Total Energy and Force Methods

2018

9th – 11th January 2018

Selwyn College, Cambridge

Total Energy and Force Methods

The workshop focuses on the most recent developments in the field of electronic structure methods from the first-principles perspective, their diverse applications and mathematical foundations. It is organized within the “mini” series associated to the “Total Energies and Forces” conference, held at ICTP in Trieste every two years. While the Trieste conferences take place on odd-numbered years since 1987, the alternates are held on even-numbered years, each time in a different location. The previous most recent workshops of this series took place in Madrid (2000), Tenerife (2002), Paris (2004), Cambridge (2006), Bonn (2008), Shanghai (2010), Barcelona (2012), Lausanne (2014) and Luxembourg (2016).

The numerous approaches that are developed and used in the electronic-structure community provide the foundation for computing many physical and chemical properties of solids, liquids, and low-dimensional systems. However, there are numerous challenging applications for which the level of approximation is insufficient or where computational costs are prohibitive for accurate quantitative prediction of material properties. Therefore, continued efforts are devoted to an improvement of existing methods and the development of new methods.

The core areas for the conference are

(i) Theory and methods: Density-functional theory, time-dependent DFT, many-body techniques for real materials, quantum Monte Carlo, ab-initio molecular dynamics, large scale and multiscale simulations, quantum-chemistry methods, mathematical foundations and modern band theory.

(ii) Applications: nanoscience, biochemistry and biomaterials, magnetism and spintronics, geophysics, functional materials, surfaces, spectroscopies, catalysis and electrochemistry, chemical reactions and kinetics, materials design.

(iii) Data: high throughput computation, energy landscape sampling, data mining, machine learning, materials discovery and design.

Programme

	9th January 2018	**10th January 2018**	**11th January 2018**
08:30		*Coffee*	*Coffee*
		Session 1 - Chair : Mike Finnis	Session 1 – Chair : Richard Needs
09:00		Michele Ceriotti	Katarzyna Pernal
09:45	*Registration*	Eric Cancès	Andreas Grüneis
10:30	Welcome	*Coffee break*	*Coffee break*
	Session 1 – Chair : David Vanderbilt	Session 2 – Chair : Emilio Artacho	Session 2 – Chair : Chris Pickard
11:00	Bogdan Bernevig	Mariana Rossi	Michael Medvedev
11:45	Daan Frenkel	Motoko Kotani	Garnet Chan
12:30	*Lunch*	*Lunch*	*Lunch*
	Session 2 – Chair : Michiel Sprik	Session 3 – Chair : Gábor Csányi	
14:00	George Booth	Giuseppe Carleo	
14:45	Atsuto Seko	Kieron Burke	
15:30	*Coffee break*	*Coffee break*	
	Session 3 – Chair : Nicola Marzari	Session 4 – Chair : Mike Payne	
16:00	Luca Ghiringhelli	Fabio Pietrucci	
16:45	Gus Hart	Kristjan Haule	
19:00		*Drinks reception*	
19:30		*Workshop dinner*	

The workshop will be held in the Diamond Room in Selwyn College.
Coffee will be served in the Diamond Room and lunch will be served in the cafeteria.
The Reception will be in the New SCR, and Dinner will be served next door, in the Hall.

Talks

Tuesday **9th January 2018**

11:00 **Bogdan Bernevig (Princeton University)**

Topological Quantum Chemistry

The past decade has seen tremendous success in predicting and experimentally discovering distinct classes of topological insulators (TIs) and semimetals. We review the field and we propose an electronic band theory that highlights the link between topology and local chemical bonding, and combines this with the conventional band theory of electrons. Topological Quantum Chemistry is a description of the universal global properties of all possible band structures and materials, comprised of a graph theoretical description of momentum space and a dual group theoretical description in real space. We classify the possible band structures for all 230 crystal symmetry groups that arise from local atomic orbitals, and show which are topologically nontrivial. We show how our topological band theory sheds new light on known TIs, and demonstrate the power of our method to predict a plethora of new TIs.

11:45 **Daan Frenkel (University of Cambridge)**

Computing the Edwards Entropy: irrelevant for computational materials science?

