dissociation at surfaces may also have a general relevance to catalysis.

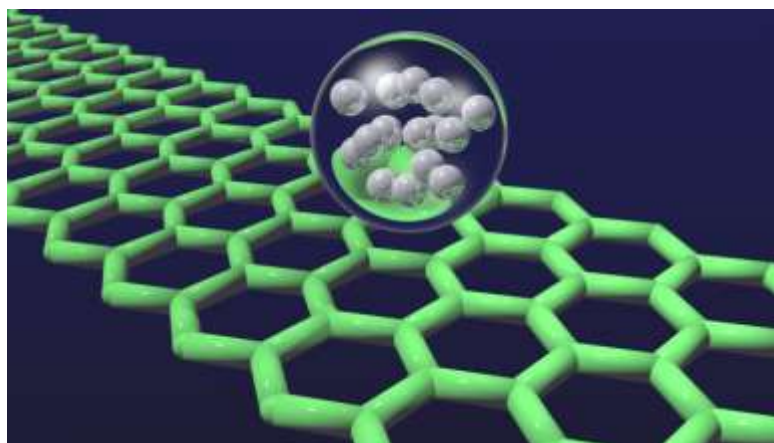


Figure: Path-integral molecular dynamics of a hydrogen atom at graphene. The atom is represented by multiple images connected by harmonic springs in a ring-polymer. Each of these images runs simultaneously, making the calculations extremely expensive.

Water Adsorption on Stoichiometric and Reduced Surfaces of Ceria

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e05-react-par

The presence of water plays an important role on the redox properties of Ceria in its widespread usage. *Ab initio* simulation techniques based on DFT-GGA+U are employed to investigate the ceria-water interaction including associative and dissociative adsorption of water at different water coverage and the formation of oxygen vacancies on dry and wet low index CeO₂ surfaces. The results indicate that on stoichiometric surfaces dissociative adsorption depends strongly on the water coverage, while associative adsorption is less dependent on coverage due to weaker interactions between the adsorbed molecules. In general the coordination of surface cerium controls the adhesion of water while the hydrogen bonding network dictates the orientation of the molecules. The adsorption energy increases on reduced surfaces because oxygen vacancies act as active sites for water dissociation. Crucially, by calculating the heat of reduction of dry and wet surfaces, we show that water promotes further reduction of ceria surfaces and is therefore central to its redox chemistry. Finally we evaluate water desorption as a function of temperature and pressure on CeO₂{111}, CeO₂{110} and CeO₂{100} surfaces. Such understanding will help experiment interpret the complex surface/interface redox processes of ceria, which will inevitably include water.

Computation Modeling Studies of YSZ Materials for Catalytic Methane Oxidation

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e05-react-cat

This research examines the structure, features and catalytic activity of YSZ (yttrium doped zirconia) relevant to the industrially valuable process of methane reforming by partial oxidation to synthesis gas (CO, H₂). Natural gas, primarily methane, reforming is carried out over a variety of catalysts, including oxide supported precious and transition metal particles. YSZ is a frequently exploited support material owing to its thermal, mechanical and chemical stability. YSZ materials are an active component of the catalytic system, indeed they have significant catalytic activity in their own right. YSZ is able to act as an oxygen conductor and has been shown to stabilise reactive oxygen species on its surfaces, leading to a range of potential active sites for oxidation reactions.

There is some debate as to the specific intermediates, pathways and mechanisms involved in methane to syngas conversion over these materials. This research utilises computational electronic structure techniques (DFT, hybrid functionals) to address these questions. Previous work has identified important structures likely to be present at the surface of this material, predominantly {111} terraces and steps. These structures contain defects in the form of dopant yttrium ions and oxygen vacancies. The vacancies are able to adsorb and stabilise various active oxygen species such as superoxide (O₂⁻). Computational techniques have been applied to a variety of significant reactions in the catalytic processes, including the initial hydrogen abstraction from methane by surface oxygen species, further dehydrogenation over the surface and interactions of other important species (H₂O, H₂, CO, CO₂, H₂CO, etc) with the surface. Activation barriers and reaction energies are being calculated in order to identify those reactions likely to predominate in the catalytic process.

Adsorption of magnetic molecules on insulating surfaces

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e05-surfin-*shl*

We have investigated the adsorption of Co-salen, a small paramagnetic molecule, on the NaCl (001) surface, where we determined the adsorption sites and orientations of the molecule which were confirmed with experimental observations taken with atomic resolution non-contact Atomic Force Microscopy (NC-AFM) [1]. We demonstrated that well prepared and characterized Cr tips can provide atomic resolution on the bulk NaCl(001) surface with dynamic atomic force microscopy in the noncontact regime at relatively large tip-sample separations. At these conditions, the surface chemical structure can be resolved yet tip-surface instabilities are absent. Our calculations demonstrate that chemical identification is unambiguous, because the interaction is always largest above the anions. This conclusion is generally valid for other polar surfaces, and can thus provide a new practical route for straightforward interpretation of atomically resolved images.[2]

