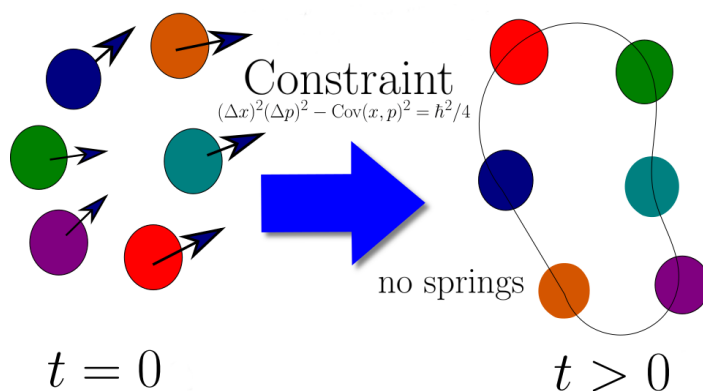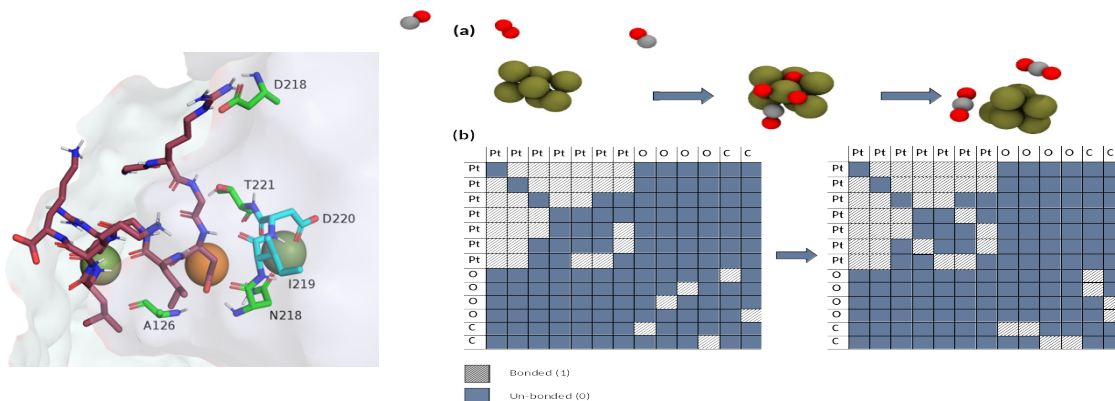# Royal Society of Chemistry, Theoretical Chemistry Group Graduate Meeting

School of Chemistry,
University of Nottingham,
July 31st 2019

Royal Society of Chemistry, Theoretical Chemistry Group Graduate Meeting

Wednesday July 31st 2019, School of Chemistry, University of Nottingham

All lectures will take place in X1, School of Chemistry and the posters will be presented in the foyer area outside the lecture theatre.

The Coulson prize will be awarded for the best presentation at the meeting and prizes will be awarded for the best posters.

Programme

11:00	Arrival
11:30 – 12:30	Keynote Lecture: Prof. Kieron Burke, University of California Irvine *"Density functional theory: From deep understanding to machine learning"*
12:30 – 13:30	Lunch and Poster Session
13:30	*"Theory and Computation in Two-Photon X-ray Spectroscopy"* Adam Fouda, University of Nottingham
13:55	*"New insights on the role of single sulfur vacancy on gaseous adsorption and potential water splitting over MoS_2 edges"* Francis Enujekwu, University Nottingham, UK and Ningbo
14:20	*"A computational screening of porous materials for biogas upgrading"* Joseph Glover, University of Nottingham
14:45	*"Solvent effects on non-covalent interactions: functional group interaction profiles"* Mark Driver, University of Cambridge
15:10 – 15:30	Coffee and Posters
15:30	*"A novel, linear-scaling method for non-covalent interactions"* Robert Shaw, University of Sheffield
15:55	*"A Self-Interaction Correction Through A Constrained Minimisation of The Total Energy"* Tom Pitts, Durham University

16:20 *"Constant-Uncertainty Molecular Dynamics – A Practical Method for Approximating Quantum Dynamics?"*
Sundeep Popat, University of Cambridge

16:45 "**Active Search for Computer-Aided Drug Design**"
Steve Oatley, University of Nottingham

17:10 – end Drinks Reception and Prizegiving

Posters

P1.   "*Using machine learning to build potential energy surfaces for use in quantum molecular dynamics*"
Adam N. Hill, University of Sheffield

P2.   "*Approximations for Non-Adiabatic Electronic States*"
Benjamin Pearce, Durham University

P3.   "*Molecular Simulation to Accelerate Discovery of $\alpha_V\beta_6$ Integrin Inhibitors*"
Ellen E. Guest, University of Nottingham

P4.   "*On the formation of urea in the ISM*"
Eren C. S. Slate, University of Sheffield

P5.   "*Electron Transfer in Transition Metal Complexes*"
Heather Carson, University of Sheffield

P6.   "*Automatic Prediction and Characterisation of Complex Chemical Reactions*"
Idil Ismail, University of Warwick

P7.   "*Ab initio Relaxation Dynamics of Pentagonal Bipyramidal Dysprosium(III) Single Molecule Magnets*"
Jon Kragskow, University of Manchester

P8.   "*Computational Studies of Incorporation of Pu and Ce into Ceramic Matrices Such as Zirconolite*"
Jonathan Tanti, University of Manchester

P9.   "*Modelling Electrostatic Cohesion of Pharmaceutical Powders*"
Joshua Baptiste, University of Nottingham

P10.   "*Studying covalency in transition metal and actinide complexes using DMRG-CASSCF*"
Letitia Bernoschi, University of Manchester

P11.   "*Modelling Conjugated Polymers containing Diketopyrrolopyrrole and Thiophene*"
Ling Jiang, University of Nottingham, Ningbo

P12.   "*Towards understanding the role of lead-based modifiers in rocket propellants*"
Lisette R. Warren, University of Edinburgh

P13.   "*Creating Versatile Photoswitches: Shedding Light on Design Parameters of Hemithioindigos*"
Martin Lea, University of Warwick

P14.   "*Investigating the autooxidation accelerating reactions of peroxides and peroxyl radicals using quantum chemistry calculations*"
Matthew R. Dwyer, University of Sheffield

P15.   "*Identifying Conical Intersections using TDDFT*"
Max Winslow, Nottingham Trent University

P16.   "*Aromaticity; Anti-Aromaticity; and Chemical Boning from Magnetic Shielding Calculations*"
Muntadar Al-Yassiri, University of York

P17.   "*Investigating reaction dynamics using the Reaction Path Hamiltonian*"
Raphael Chantreau Majerus, University of Warwick

P18.   "*Density functional correlation theories based on the Unsöld approximation*"
Zack M. Williams, University of Bristol

P19.   "*Exchange-correlation functionals from the integration of density and wave function theories*"
Timothy Callow, Durham University

P20.   "*Evaluating the Role of Electrostatics in Lignin-degrading Peroxidases with QM/MM*"
Jonathan Colburn, University of St Andrews

P21.   "**Adsorption of Uranyl(VI) on the Stoichiometric and Oxidised Mackinawite {001}-S Surface**"
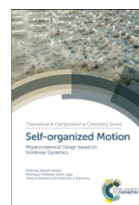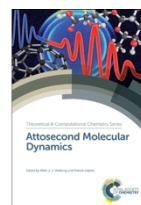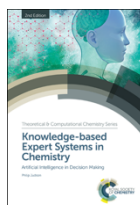Naomi Ofili, University of Manchester

Sponsors

We are grateful for support from

PRESENTATIONS

Theory and Computation in Two-Photon X-ray Spectroscopy

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An understanding of the evolution of the electronic structure of molecular systems on an ultrafast time scale underpins many modern technological developments. At the forefront of driving our understanding in electronic structure and its response to polyatomic nuclear dynamics, is the cooperation between cutting edge x-ray spectroscopy experiments and simulation. Spectroscopy with high energy x-rays is atom specific and sensitive to both intermolecular and intramolecular environments, and these techniques are emerging as one of the most powerful analytical tools for the study of geometric and electronic structure, elucidating chemical bonding and probing the properties of materials. For example, X-ray studies have determined the first coordination shell of liquid water [1] and monitored the bond breaking of a carbon monoxide molecule absorbed on a metal surface in real-time [2].