In 1989, Sir Sam Edwards introduced the concept of `granular entropy', defined as the logarithm of the number of distinct packings of N granular particles in a fixed volume V. The proposal was rather controversial but much of the debate was sterile because the granular entropy could not even be computed for systems as small as 20 particles - hardly a good approximation for the thermodynamic limit.

In my talk I will describe how, using a novel algorithm, granular entropies of much larger systems can now be computed. This is of course nice, but most materials scientists can survive quite well without ever having to worry about granular entropy...

However, it turns out that the same new numerical tool enables numerical predictions that can be of considerable interest for materials science.

14:00 **George Booth (King's College London)**

Data-driven wavefunctions for electronic structure

The wavefunction is a 3N dimensional object containing all the information about the electronic structure and properties of the system. Wavefunction parameterizations of electronic structure generally sacrifice this full exponential flexibility (and thus accuracy) to allow for tractable computation of a small, polynomially-complex representation of the state. Here, we discuss a new approach we are developing, whereby an exact wavefunction parameterization underpins a data-driven description of a wave function, allowing systematic improvability with implicit exponential parameters and circumventing the difficult non-linear explicit optimization of parameters in standard (and approximate) wavefunction parameterizations. This data represents a subset of N-electron coordinate configurations and their associated probability amplitudes, which gives rise to extensive, well-defined wavefunctions in the thermodynamic limit. This is applied initially to lattice models, and we will discuss possibilities for the future.

14:45 **Atsuto Seko (Kyoto University)**

Linearized machine learning interatomic potentials for metals and recommender system for the discovery of unknown materials

Our applications of machine learning to materials data will be shown. The first application is the construction of machine learning interatomic potentials (MLIPs). MLIP based on a large dataset obtained by density functional theory (DFT) calculation has great potential for improving the accuracy and transferability effectively. Therefore the MLIP has also been increasingly applied to a wide range of materials regardless of their type of chemical bonding. In this study, accurate MLIPs of 31 elemental metals using linearized MLIP frameworks will be shown [1].

The second application is the prediction of the relevance of chemical compositions where stable crystals can be formed, i.e., chemically relevant compositions (CRCs) [2]. Herein we adopt recommender system approaches to estimate CRCs. This approach significantly accelerates the discovery of currently unknown CRCs that are not present in the training database.

[1] A. Seko et al., Phys. Rev. B 90, 024101 (2014), A. Seko et al., Phys. Rev. B 92, 054113 (2015). A. Takahashi, A. Seko and I. Tanaka, Phys. Rev. Mater. 1, 063801 (2017). A. Takahashi, A. Seko and I. Tanaka, arXiv: 1710.05677.

[2] A. Seko et al., arXiv:1711.06387, A. Seko et al., arXiv:1710.00659, A. Seko et al., Phys. Rev. B 95, 144110 (2017).

16:00 **Luca Ghiringhelli (FHI Berlin)**

SISSO: a compressed-sensing method for systematically identifying efficient physical models of materials properties

The lack of reliable methods for identifying descriptors — the set of parameters capturing the underlying mechanism of a materials property — is one of the factors hindering efficient materials development. Here, we propose a systematic approach for discovering physically interpretable descriptors and predictive models, within the framework of compressed-sensing based dimensionality reduction. SISSO (sure independence screening and sparsifying operator) tackles immense and correlated features-spaces, and converges to the optimal solution from a combination of features relevant to the materials' property of interest. The methodology is benchmarked with the quantitative prediction of the ground-state enthalpies of octet binary materials (using ab initio data) and applied to the showcase example of predicting the metal-insulator classification (with experimental data). Accurate predictive models are found in both cases. For the metal-insulator classification model, the interpretability and predictive capability are tested beyond the training data: It perfectly rediscovers the available pressure-induced insulator→metal transitions and it allows for the prediction of yet unknown transition candidates, ripe for experimental validation. Being a step forward with respect to previous model-identification methods, SISSO could become the long-sought enabler of rational materials development.