We have extended our investigation to the adsorption of Salen complexes on a magnetically ordered surface, and their effect on the local spin ordering on the surface and in the molecule. We will compare and contrast the behavior of Salen complexes with a Co(II) ($s=1/2$) metal coordination atom adsorbed on the anti-ferromagnetic NiO (001) surface, with the previous data with a NaCl substrate. These theoretical studies will be performed in collaboration with experimental groups (Dr. A. Schwarz, Hamburg University) studying these systems with atomic and molecular resolution non-contact atomic force microscopy and magnetic exchange force microscopy, which can resolve the local spin ordering in the system [3]. Our detailed understanding of the adsorption behavior of a prototype molecular magnet is an important step towards understanding magnetic ordering and switching processes mediated by single molecule adsorption on insulators. This understanding is crucial for the development of single molecule devices that rely on spin ordering and molecular spintronics architectures.

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The Energy Landscape of Zeolitic Imidazolate Frameworks (ZIF) with Functionalized Linkers

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e05-surfin-ben

Zeolitic imidazolate frameworks (ZIF) constitute a well-documented class of hybrid inorganic-organic materials.^[1] They have gained attention as extended analogues of zeolites, where Zn^{2+} ions play the role of silicon and imidazoles (Im) form bridges that mimic the role of oxygen. Research efforts are driven by the prospect of expanding their functionality, enhancing adsorption and catalytic properties.

Recently, the family of lithium-boron ZIF (BIF) has been reported, where Zn^{2+} ions are replaced with Li^+ and B^{3+} respectively, resulting in the chemical composition of $LiB(Im)_4$. These lightweight structures possess enhanced gas adsorption capacity per mass unit and provide more different catalytic sites.^[2] It is striking that the new topologies (>20 today) and possibility to tune properties in the Zn-based family has been achieved successfully through the judicious choice of linkers.^[3] In contrast, only 4 distinct topologies of BIFs are known so far (including SOD and RHO) highlighting the need of rationalizing the energy landscape of these frameworks. The factors determining the energy ranking of particular topologies (such as linker-linker interactions, intra-framework linker packing, etc.) are crucial issues, still to be elucidated.

We use DFT level of theory with the dispersion correction (DFT-D),^[4] which proved to be accurate enough in our previous works on ZIFs.^[5] In the first step, a cross-linked study of 7 methyl-substituted linkers and 7 topologies is presented. We reveal linkers have a profound impact on the relative energies of BIFs. In addition, linkers containing other functional groups (i.e. $-NH_2$ and $-OH$) are explored. In the second step, the analysis of hypothetical structures reveal the structure-directing role of functional groups with their selective clustering at either the 4-member or the 8-member rings. Furthermore, the impact of various structural characteristic is analyzed and strategies are proposed for the stabilization of not-yet-synthesized BIFs.

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Structure prediction of molecular organic crystals

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e05-surfin-day

Ab initio crystal structure prediction has been a long-term goal in the field of computational chemistry and has fueled the development of methods for modeling the crystal structures of organic molecules. The principal method used for crystal structure prediction is based on global searches of the lattice energy surface and the application of such methods to organic molecular crystals is now becoming reliable for some classes of molecules. However, application of these methods presents a great computational challenge due to the competing demands presented by the large number of possible crystal structures available to any given molecule and the typically small energy differences between these structures. A strategy to that has been adopted is to generate trial crystal structures using simple model potentials, followed by successive lattice energy minimization using more accurate methods on a smaller set of the low energy structures. Dispersion-corrected density functional theory offers a promising approach for the final ranking of the most promising structures.

The talk will outline the methods used in crystal structure prediction and their validation on a range of types of crystal structures. Much of the development and validation has focused on the crystal structures and polymorphism of pharmaceutical molecules and progress in treating more complex molecules has been rapid in recent years.¹ We will also present promising results on the application of structure prediction to guiding the design and discovery of microporous molecular materials.²

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Hydrogen bonding and proton transfer dynamics at the liquid water-ZnO interface from first principles

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Understanding hydrogen bonding and the dynamics of proton transfer at water-solid interfaces is important to many areas of science, such as electrochemistry and heterogeneous catalysis. Studies at well defined solid surfaces also have potential to reveal insight that might be relevant to proton transfer in biological membranes. In this context, the water-ZnO(10-10) interface is an intensively studied system where the protons transfer to and from the surface on a picosecond time-scale. Yet, the detailed mechanisms of how proton transfer occurs and the relation with hydrogen bonding are unknown. Here, we report the first density functional theory (DFT) molecular dynamics study of a liquid water film on ZnO(10-10) and of a water monolayer on ZnO(10-10). In the liquid film simulation we observe a coverage increase compared to the monolayer study and also a pronounced layering in the density. In addition, water molecules in the adsorption layer of the liquid film simulation have on average a larger coordination number. Finally, we investigate the relation between hydrogen bonding and proton transfer and we find that if a water molecule is a hydrogen bond donor it is energetically favourable in the intact state, whereas if it is an acceptor it is favourable in the dissociated state. Analysis of the physical origin of this effect implies that the correlation between hydrogen bonding and proton transfer observed here is likely to be of general importance.