The nature of excited states and non-adiabatic dynamics can be probed using two-photon x-ray processes, providing information on fluorescent and non-fluorescent transitions and photochemical pathways following electronic excitation a to higher energy state. These techniques include transient x-ray absorption spectroscopy (tr-XAS) and resonant inelastic x-ray scattering (RIXS). We will present how state of the art theory and computation can support experimental measurements, providing key insights into the underlying electronic structure and dynamics. In particular it will be shown how density functional theory (DFT) based methods can be coupled with on-the-fly quantum dynamics to probe ultra-fast nonadiabatic dynamics [3] and how a similar protocol can be used to accurately simulate gas-phase water RIXS, when combined with Kramer and Heisenburg's cross-section scattering theory and considering the effects of core-excited ultra-fast dissociation [4]. The optimal basis sets required to study core hole states have also been benchmarked [5], and these approaches were applied to the interpretation of experimental x-ray photoelectron spectroscopy (XPS) in ether functionalised ionic liquids [6]. These methods have been extended to tackle open-shell systems, and in ongoing collaborative RIXS study using multi-configurational quantum chemistry combined with high resolution experiments.

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New insights on the role of single sulfur vacancy on gaseous adsorption and potential water splitting over MoS₂ edges

Francis M. Enujekwu [a,b,c], Joseph Glover [a], Collins I. Ezeh [b] , Elena Besely [a], Michael George [a,b], Mengxia Xu [b,c], Nick Besely [a], Hainam Do [b,c], Tao Wu [b,c]

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According to statistical thermodynamics, the presence of elemental vacancies in materials have redefined the chemical and physical properties of such material; and as such, enables the surface of the investigated material for various applications. Single vacancy, or a missing Sulfur atom in Molybdenum disulfide (MoS_2_SV) is one of the most typical kind of defects that possesses highly reactive sites, particularly for gaseous adsorption and conversion. In this study, the adsorption of different gas molecules (CO_2, N_2, H_2, CH_4 and H_2O) on MoS_2_SV surface is investigated using first-principles calculations and Grand Canonical Monte Carlo (GCMC) simulations.

Density functional theory (DFT) simulation reveals that the highest CO_2 adsorption energies obtained after geometry optimization were -0.139 eV and -0.908 eV for perfect MoS_2 surface ($PMoS_2$) and MoS_2_SV respectively. Further observation depicts that the adsorption of H_2O and N_2 molecules on MoS_2_SV is 3.5 and 5.1 times weaker than CO_2 adsorption, respectively. This suggests MoS_2_SV to be a suitable adsorbent for selective adsorption and separation of CO_2 over H_2O and N_2. Moreover, optimized MoS_2_SV configuration stipulates that adsorption of CO_2 and H_2O was via dissociative chemisorption, in contrast to optimized $PMoS_2$ configuration, for which physisorption was the only adsorption mechanism.

Classical GCMC simulations further investigated the adsorption properties of $PMoS_2$ and MoS_2_SV between 0 – 100 bar. Little or no differences were observed for the adsorption of N_2, H_2 and CH_4 molecules across both surfaces. A small increase of 0.05 wt% was observed for H_2 at 77K on the MoS_2_SV surface. In agreement with DFT results, the GCMC simulation also demonstrated that $MoS2\_SV$ enhances the adsorption of CO_2 and H_2O at 1 bar, 298 K relative to that of the pure surface. We observe CO_2 loadings of 2.07 wt% and 0.55 wt% and H_2O loadings of 41.78 wt% and 0.01 wt% for the $MoS2\_SV$ and $PMoS_2$ surfaces respectively. Conclusively, this study suggests the potential application of MoS_2_SV for carbon capture and water splitting.

A computational screening of porous materials for biogas upgrading

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Biomethane derived from biogas can be used as source for energy storage and transport applications. Mainly composed of CH_4 (50-70%), biogas also contains large quantities of CO_2 (35-50%) and small amounts of various trace gases such as H_2S, N_2, H_2 and NH_3. Therefore, it is essential to employ purification methods to remove unwanted impurities and increase the calorific content of the gas. While conventional methods (ads/absorption, cryogenic sieving, pressure swing adsorption, etc.) are highly effective at producing biomethane content with greater than 95% purity,[1] they suffer from high investment and operational costs. In recent years, membrane technology has received much attention due its promise as a cheaper alternative. The use of mixed matrix membranes (MMM), made from organic polymers and porous filler particles, combines the exceptional mechanical properties of pure organic membranes and high selectivity, permeability and tuneability provided from inorganic membranes, into one hybrid.[2] Typical porous filler particles include carbon-based materials, zeolites, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs) and more. However, with such breadth of choice, one of the main challenges of designing new MMMs is knowing which filler particles will provide high permselectivity and be compatible with the organic polymer.

Screening candidates for biogas separation
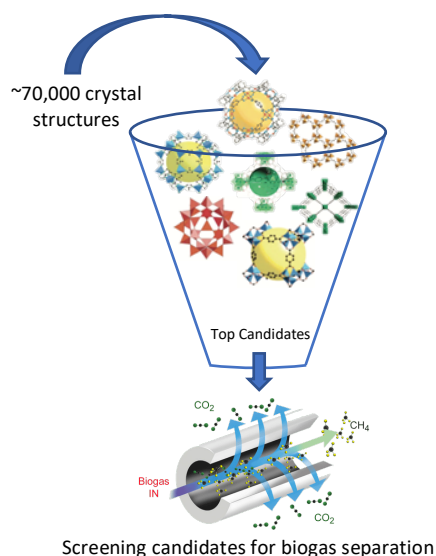
In these situations, the use of high-throughput computational modelling can be an effective and rational means of identifying real and hypothetical candidates for separation and storage applications.[3-6] In this work, a multi-level screening protocol combing various classical simulation techniques is used to screen ~70,000 MOFs and COFs as MMM filler particles for biogas upgrading. Initial candidates are quickly screened based on their permeabilities at infinite dilution, to assess the interaction strength between guests and the frameworks. Strong candidates are then subject to more accurate grand-canonical Monte-Carlo and equilibrium molecular dynamics simulations at working conditions of 10 bar and 298 K. This approach aims to develop a better understanding of the structure-performance relationships that govern CH_4 separation from biogas with the hope of aiding both computational and experimental design of novel membranes. In addition, we are able to identify promising experimental crystal structures that may not have been previously considered for separation applications.

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Solvent effects on non-covalent interactions: functional group interaction profiles

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Hydrogen bond donor (α) and acceptor (β) parameters have been developed using experimental measurement of the equilibrium constants for formation of 1:1 complexes in non-polar solvents [1]. These parameters correlate with the _ab initio_ calculated molecular electrostatic potential surfaces (MEPS) of molecules. This correlation has been used to develop a coarse graining method (footprinting) that converts the calculated MEPS of a molecule into a set of Surface Site Interaction Points (SSIPs) that describe all intermolecular interactions that the molecule can make with its environment [2].

Consideration of the binding equilibria between all SSIPs of all molecules within a liquid phase provides an approach to evaluate the solvation free energy of a molecule within a solution [3]. The free energy of interaction between a pair of solute SSIPs in a solvent varies with solute SSIP values. This can be used to generate a Functional Group Interaction Profile (FGIP) for the solvent. The FGIP shows the behaviour of all possible solute-solute interactions in a particular solvent or solvent mixture graphically, providing a useful guide for understanding experimental systems where non-covalent interactions play a role.

This analysis can be performed for single component or multi component solvent systems following a highly automated workflow. This allows exploration of solvent systems, to provide selection criteria before experimental work is undertaken. The FGIP for water at 298K is shown below, with energies on the contours in kJmol^{-1}.

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A novel, linear-scaling method for non-covalent interactions

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We present the ALMO+RPAd method [1], providing coupled-cluster accuracy interaction energies while scaling linearly with the number of molecular fragments. The calculation of interaction energies is a difficult problem in quantum chemistry, as the small energy differences require the highest accuracy methods to be used. These typically scale as order N^6 or higher, where N is the number of basis functions. However, systems of practical interest are typically in the condensed phase, where there are hundreds of molecules affecting every single interaction. In addition, traditional methods result in a basis set superposition error (BSSE) that must be corrected for, requiring multiple additional calculations.