16:45 **Gus Hart (Brigham Young University)**

Adventures in k-point convergence

Computational materials discovery approaches, such as high throughput and machine learning, rely on accurate relative energies between competing crystal structures or different atomic configurations. Integration errors due to k-point grids are the largest source of DFT errors when computing relative energies. In the case of metals, k-point convergence is particularly slow due to the Fermi surface. Accuracy is very sensitive to the Fermi level approximation but not sensitive to band crossings (perhaps surprisingly). Smearing methods are only marginally useful, despite extensive efforts to improve them. I will review the special point methods and smearing approaches that have been developed to speed convergence and describe a research program for significant improvement of band integration for metals.

Wednesday 10th January 2018

09:00 **Michele Ceriotti (EPFL)**

A Generally-Applicable Machine-Learning Scheme for Materials and Molecules

Determining the stability of molecules and condensed phases is the cornerstone of atomistic modelling, underpinning our understanding of chemical and materials properties and transformations. I will show that a machine-learning model, based on a local description of chemical environments and Bayesian statistical learning, provides a unified framework to predict atomic-scale properties. It captures the quantum mechanical effects governing the complex surface reconstructions of silicon, predicts the stability of different classes of molecules with chemical accuracy, and distinguishes active and inactive protein ligands with more than 99% reliability. The universality and the systematic nature of this framework provides new insight into the potential energy surface of materials and molecules. I will also discuss how the method can be extended to yield a "symmetry-adapted" Gaussian process regression approach that is capable of learning tensorial properties without the need of defining explicitly a local reference frame.

09:45 **Eric Cancès (École des Ponts – ParisTech)**

Error estimators for first-principle total energy calculation

The error between the computed value of a given physical quantity of interest (QOI), e.g. the dissociation energy of a molecule, and the exact one, has several origins: a model error (resulting from the choice of a non-extremely accurate, but computationally tractable, model, e.g. Kohn-Sham with B3LYP functional), a discretization error (resulting from the choice of a finite basis set), an algorithmic error (due to the choice of stopping criteria in Self-Consistent Field and other iterative algorithms), an implementation error (due to possible bugs or inappropriate data structures giving rise to uncontrolled round-off errors), a computing error (due to random hardware failures such as miswritten or misread bits).
Quantifying these different sources of errors is key for two reasons. First, guaranteed estimates on these five components of the error would allow one to supplement the computed value of the observable returned by the numerical simulation with guaranteed error bars. Second, they would allow one to choose the parameters of the simulation

(approximate model, discretization parameters, algorithm and stopping criteria, data structures, etc.) in an optimal way in order to minimize the computational effort required to reach the target accuracy (error balancing).
In this talk, I will present recent results on the analysis of discretization and algorithmic errors, and on balancing between these two sources of errors. I will also present preliminary works on the mathematical analysis of discretization error cancellation, on which electronic structure calculation heavily relies.

11:00 **Mariana Rossi (FHI Berlin)**

Anharmonic and quantum effects in (bio)organic systems with first-principles accuracy

Bio-organic materials are desirable tools for the use in technological and medicinal applications due to their abundance, low cost, low toxicity, and ease of fabrication. These systems, however, present an immense challenge for theoretical modelling due to the large conformational space they can explore at finite temperatures and the inherent anharmonicity of their intra and intermolecular interactions. Moreover, the presence of light atoms in organic components increases the importance of nuclear quantum effects.
In this talk, I will discuss our recent efforts in order to address the challenges mentioned above, all of them based on density functional theory and molecular dynamics calculations. I will discuss the challenges in exploring the conformational space of organic/inorganic interfaces and discuss our recent methodological developments within the field of path integral molecular dynamics — a theory that allows the simulation of the quantum nature of nuclei in high-dimensional systems. These developments, associated with a recent implementation of electric response within the framework of density functional perturbation theory in the FHI-aims code and molecular dynamics simulations also allows us to obtain vibrational spectroscopic signals for periodic systems, including anharmonicities.

11:45 **Motoko Kotani (Tohoku University)**

Mathematical challenges for materials design

New approaches for materials development is expected in the digitalized society. Information science and date science would be useful tools for smart design. Materials are however rather complicated system. We need deep understanding of the relation between structures and functions. I would like to discuss some emergent results for materials design by applying advanced mathematical concepts.

14:00 **Giuseppe Carleo (ETH Zürich)**

Machine learning methods for quantum many-body physics

Machine-learning-based approaches are being increasingly adopted in a wide variety of domains, and very recently their effectiveness has been demonstrated also for many-body physics [1-4]. In this talk I will present recent applications to quantum physics.
First, I will discuss how a systematic machine learning of the many-body wave-function can be realized. This goal has been achieved in [1], introducing a variational representation of quantum states based on artificial neural networks. In conjunction with Monte Carlo schemes, this representation can be used to study both ground-state and unitary dynamics, with controlled accuracy. Moreover, I will show how a similar representation can be used to perform efficient Quantum State Tomography on highly-entangled states [5], previously inaccessible to state-of-the art tomographic approaches.
I will then briefly discuss, recent developments in quantum information theory, concerning the high representational power of neural-network quantum states.

[1] Carleo, and Troyer -- Science 355, 602 (2017).
[2] Carrasquilla, and Melko -- Nat. Physics doi:10.1038/nphys4035 (2017)
[3] Wang -- Phys. Rev. B 94, 195105 (2016)
[4] van Nieuwenburg, Liu, and Huber -- Nat. Physics doi:10.1038/nphys4037 (2017)
[5] Torlai, Mazzola, Carrasquilla, Troyer, Melko, and Carleo -- arXiv:1703.05334 (2017)

14:45 **Kieron Burke (UC Irvine)**

Recent developments in electronic structure from a DFT perspective

I will review some recent aspects of electronic structure theory from a DFT perspective. As DFT is used in more than 30,000 scientific publications each year, and has predicted both new catalysts and the world's highest temperature superconductors, there is tremendous value in trying to understand it, improve its performance, lower its computational cost, and expand its range of applicability. I will highlight some recent work from my group in each of these areas.

16:00 **Fabio Pietrucci (Université Pierre et Marie Curie)**

A general approach to the simulation of structural transformations in solids, liquids and nanostructures

We recently developed a distance metric able to differentiate structures belonging to different ordered or disordered forms of a material. We tested the approach on a number of crystalline polymorphs, amorphous forms and liquids over a range of ionic, covalent, metallic and molecular materials. We further employed the metric to build a two-dimensional space of collective variables, that in combination with enhanced sampling approaches (like metadynamics and umbrella sampling) allow to study structural transformations in a simple and general way. We demonstrated our methodology on several challenging transitions of water (TIP4P/2005 model), obtaining in particular the crystallization of liquid and amorphous water without supercooling – in fact, even above the melting temperature, i.e., in unfavorable thermodynamic conditions. Our approach may help bridging the gap between the rich information provided by crystal structure prediction tools and the poor understanding of viable kinetic routes for the synthesis of new materials.

S. Pipolo, M. Salanne, G. Ferlat, S. Klotz, A.M. Saitta, F. Pietrucci, Phys. Rev. Lett. (in press), arXiv 1703.00753
M. Fitzner, G.C. Sosso, F. Pietrucci, S. Pipolo, A. Michaelides, Nat. Commun. (in press)
F. Pietrucci, Rev. Phys. 2, 32 (2017)
F. Pietrucci and R. Martonak, J. Chem. Phys. 142, 104704 (2015)

16:45 **Kristjan Haule (Rutgers University)**

Structural predictions for correlated electron materials using functional dynamical mean field theory approach

Materials with strong electronic correlations have long resisted abinitio modelling due to their complexity arising from non-perturbative strength of the interaction. The Dynamical Mean Field Theory in combination with the Density Functional Theory has recently allowed accurate modelling of the electronic structure of many complex materials, such as the heavy fermions, transition metal oxides, iron superconductors, etc. The stationary implementation of the Dynamical Mean Field Theory functional [1,2] and its derivative [3] has been recently achieved, which allows one to predict forces for structural relaxation at finite temperature across the metal-insulator transition, and prediction of the coupling between magnetism and phonons at finite temperature. We will show how the electronic correlations enhance the electron-phonon coupling strength in FeSe[4], how the coupling of magnetism and crystal structure in rare earth nickelates leads to the metal insulator transition[5], and why is the BCC structures of elemental iron stable at high temperature[6].