By using absolutely localised molecular orbitals [2] and a pairwise random phase approximation, we have been able to develop a BSSE-free method for calculating interaction energies that scales linearly with the number of fragments. It is possible to perform calculations involving over 3500 orbital basis functions on a single compute core in under ten minutes. Benchmarks over several non-covalent interaction datasets demonstrate that, when compared with coupled cluster results, the new method outperforms MP2, dispersion-corrected DFT, and SAPT2 in terms of accuracy, while offering speedups of at least two times. Moreover, it naturally decomposes the energy into physically distinct contributions that agree qualitatively with those of the established symmetry-adapted perturbation theory decomposition.

Finally, we have derived analytical derivatives for the method, and have written a highly-parallelised code, Gamma, to perform the calculations. In this way, the geometry optimisation of a cluster of 100 water molecules was able to be performed in under half an hour across two compute nodes with 16 cores each. Results on smaller water clusters suggest good agreement with coupled cluster geometries.

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A Self-Interaction Correction Through A Constrained Minimisation Of The Total Energy

Tom Pitts [a], Nikitas Gidopoulos[b]

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[b] *Department Of Physics, Durham University, Durham, County Durham, DH1 3LE, UK*

Self-interactions are a known failing of many commonly used density function approximations. Self-interactions arise from a spurious interaction of an electron with itself. This self-interaction effect manifests as an incorrect decay in the Kohn-Sham potential, in a self-interaction free system the Kohn-Sham potential decays as $(N-1)/r$, while in approximations such as LDA and PBE this decay is instead N/r. This incorrect asymptotic decay affects the calculation of one electron properties, notably the Highest Occupied Molecular Orbital(HOMO) energy from which the Ionisation potential can be obtained. Self-interacting density functional approximations typically underestimate ionisation energies by $\approx 4eV$, even for functionals providing accurate total energies. A correction for self-interacting functionals was proposed by Gidopoulos and Lathiotakis[1] which aimed to correct self-interactions in any given functional will be the subject of this presentation.
In this self-interaction correction method the Hartree exchange and correlation Kohn-Sham potential of a Density Functional Approximation for a finite N-electron system is replaced by the electrostatic potential of an effective charge density that is everywhere positive and integrates to a charge of $N-1$ electrons. This constraint enforces the correct asymptotic decay on the Kohn-Sham potential and improves the calculation of ionisation potentials.
In this talk I will present the methods of enforcing these constraints in the Kohn-Sham approximations and demonstrate the improvements to the calculation of ionisation potentials for the functionals LDA, PBE and B3LYP for a range of molecules[2]. This corrections reduces errors in the ionisation potential from $\approx 4eV$ to $\approx 1.5eV$ and exhibits an insensitivity to original functional used. The energetics of the functional being constrained are shown to differ by no more that 0.1meV. Therefore this method preserves the original uncorrected total energies of functional approximation while significantly improving the calculation of ionisation energies.
Recent work will then be covered with an introduction to a functional that is a hybrid of Hartree Fock and a self-interaction free constrained PBE potential. Here both elements of the hybrid are self-interaction free and for a hybrid coefficient of 0.5 this method demonstrates further improvements over the original constrained method in calculation of ionisation potentials, reducing the error to $\approx 0.5eV$. Further investigation will reveal that this accuracy is present, not just for the HOMO, but for all the occupied orbitals.
Finally, current work will be presented on a first order correction to the total energy for the difference in energy between an unconstrained self-interaction contaminated calculation and the constrained self-interaction free method. This energy correction will be shown to be $\approx 10^{-6}eV$ and minimising the energy of this correction will be shown as another method of correcting for self-interaction effects in a density functional approximation.

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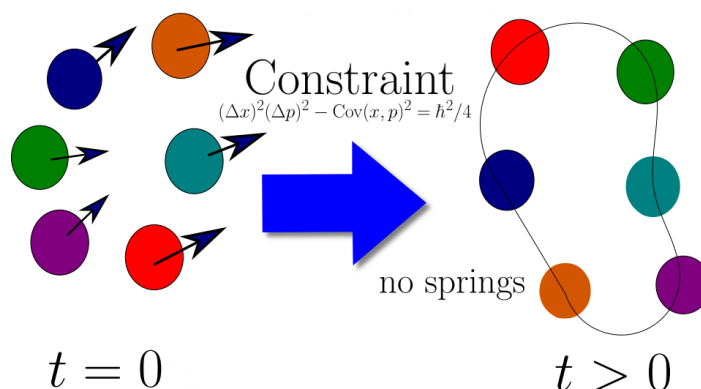# Constant-Uncertainty Molecular Dynamics – A Practical Method for Approximating Quantum Dynamics?

Sundeep Popat [a,b] and Stuart C. Althorpe [a]

[a] *Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom*
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Constant-uncertainty molecular dynamics [1] (CUMD) has been proposed as a "simple and efficient" method in which quantum effects can be incorporated into classical molecular dynamics simulations. The method has been shown to give better agreement with exact quantum mechanical results compared to ring-polymer molecular dynamics [2] (RPMD) for one-dimensional test systems. The method uses RPMD to set up an ensemble of classical particles and then evolves them subject to a constraint between the positions and momenta of the particles (based on the uncertainty principle). We find that the constraint cannot be integrated as it contains terms which are non-linear with respect to momenta; this results in the method using an ad-hoc fix, causing it to be inefficient and algorithmically unstable. As a result, it is unlikely that CUMD can be extended to larger, more realistic systems. However, we use the first step in the method (momenta rescaling of the RPMD beads) as a method in its own right and test it on further 1D and 2D systems.

Figure 1: Idea behind Constant-uncertainty molecular dynamics.

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Active Search for Computer-Aided Drug Design

S. A. Oatley [1], D. Oglic [2,3], S. Macdonald [4], T. McInally [1], R. Garnett [5], T. Gärtner [2], J. Hirst [1]

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[2] *School of Computer Science, University of Nottingham, Nottingham, UK*
[3] *Institut für Informatik III, Universität Bonn, Bonn, Germany*
[4] *GlaxoSmithKline, Stevenage, UK*
[5] *Department of Computer Science and Engineering, Washington University in St. Louis, St. Louis, USA*

Chemical space is large, to the point of precluding its explicit enumeration. Thus, it represents a so-called intensionally defined design space. Search strategies for intensionally designed spaces are a current area of interest in machine learning. In the context of a drug design problem, we have investigated the application of a data-driven adaptive Markov chain approach, where the acceptance probability is given by a probabilistic surrogate of the target property, modelled with a maximum entropy conditional model.[1,2] We apply the approach to a lead discovery search for inhibitors of an α_v integrin, using a molecular docking score[3] as the optimisation function. α_v integrins are currently an important target for the treatment of a number of fibrotic diseases e.g. idiopathic pulmonary fibrosis, an increasingly prevalent lung disease. These integrins are large, bidirectional transmembrane signalling proteins that share a common RGD binding motif. Our algorithm is (i) soundly based in machine learning; (ii) proposes structures from an implicitly defined space of potential designs; (iii) is guaranteed to converge; and (iv) achieves a large structural variety of proposed target structures, some of which provoke significant interest from a medicinal chemistry perspective.
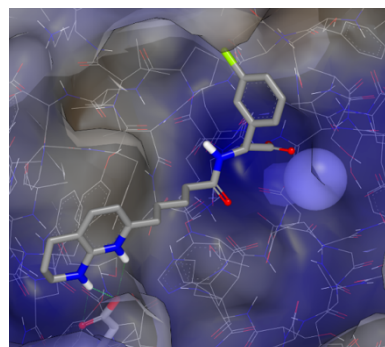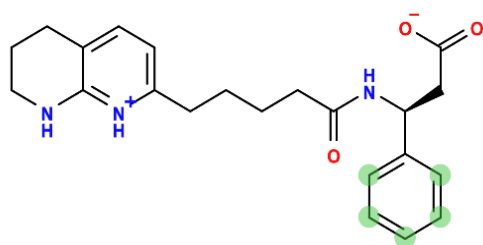
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(2)   Oglic, D.; Oatley, S. A.; Macdonald, S. J. F.; McInally, T.; Garnett, R. Active Search for Computer-Aided Drug Design. *Mol. Inform.* **2018**, *In Press*.
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POSTERS

Using machine learning to build potential energy surfaces for use in quantum molecular dynamics

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Quantum molecular dynamics studies of chemical systems allow theoreticians to explore the behaviour of modern-day chemistry in ways that are not feasible in a lab. It is possible to: predict the results of an experiment performed at extreme temperatures and pressures; calculate reaction kinetics; predict reaction pathways; and even calculate product ratios. To do so, information about the energy of a chemical system at a large number of different geometries is needed, and although electronic structure calculations have become relatively fast to compute on modern supercomputers, the systems of interest have also grown significantly more complex.