[1] Kotliar, G. et.al. Electronic structure calculations with dynamical mean-field theory, Rev. Mod. Phys. 78, 865 (2006).
[2] Haule, K. and Birol, T., Free Energy from Stationary Implementation of the DFT+DMFT Functional, Phys. Rev. Lett. 115, 256402 (2015).
[3] Haule, K and Pascut G.L., Forces for structural optimizations in correlated materials within a DFT+embedded DMFT functional approach''. Phys. Rev. B 94, 195146 (2016).
[4] Mandal, S. and Cohen, R.E. and Haule, K., Strong pressure-dependent electron-phonon coupling in FeSe, Phys. Rev. B 89, 220502(R) (2014).
[5] Haule, K. and L. G. Pascut, Mott Transition and Magnetism in Rare Earth Nickelates and its Fingerprint on the X-ray Scattering, Scientific Reports 7, 10375 (2017).
[6] Han, Q. and Birol, T. and Haule K. The phonon softening due to melting of the ferromagnetic order in elemental iron'', arXiv:1705.06877.

09:00 Katarzyna Pernal (Lodz University of Technology)

Correlating electrons via adiabatic connection approach: a general formalism, approximations, and applications

Electronic systems are usually described by assuming a certain model capturing only partially electron correlation effects. To assure a quantitative description one faces a problem of accounting for electron correlation missed by the assumed model. Over years different approaches have been developed, the perturbative approach being one of the most often used. In my talk I will present another, fairly general, approach based on the adiabatic connection formalism. The idea itself is not novel but it has not been realized till recently that by combining the adiabatic connection (AC) with the extended random phase approximation one obtains a general tool capable of accounting for electron correlation in a broad class of multireference wavefunctions, even when electrons are strongly correlated. I will show that the AC-based approximation yields excellent results when applied to multireference models, exceeding in accuracy second-order perturbation-theory-based approximations.

09:45 Andreas Grüneis (MPI Stuttgart)

Recent progress in applying coupled cluster theories to ground and excited state properties of solids and surfaces

This presentation will review recent progress in applying periodic coupled cluster theories to the study of surfaces and solids. We will briefly discuss methods that reduce the computational cost and accelerate convergence of calculated properties towards the complete basis set as well as thermodynamic limit [1-4]. These recent developments have enabled an increasing number of ab-initio studies and allowed for assessing the accuracy of coupled cluster theories by comparing to experimental findings as well as quantum Monte Carlo results. The presented applications will include phase transitions of solids [5], molecular adsorption energies [6-7], hydrogen dissociation on silicon surfaces as well as ground and excited state studies of defects in solids.

[1] A. Grüneis, Phys. Rev. Lett. 115 066402 (2015).
[2] G. H. Booth, T. Tsatsoulis, G.K.L. Chan, A. Grüneis, J. Chem. Phys. 145 084111 (2016).
[3] K. Liao, A. Grüneis, J. Chem. Phys. 145 141102 (2016).
[4] F. Hummel, T. Tsatsoulis, A. Grüneis, J. Chem. Phys. 146 124105 (2017).
[5]. A. Grüneis, J. Chem. Phys. 143, 102817 (2015).
[6] T. Tsatsoulis, et al. , J. Chem. Phys. 146 204108 (2017).
[7] Y. S. Al-Hamdani, et al., J. Chem. Phys. 147, 044710 (2017).

11:00 Michael Medvedev (Russian Academy of Sciences)

Accuracy of DFT self-consistent electron densities

The theorems at the core of density functional theory (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density [1]. For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional.

We have examined the other side of the coin — the energy-minimizing electron densities for atomic species, as produced by more than a hundred DFT functionals [2]. Self-consistent electron densities produced by these functionals were compared to the CCSD-full ones by means of three local descriptors: electron density (RHO), its gradient norm (GRD) and its Laplacian (LR); aug-cc-pωCV5Z basis set was used for all calculations.

We have found that, reflecting theoretical advances, DFT functionals' densities became closer to the CCSD-full ones, until in the early 2000s this trend was reversed by flexible functionals with forms chosen to be suitable for empirical fitting.