The common pre-requisite for carrying out a quantum dynamics study is a potential energy surface (PES) that associates nuclear positions and energy, usually constructed from high-level ab initio calculations and fit using physically motivated functions.[1] This fitting process is tailored to individual systems and is a painstakingly slow process. Machine learning (ML) algorithms offer a number of potential advantages for the construction of PESs: firstly, they represent more of a "black-box" approach to the fitting that promises an easier route to accurate surfaces; second, reducing the dimensionality of the problem holds the promise of constructing a surface from significantly fewer points.

When using a ML algorithm to build a potential energy surface, three areas need to be considered: data generation; molecular representation, and the algorithm itself. For a simple proof of concept, the PES of H_2O has been fit using a simple feed forward neural network with two hidden layers (64 nodes each). A dataset of ~1300 geometries [calculated at the CCSD(T)/aug-cc-pVTZ level] represented as internal coordinates was randomly sampled to generate a training, validation, and test set. These were used to train and evaluate the model.

Ab initio calculations on more complicated systems, and at higher levels of theory, cost significantly more than those on water and thus it is desirable to reduce the number of calculations required to produce an accurate PES. We are exploring novel ways of sampling a PES to concentrate computational effort on the more chemically interesting regions. Combining new sampling methods with ML fitting of the surface represents a promising route to the minimal amount of information required to produce an accurate surface.

References

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Approximations for Non-Adiabatic Electronic States

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The Born-Oppenheimer (BO) approximation[1] is used as the basis for most quantum mechanical studies of molecules and solids, and has proved to be very successful for a wide range of systems. However, when considering phenomena which depend on the coupling between the electronic and nuclear wavefunctions, the BO approximation breaks down. An approach to go beyond the BO level is to use the exact factorisation theorem[2], which demonstrates that the decomposition of the total wavefunction into a product of an electronic and nuclear wavefunction can in principle be exact.

Using a variational approach, exact equations for the electronic and nuclear wavefunctions can be derived; the nuclear equation retains the algebraic structure of the BO approximation, however, the electronic equation contains additional terms which couple it to the nuclear wavefunction[3]. These extra terms account for electron-nuclear correlations which are beyond the scope of traditional BO.

The exact non-adiabatic equations are difficult to solve and one must therefore resort to approximation techniques. A promising method of incorporating non-adiabatic effects rather than solving the complicated exact electronic equation is to choose the electronic wavefunction to be an eigenstate of the sum of the electronic Hamiltonian and an optimised effective local potential.

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Molecular Simulation to Accelerate Discovery of αVβ6 Integrin Inhibitors

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Idiopathic pulmonary fibrosis (IPF), a chronic disease characterised by progressive scarring of the lungs, has a survival rate of two to four years upon diagnosis [1]. With increasing incidences of IPF each year, the urgent need for new treatment motivates research into antagonists of the RGD binding integrin, αVβ6, a protein linked to the initiation and progression of IPF. All-atom molecular dynamics (MD) simulations provide an understanding of how the dynamic changes of active site residues in αVβ6 contribute to ligand binding. In order to perform MD simulations of potential antagonists using the CHARMM force field [2], parameters for new atom types have been developed and validated by comparison with target data calculated at the MP2/6-31G* level of theory.

MD simulations of αVβ6 in complex with its natural ligand, pro-TGF-β1, show a bidentate Arg-Asp interaction between the ligand and the receptor. There is also a metal chelate interaction between an aspartate on the ligand and a Mg^{2+} ion in the active site. These interactions are typical of RGD binding ligands. Additional binding site interactions, which are not observed in the static crystal structure [3], are identified. This demonstrates how MD simulations can help identify active site residues to target when designing antagonistic compounds. Our interest focuses on how these interactions compare with those of an RGD mimetic. This mimetic serves as a framework for a series of potential αVβ6 antagonists [4]. Starting from docked complexes [5], MD simulations have been performed for each of these compounds and the persistence of binding interactions compared with experimental pIC_{50} values [4].
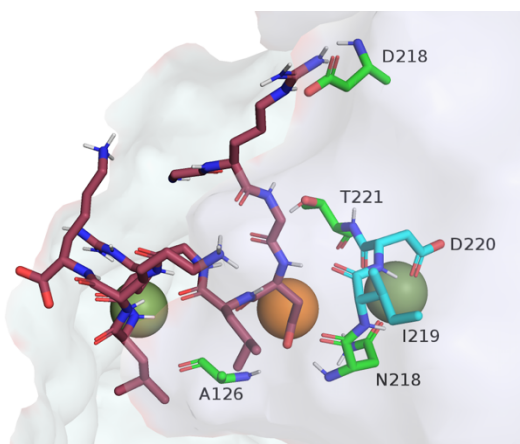

Figure: Active site residues that form interactions with pro-TGF-β1 (pink backbone) over a 50 ns MD simulation. Interacting residues in the crystal structure are shown in light green. Residues that are not shown as interacting in the crystal structure, but gain an interaction during MD are shown in light blue. The Mg^{2+} MIDAS ion is shown in orange and Ca^{2+} ions are shown in dark green.

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On the formation of urea in the ISM

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The interstellar medium (ISM) contains vast dust clouds, some of which are incredibly chemically diverse. The dust grains in such clouds are covered by ices made up from a range of small species, including H_2O, CO, H_2CO, CO_2, MeOH, CH_4 and NH_3. These ices photodissociate into radicals which undergo reactions to form larger, more complex molecules. One such complex molecule is urea.

Urea can act as a precursor to pyrimidine base formation and so has implications for the prebiotic origins of life.[1] While it has yet to be detected in the ISM it has, however, been identified as a product of the famous Urey-Miller experiment of the 1950's as well as on the surface of meteorites.[2,3] Irradiation experiments involving mock ISM ices have found urea as a product but as yet the exact formation route is unknown.[4] We have used computational methods to try and elucidate the potential formation routes and have found radical-radical or charged species chemistry to be the most promising.

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Electron Transfer in Transition Metal Complexes

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Human-induced climate change in combination with the ongoing depletion of fossil fuels means there is an urgent requirement to find alternative and more sustainable ways to store and distribute energy. As solar radiation is one of the most abundant and inexhaustible energy sources available, it makes sense to use materials which utilize the power of the sun. In theory, an artificial photosynthesis system could be designed to mimic this natural phenomenon and synthesize fuel (either directly or as electricity).

During artificial photosynthesis, when a photon absorbs light the energy is transported to the reaction site via electron transfer (ET). This fundamental process is vital for the efficiency of artificial photosynthetic systems. Thus, we need to increase our understanding of ET in order to improve artificial photosynthetic systems, which can be achieved through external perturbation of the process, such as with IR photons.

Platinum trans-acetylide complexes, made up of a donor (D), a bridge (B), and an acceptor (A) unit, can be used to follow ET and help explore this concept of control and why it is possible.[1] By exciting acetylide bonds within these complexes, decay pathways between different electronic states can be altered leading to more desirable outcomes of ET after excitation.[2] Previous work carried out by the Weinstein and Meijer groups focused on donor-bridge-acceptor molecular triads such as PTZ-CH_2-Ph-CC-Pt-CC-NAP, where PTZ is the donor phenothiazine and NAP is the acceptor naphthalene-monoimide. Using theoretical calculations, such as time-dependent density functional theory (TD-DFT), this work will focus on how the excited state dynamics have been understood in these complexes and the assignment of various different states upon excitation. As well as the identification of key normal modes in the system using non-adiabatic coupling calculations, and through the excitation of these modes show how the excited state dynamics can be influenced.

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Automatic Prediction and Characterisation of Complex Chemical Reactions

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The automated prediction and construction of catalytic reaction pathways has gained increasing interest over the past decade. However, despite the remarkable advances made in computational chemistry, the complete exploration of all possible reaction paths remains an outstanding challenge, with previous studies finding that such manual, exhaustive explorations to be largely error prone and generally unfeasible [1]. In this work, we employ a novel approach using stochastic graph-based methods to allow for the complete and automated sampling of the potential energy surface (PES) of chemical reactions involving the oxidation of carbon monoxide using Platinum-based catalysts. Using our conceptual knowledge of chemistry, we employ simple chemical heuristics to improve the efficiency of sampling chemical space by disregarding all chemically irrelevant elementary reactions. The development of such unbiased methods will allow for unprejudiced discoveries in molecular reactivity, with the potential to uncover previously unknown chemical intermediates and mechanisms. The catalytic oxidation of Carbon monoxide molecules over Platinum nanoparticle catalysts is investigated using the Large-scale Atomic/ Molecular Massively Parallel Simulator (LAMMPS) and the ReaxFF forcefield [2]. The results of these simulations will help to identify the complete dynamic process of reaction mechanisms, providing atomic scale insights in enumerating all chemically sensible reaction paths that give rise to carbon dioxide. This will in turn provide us with the necessary information to help inform a better strategy to optimise catalytic design in order to maximise product selectivity and increase the overall yield.
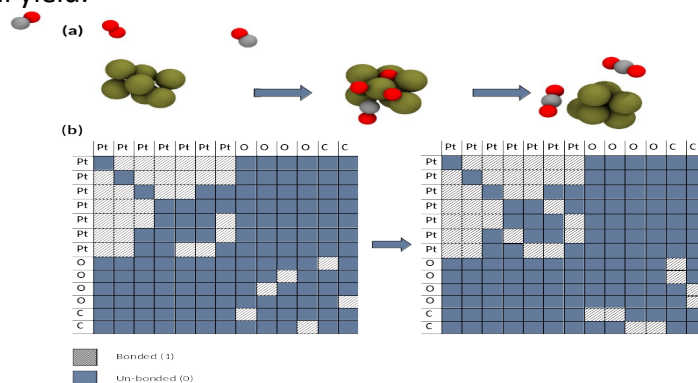

Fig 1. Schematic illustration of a graph-based reaction-path sampling simulation representing the catalytic oxidation of carbon monoxide over a platinum nanoparticle catalyst ($Pt_7 + 2CO + O_2 \rightarrow Pt_7 + 2CO_2$).

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Ab initio Relaxation Dynamics of Pentagonal Bipyramidal Dysprosium(III) Single Molecule Magnets

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The rapid pace of the development of single molecule magnets (SMMs) has resulted in a plethora of metal-based complexes with extraordinary magnetic properties. One benchmark of these properties is the maximum temperature at which magnetic hysteresis is observed (Blocking Temperature T_B) before relaxation of the molecular spin becomes too fast. For practical applications, a high value of T_B is desired. The design of SMMs has principally focussed on obtaining large energy barriers to magnetic relaxation (U_{eff}), which can be achieved following simple crystal field arguments [1,2], however little focus has been paid to the actual mechanism(s) of magnetic relaxation.

Two mechanisms operating in the temperature region around 77 K are the Orbach and Raman mechanisms. Both involve the coupling of the spin to molecular and lattice vibrations (phonons), and therefore investigating the structural links between vibrations and relaxation is key to guiding the future design of SMMs. Recently, a large value of T_B of 60 K was measured for $[Dy(Cp^{ttt})_2][B(C_6F_5)_4]$, with $Cp^{ttt} = \{C_5H_2{}^tBu_3\text{-}1,2,4\}$ [3]. Above 60 K relaxation was attributed to ring C-H vibrations facilitating an Orbach mechanism, and subsequent replacement of the ring hydrogens with heavier substituents disabled the C-H-mediated relaxation pathway resulting in even higher blocking temperatures [4,5].

Herein, we study the relaxation dynamics of hepta-coordinate Dy^{III} complexes $[Dy(OAr)_2(py)_5][BPh_4]$ (Ar = $CHCH_3C_6H_5$) (**1Λ, 1Δ**) (T_B = 23 K), and investigate their relaxation dynamics with reference to the structurally similar complex $[Dy(O^tBu)_2(py)_5][BPh_4]$ (**2**) (T_B = 14 K) [6]. We quantify the similarity of vibrations between dissimilar molecules using the Vibrational Projection analysis approach [7], to show that the O-Dy-O stretches are crucial in the Orbach regime, with the different energies of these modes resulting in faster or slower relaxation rates. Additionally, we see qualitative agreement with the experimental data, predicting faster relaxation of **1Λ, 1Δ** than **2** in the Orbach region (Fig. 1). Future work involves investigating the Raman relaxation process in order to explain the differences in blocking temperature between the two compounds.
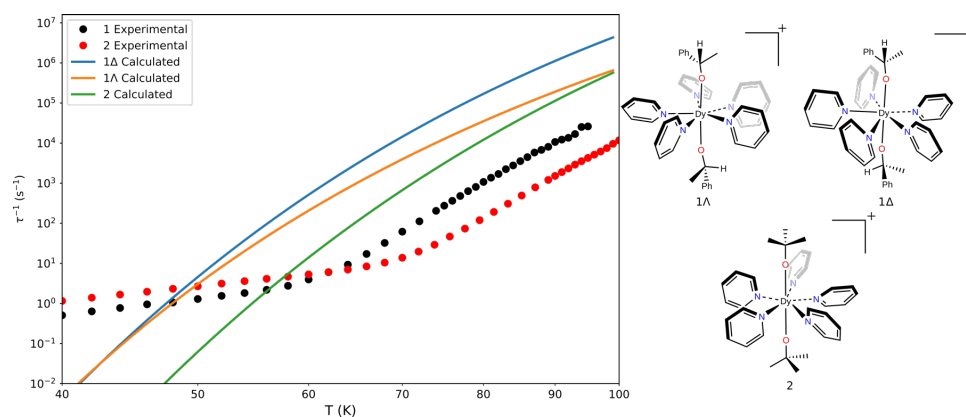

Fig. 1 Left - *Ab initio* and experimental relaxation rate data for **1Λ , 1Δ** and **2**. Right – structures of **1Λ , 1Δ** and **2** from X-ray Crystallography

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Computational Studies of Incorporation of Pu and Ce into Ceramic Matrices Such as Zirconolite

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Solutions to the long-term storage of highly radioactive waste products, formed through the nuclear cycle, are required to allow for the continued safe use of nuclear energy. The long-term solution for the storage of highly radioactive waste must be stable and be able to withstand radiation damage, without destructive changes occurring in structural composition. Various forms of solid storage devices have been considered – such as glasses and ceramics which allow for the immobilisation of radioactive materials.

The ceramic zirconolite ($CaZrTi_2O_7$) has been the focus of experimental research for several decades and its candidacy as a potential nuclear waste-form has developed over time, with experimental evidence of the system's long-term damage response to radioactive decay considered. Naturally occurring zirconolite has been found to contain actinides, such as uranium and plutonium, substituted onto the cationic sites. In this work, computational chemistry in the form of the Periodic Electrostatic Embedded Cluster Method (PEECM), utilising Density Functional Theory (DFT) and hybrid DFT, has been employed to determine the changes to zironolite-2M (Fig. 1) upon substitution of early actinides and cerium into the zirconolite lattice. Zirconolite is able to accommodate actinides on its Zr^{4+} and Ca^{2+} sites, with cations (Fe^{3+}, Mg^{2+}, Al^{3+}) able to be substituted onto the Ti-site for charge balancing.

The calculated band gap – determined via a Projected Density of States (PDOS) – shows good agreement with experimental literature and also shows agreement with previous computational and experimental work regarding the composition of the valence and conduction bands. Energy states of f-orbitals are introduced to the PDOS following substitution and the relative energies of these states stabilise across the actinide series.

Strong correlations have been found between the substitution energy of actinides (and Fe^{3+} when required for charge balancing) and the ratio of ionic radii of the substituent and substituted ions for both Zr- and Ca-substituted systems. Pu^{4+} and Ce^{4+} substitution energies are similar, potentially justifying the use of Ce as a non-radioactive surrogate for Pu in isovalent substitutions. Double substitutions were also calculated, with similarly strong correlations found between these two parameters.

Further work will involve understanding the presence of reduced or oxidised actinides in some calculated systems. Also to this, any differences caused by changing the charge balancing species will be examined.
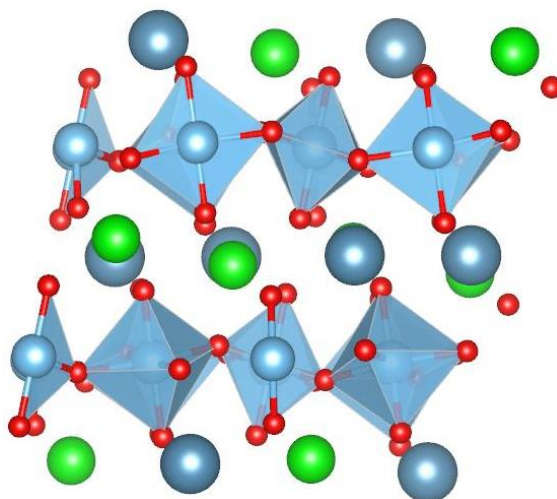

Figure 1: The 88-atom unit cell of zirconolite 2M. Dark Blue – Ca, Green – Zr, Light Blue – Ti, Red – O.

Modelling Electrostatic Cohesion of Pharmaceutical Powders

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Respiratory diseases, such as chronic obstructive pulmonary disease (COPD) and asthma, continue to affect the health of hundreds of millions of people worldwide. Treatment of these diseases is generally performed via direct inhalation of the drug molecule, with newer devices using the aerosolisation of dry powders.

The pharmaceutical powders used for aerosolisation techniques are generally composed of both carrier particles (usually lactose) and the active pharmaceutical ingredients (APIs), with both components being dielectric materials. The dielectric nature of these materials leads to the accumulation of bipolar electrostatic charges due to triboelectric charging via particle-particle and particle-wall collisions during the blending process.

The bipolar charge within the powder may lead to an unwelcome aggregation of the powder particles while also having an effect on the homogeneity of the blend which could be positive (contributing to the formation of an ordered mixture) or negative (poor mixing of the components). Following aerosolisation the charge may also have a positive effect, with the electrostatics improving the deposition of fine aerosol particles within the lungs.

In this presentation it is shown how recently developed theory on electrostatic interactions between charged, dielectric materials can be used to identify patterns of behaviour taking place during the aeroionisation of dielectric powders.

The electrostatic model used in this work was proposed by Lindgren et al. in 2018,[1] and is a generalisation of the solution, proposed in 2010 by Bichoutskaia et al.,[2] to the problem of accurately calculating the electrostatic interactions between charged spheres of dielectric materials. The model considers interactions between an arbitrary number of spheres of arbitrary size, charge, position and dielectric constant, embedded in a homogeneous dielectric medium. The solution accounts for the mutual polarisation of surface charge density on each sphere due to the presence of external charges.

In this work, we employ molecular dynamics techniques[3] that include a polarisable electrostatic force-field to run simulations which investigate the effects of bipolar charge on the interactions present in aerosolised pharmaceutical powders. A variety of systems have been studied, ranging from the simple case of predicting the outcome of a collision between two oppositely charged bodies, to more complex problems such as investigating the charge scavenging of a bipolar cloud of particles by a larger charged particle.

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Studying covalency in transition metal and actinide complexes using DMRG-CASSCF

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Covalency in actinide (An) complexes has been a subject of intensive research over the past few decades, owing mainly to its decisive influence on properties and reactivity [1–3]. In particular, the involvement of 5f orbitals in An-ligand bonding – either by orbital overlap or via accidental degeneracy [4] – has important consequences for the magnetic properties of these compounds [5].

As electron-electron repulsion and spin-orbit coupling (SOC) have similar orders of magnitude in f-block elements [5], both effects need to be accounted for at the same level of theory. In lanthanide complexes, this is achieved by a Complete Active Space Self-Consistent Field (CASSCF) calculation, followed by the addition of SOC via State Interaction (SI). The chosen active space is usually a minimal n in 7 to represent the $4f^n$ configuration, as 4f orbitals are too contracted to participate in metal-ligand bonding.

In contrast, bonding in An complexes involves the 5f, 6d and 7s orbitals and these must be included in the active space to correctly represent the electronic states. Their inclusion makes the exponentially-scaling CASSCF (as well as Restricted Active Space Self-Consistent Field – RASSCF) intractable for high-quality electronic structures. Going towards the calculation of hyperfine coupling as a probe for covalency [6], spin polarisation needs to be accounted for by correlating core electrons, further increasing the size of the active space.

Therefore, we are exploring the use of a Density Matrix Renormalisation Group (DMRG) variant of CASSCF (henceforth referred to as DMRGSCF) that allows the use of large active spaces at reduced computational cost compared to conventional CASSCF [7–9]. We start by examining the performance and accuracy of DMRGSCF for well-studied 3d complexes where the d-orbitals are heavily involved in bonding, such as vanadyl acetylacetonate (VO(acac)$_2$). The DMRGSCF results are assessed by comparison with CASSCF and experimental data. Following this, we apply the same strategy to structurally similar An compounds.

We find good agreement between CASSCF and DMRGSCF calculations with the same active space, however care must be taken when setting the DMRG-specific parameters (e.g. maximum bond dimension, number of sweeps) to ensure convergence.

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Modelling Conjugated Polymers containing Diketopyrrolopyrrole and Thiophene

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Semiconducting polymers have a great potential in organic solar cells, printed electronic circuits and organic light-emitting diodes, due to their sustainability and low density. Over the past two decades, the performance of semiconductor devices has improved and a wide range of molecular structures have been investigated. However, a major limitation in transport properties, arising from conformational and energetic disorder, is still to be addressed. For most polymeric organic semiconductors, the weak intermolecular van der Waals forces inherently cause low charge carrier mobility; increasing the local order leads to greater charge mobility. Several donor–acceptor co-polymers in less ordered microstructures have been found with unexpectedly high charge mobilities. These novel high-mobility amorphous conjugated polymers suggest that not all the factors to make a good polymeric semiconductor have been identified clearly. Alongside experiment, theory and computational approaches can provide insights into structure-property relationships in semiconducting polymers. In our work, we present computational studies on two prototypical amorphous polymers which include diketopyrrolopyrrole (DPP) and thiophene units called thieno[3,2-b]thiophene-diketopyrrolopyrrole with thiophene copolymer (TT-DPP) and poly-diketopyrrolopyrrole-bithienothiophene (PDPP-BTT). The DPP units have strong intermolecular donor−acceptor interactions, which can promote self-assembly of the polymer and enhance the charge transport. Recent studies have shown that the incorporation of DPP into oligothiophene or polythiophene backbone results in low band gap conjugated systems exhibiting high efficiency for photovoltaic devices. We have optimised force fields using ab initio forces calculated from trajectories of classical molecular dynamic simulations. We have sampled the equilibrium structures and use these to evaluate the microscopic structure in bulk, the density of states, the localization length, and the correlation between electronic and structural features of the two polymers. Our results provide guidance that is suitable for any polymer of the same type and may form the basis to establish more rigorously the structure−property relation in these materials.

Towards understanding the role of lead-based modifiers in rocket propellants

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Lead-based compounds, such as lead salicylate, are commonly used additives in double base rocket propellants containing nitroglycerin and nitrocellulose mixtures, where they are attributed with generating a steady fuel burn rate. European legislation seeks to restrict the use of lead in propellants due to land and wildlife contamination, and to minimise health risks to personnel handling and operating propellants. However, as the behaviour of lead-based additives within the propellant system is poorly understood, and attempts to simply replace the lead with other materials has met with limited success, there is now a need for a fundamental investigation into the effects of lead-based compounds on the chemical reactivity of double base rocket propellants.

This research thus aims to establish whether lead oxide (α-PbO and β-PbO$_2$) can provide catalytically active surfaces for the binding of nitroglycerin compared to tin oxide (SnO$_2$), which in contrast shows only modest catalytic function as a ballistic modifier.

The bulk electronic structure of each system has been deduced, and the most stable surface identified, to which a nitroglycerin molecule was attached in a binding study. The optimised structures have been extensively analysed, with outcomes focusing on adsorption energies and changes in electronic band structure diagrams. Results thus far indicate preferential binding of nitroglycerin to the PbO$_2$ surface versus the PbO surface. This is due to nitroglycerin binding to Pb and O vacancies exposed on the PbO$_2$ surface allowing for bond formation. In contrast, the inert and diffuse Pb lone pair located on the PbO surface prevents approach of the molecule so that only long-range interactions form.

This work has made use of the ab initio CRYSTAL17 code, with the range separated hybrid HSE06 functional and localised basis sets utilised alongside the Grimme D3 dispersion correction scheme. Future work intends to study a metallic Pb surface, and other lead-free modifiers to provide fundamental insight in the search for a non-toxic replacement.
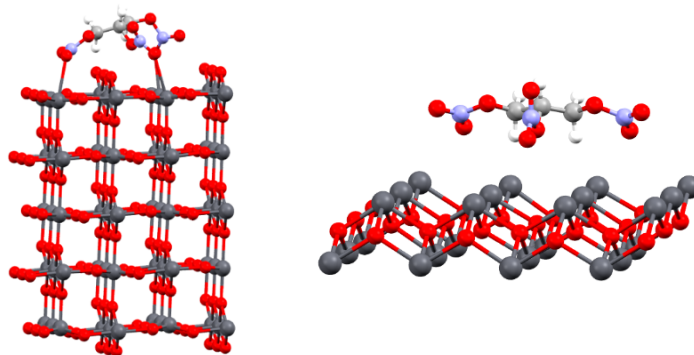
Optimised adsorption structures; Nitroglycerin bound to PbO$_2$ (left) and PbO (right) in the most stable adsorption mode.

Creating Versatile Photoswitches: Shedding Light on Design Parameters of Hemithioindigos

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The ability to reversibly modify the properties of a material in response to external stimuli is fundamental for the design of novel functional materials. Being able to manufacture and control this ability at the molecular level could lead to the realization of the next generation of nanomaterials for sensors and optoelectronics. Achieving an understanding of how chemical modifications can be used to augment or even inhibit switching will enable intuitive component design for the fabrication of tailor-made, light responsive materials and interfaces. An emerging class of photoswitching molecules Hemithioindigos (HTIs) exhibit promising photoisomerization properties which can be tuned through means of chemical functionalization. [1] Here we present a joint first-principles-based computational and spectroscopic experimental study, wherein we identify the key design parameters of HTIs that enable its switching capabilities. We investigate how these parameters are modified through the influence of functional groups. On the basis of our findings, we propose molecules with a propensity for successful switching for different applications.

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INVESTIGATING THE AUTOXIDATION ACCELERATING REACTIONS OF PEROXIDES AND PEROXYL RADICALS USING QUANTUM CHEMISTRY CALCULATIONS
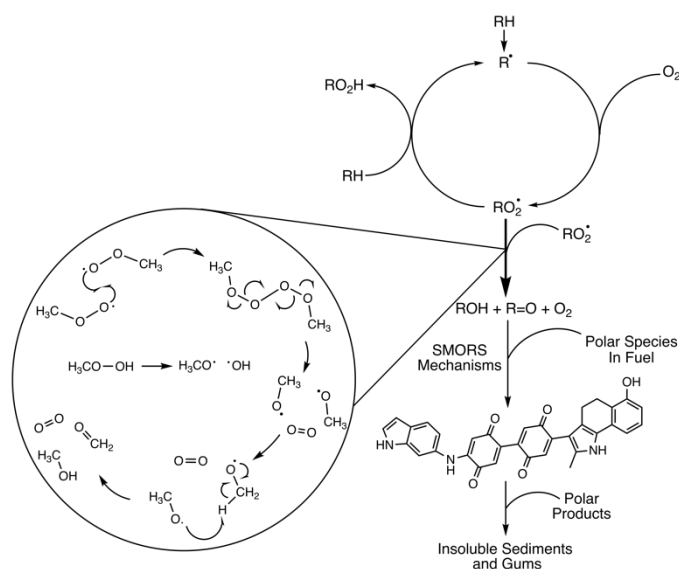
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Increases in performance and operating temperatures of jet engines has lead to the fuel being used as a coolant to remove this excess heat. As a consequence the fuel becomes thermally stressed, and undergoes autoxidation through radical reaction pathways, causing the formation of insoluble gums. Novel fuels appearing on the market, means the importance of a fuels chemistry on its thermal stability is becoming critical. This work presents a fundamental and chemically detailed approach to this problem.

The autoxidation process occurs through radical reaction mechanisms. This presents a challenge, in particular when modelling them using quantum chemistry techniques. This is particularly true for the reactions of peroxide species which link the initial oxidation process to the deposition steps. The propensity to conserve overall electronic spin angular momentum during reactions, means that high level multi-reference methods are required to properly describe them.

Multi-reference self consistent field theory calculations with second-order Rayleigh-Schrödinger perturbation corrections applied (CASPT2) were carried out to investigate the self-reaction of peroxides and peroxyl radicals. These calculations demonstrate that the reactions are intrinsically multi-reference and involve open shell bi-radicals. These reactions follow non-concerted reaction pathways which are energetically more favourable than the corresponding homolytic fission of peroxides and proceed towards the formation of oxidation product. From our calculations, the self reaction of peroxyl radicals, also appears to lead to the formation highly reactive singlet oxygen as a product. Singlet oxygen will accelerate the autoxidation of fuel by reacting directly with the hydrocarbons, acting as the initiation step.

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Identifying Conical Intersections using TDDFT

Max Winslow, David Robinson

At a conical intersection two or more electronic states become degenerate allowing a molecule in an excited state to relax via radiationless decay. The degeneracy of the surfaces cause the Born-Oppenheimer approximation to break down, therefore, CASSCF is commonly used to identify conical intersection geometries, however it is a computationally expensive method. This work looks at comparing geometries at the conical intersection obtained from CASSCF with those obtained from TDDFT approaches. These approaches can then be used to design and identify molecules that utilise the aggregated induced emission effect to be used as fluorescent probes.

Aromaticity; Anti-Aromaticity; and Chemical Boning from Magnetic Shielding Calculations

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The local and global magnetic properties were evaluated by means of one-, two-, and three-dimensional grids of points (ghost atoms) as probes of the local isotropic chemical shielding. The work is dedicated to assessing the aromaticity/antiaromaticity and/or the magnetic behaviour about the bonds of some 1,3-dipolar hypervalent molecules; (S0; S1; S2; and T1) naphthalene; azulene, anthracene, phenanthrene, some cyclic oxocarbon dianions, pyrazine, triazine, and S2N2.

Obtaining the visualised results as 2D magnetic shielding maps and the 3D isosurfaces show the ability to recognise, for instance, the aromaticity degree of different electronic states of naphthalene as S2 > Gs > T1 > S1. Also, the bonds' magnetic features can be assessed, in an accurate manner, depending on the different type of 2D magnetic evaluations.

The work depended on the _off-nucleus_ NMR isotropic shielding σiso calculations, which first was introduced by Johnson and Bovey who employed it on the benzene molecule [1]. Since the aromaticity concept cannot be directly determined by experimental means, we employed the _off-nucleus_ isotropic shielding evaluation to assess the magnetic criterion of the mentioned molecules. The _off-nucleus_ shielding investigation can be used to examine the isotropic shielding σiso at any selected point of the molecular space. This work depended on employing multidimensional grids as one-dimensional line lies on the bonds; two-dimensional grid placed at different places and different orientations through the molecular space; and three-dimensional grid which immerses the whole molecular structure. Each point of the applied grids serves as an effective probe feeling the local isotropic shielding and then the total aromaticity[2-3], and magnetic profile of bonding[4].

Computationally, the complete active space self-consistent field (CASSCF) and the Møller–Plesset perturbation theory (MP2) methods have been performed by means of the Dalton[5] and Gaussian[6] program packages. The techniques include setting and calculating ghost-atoms as Consequently, the results can be visualised and represented as one, two or three dimensions.

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Investigating reaction dynamics using the Reaction Path Hamiltonian

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The Reaction Path Hamiltonian was first derived in 1980, by Miller, Handy and Adams [1]. They had derived a classical Hamiltonian for a reacting molecular system based on the principle that the reaction valley describes all mechanistic and dynamic steps accompanying a chemical reaction. By using the Reaction Path Hamiltonian, one can ideally get insight into qualitative features of reaction mechanism and reaction dynamics such as vibrationally adiabatic potential, energy dissipation during the reaction, and translational-vibrational energy transfer during the reaction. With respect to the project, the objective is to construct the Reaction Path Hamiltonian for a given reaction, using information obtained through a climbing image nudged elastic band calculation, in order to compare the kinetics with a more set in stone method; Transition State Theory. Once the Reaction Path Hamiltonian has been constructed using the Hessian, the rate of reaction of a given reaction can be investigated [2]. In order to do this an ensemble of trajectories that cross the dividing surface are obtained by sampling initial positions and momenta from the Boltzmann distribution on the dividing surface. Each initial condition is then propagated forward and backward in time using Hamilton's equations from the Reaction Path Hamiltonian and information can be gathered about the rate.

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Density functional correlation theories based on the Unsöld approximation

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We present Unsöld-W12 (UW12) an approximate method for including explicit correlation in density functional theory [1, 2]. The approximation has a similar form to second-order Møller–Plesset (MP2) theory, without the dependence on virtual orbitals. Therefore, unlike double hybrid functionals, the approximation does not suffer from poor basis set convergence and is fully self-consistent.

We showcase two exchange—correlation functionals based on this approach; XCH-BLYP- UW12 and fB-LYP-osUW12, demonstrating their performance for small systems. These functionals, among other advantages contain an exceptionally small amount of self-interaction error; the cause of many problems in density functional theory.

We also consider possible new functional forms for the approximation.

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Exchange-correlation functionals from the integration of density and wave function theories

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Accurate and reliable approximations for the exchange-correlation (xc) functional are critical to the success of density functional theory (DFT). One of the limitations of the most-widely used approximations is that it is difficult to systematically improve them. By contrast, approximations in wave function theory (WFT) lend themselves directly to systematic improvement, as they are constructed from many-body perturbation theory (MBPT). Our work integrates techniques from wave function theory into DFT, to develop approximations for the xc-potential that can be systematically improved.

In our work, we start with an energy difference which is a wave function-based expression, and a functional of a local potential. The minimizing potential of this energy difference is the Kohn-Sham (KS) potential from DFT; this draws the two theories (DFT and WFT) together [1]. This energy difference contains the fully-interacting wave function, which we must approximate to yield approximations for the KS potential. In theory, we could use any approximation for the wave function, such as the first-order Møller-Plesset wave function [2], to find the corresponding KS potential. However, the main emphasis of this talk concerns the construction of approximations for the interacting wave function, and thus the energy difference, using MBPT. Our model is based on a weakly-interacting wave function, whose zeroth-order term is represented by a class of Hamiltonians; minimizing the energy difference over this class of Hamiltonians yields a corresponding class of KS potentials. The aim is to make a judicious choice for the zeroth-order Hamiltonian such that the expansions for the interacting state and KS potential converge fast.

We consider the physical relationship between the second-order energy difference, and the correlation energy between the weakly-interacting and non-interacting states, to guide our choice of zeroth-order Hamiltonian [3]. Arguing that making the magnitude of correlation energy small will yield fast-converging expansions, we derive in a novel manner the exchange-only optimized effective potential. This choice constrains the correlation energy described above so it is not uncontrolled, but it does not minimize it. The main result of this work is a new KS potential containing exchange and correlation character to first-order, which is obtained by minimizing the magnitude of the second-order correlation energy.

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Evaluating the Role of Electrostatics in Lignin-degrading Peroxidases with QM/MM

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The biodegradation of lignin, a complex and highly recalcitrant biopolymer, involves radical mediated oxidative depolymerisation. This process is catalysed almost exclusively by heme peroxidase enzymes. It is believed that the ability to support high redox potentials is what confers this unique property. Here we apply QM/MM methodology to compute the one-electron redox potentials of a variety of heme peroxidase enzymes, including lignin peroxidase, manganese peroxidase versatile peroxidase. We aim to rationalise this property in terms of the enzyme structure, particularly the electrostatic environment. Currently our results correctly predict the experimentally characterised high redox potential of lignin peroxidase (1) relative to other peroxidases, however, attempts to understand the source of this difference suggest the need to rethink existing explanations involving the role of charged amino acids, and may have implications generally for interpreting electrostatic effects in electronic embedding calculations.
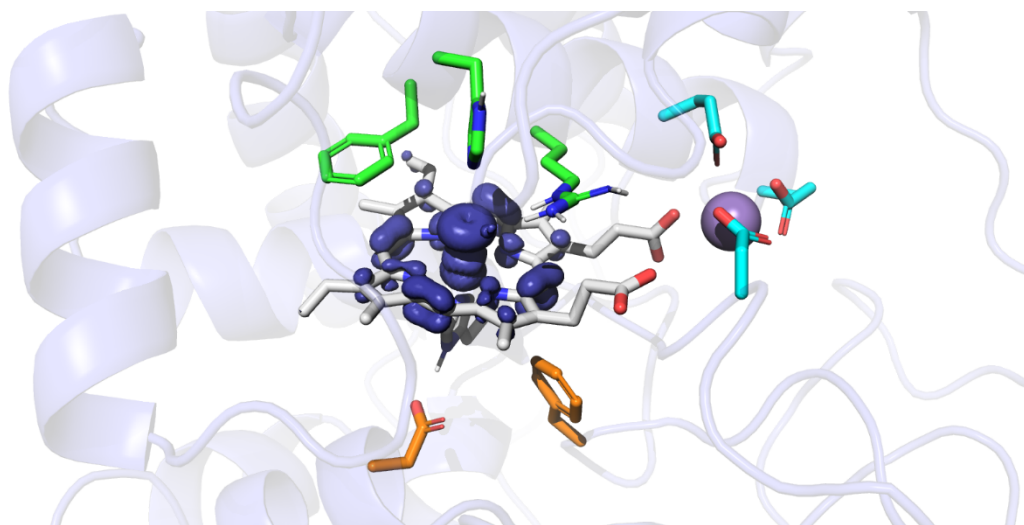
Figure 1; Minimised structure of the active oxidising species in manganese peroxidase, compound I, sampled from a classical molecular dynamics trajectory. Superimposed on the heme moiety (sticks) is the spin density, which is delocalised over the porphyrin ring, consistent with the expected cationic radical electronic structure.

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Adsorption of Uranyl(VI) on the Stoichiometric and Oxidised Mackinawite {001}-S Surface

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Uranium is a key element used in the nuclear power industry. It is important that we understand how it interacts with the environment in order to prevent and control its migration in the event of its accidental release. Uranium's speciation and mobility is significantly affected by its interaction with naturally occurring minerals. Using plane wave density functional theory, we model the interaction between the uranyl ion (U(VI)O_2^{2+}), coordinated by H_2O and OH^- ligands, with the iron sulfide mineral mackinawite in its pure form and two oxidised forms.

Our results show that for mononuclear uranyl complexes, outer-sphere and monodentate inner-sphere adsorption is most stable on the stoichiometric {001}-S surface. We observe an overall increase in adsorption energy for equivalent adsorption modes as stoichiometric mackinawite is oxidised. We also identify adsorption structures on oxidised mackinawite that match well with previously acquired EXAFS data, highlighting the predictive capability of theoretical calculations.[1]

Our results have implications for the use of mackinawite as a scavenger material for uranium and how the process is affected by exposure of mackinawite to oxygen from the air.
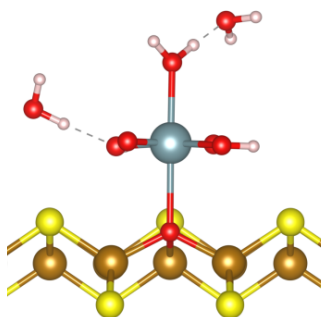
Monodentate coordination of the uranyl complex on the oxidised mackinawite {001}-S surface.

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