During the year 2017, this result was extensively discussed in the scientific literature and significantly broadened [3-11].

[1] P. Hohenberg, W. Kohn, Inhomogeneous electron gas. Phys. Rev. 136, B864–B871 (1964).
[2] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, K. A. Lyssenko, Density functional theory is straying from the path toward the exact functional. Science. 355, 49–52 (2017).
[3] K. R. Brorsen, Y. Yang, M. V. Pak, S. Hammes-Schiffer, Is the Accuracy of Density Functional Theory for Atomization Energies and Densities in Bonding Regions Correlated? J. Phys. Chem. Lett. 8, 2076–2081 (2017).
[4] T. Gould, What Makes a Density Functional Approximation Good? Insights from the Left Fukui Function. J. Chem. Theory Comput. 13, 2373–2377 (2017).
[5] K. P. Kepp, Comment on "Density functional theory is straying from the path toward the exact functional." Science (2017).
[6] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, K. A. Lyssenko, Response to Comment on "Density functional theory is straying from the path toward the exact functional." Science. 356, 496–496 (2017).
[7] P. Verma, D. G. Truhlar, Can Kohn–Sham density functional theory predict accurate charge distributions for both single-reference and multi-reference molecules? Phys Chem Chem Phys. 19, 12898–12912 (2017).

[8] P. D. Mezei, G. I. Csonka, M. Kallay, Electron density errors and density-driven exchange-correlation energy errors in approximate density functional calculations. J. Chem. Theory Comput. (2017), doi:10.1021/acs.jctc.7b00550.
[9] I. Mayer, I. Pápai, I. Bakó, Á. Nagy, Conceptual Problem with Calculating Electron Densities in Finite Basis Density Functional Theory. J. Chem. Theory Comput. (2017), doi:10.1021/acs.jctc.7b00562.
[10] D. Hait, M. Head-Gordon, How accurate is density functional theory at predicting dipole moments? An assessment using a new database of 200 benchmark values. ArXiv170905075 Cond-Mat Physics (2017) (available at http://arxiv.org/abs/1709.05075).
[11] Y. Wang, X. Wang, D. G. Truhlar, X. He, How Well Can the M06 Suite of Functionals Describe the Electron Densities of Ne, Ne6+ and Ne8+? J. Chem. Theory Comput. (2017), doi:10.1021/acs.jctc.7b00865.

11:45 **Garnet Chan (Caltech)**

Predictive accuracy in the condensed phase

I will describe recent developments in diagrammatic methods aimed at reaching predictive accuracy in materials.
In particular I will describe coupled cluster theory for materials spectroscopy, and if time permits, its extension to finite temperature and non-equilibrium condensed phase phenomena.

Posters

Tuesday **9th January 2018**

Benjamin Ramberger

The random phase approximation (RPA) is a perturbational approach to evaluate the ground state energy of matter. It is growing popular recently as it describes many systems more realistically than density functional theory (DFT). However, in condensed matter simulations, forces beyond DFT have been rarely available, thus limiting the application of other methods like the RPA. Here we present our recent advances on the computation of interatomic forces in the RPA, including the work in PRL 118, 106403 (2017). There we show that the first derivative of the RPA energy with respect to the Green's function is the self-energy in the G0W0, which allows us to write compact equations for the RPA forces and calculate them efficiently. Furthermore, position dependent overlap operators are incorporated in the present framework, allowing us to implement the RPA forces in the projector augmented wave (PAW) formalism. We also sketch that our approach could be easily adapted for other methods like second-order Møller-Plesset (MP2) perturbation theory. Finally we give examples of recent applications, e.g. assesing the quality of different density functionals with RPA molecular dynamics [PRL 119, 145501 (2017)].

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Tobias Schäfer

Low-Complexity Algorithms for Ground State Energy Calculations in Second-order Møller-Plesset Perturbation Theory (MP2) in the Plane Wave Basis applied to 3D Periodic Materials

Hartree-Fock plus Second-order Møller-Plesset perturbation theory (HF+MP2) is a standard approach in materials physics and quantum chemistry to evaluate the energy of matter. However, this is computationally very demanding since conventional MP2 implementations scale with the fifth power of the system size, $O(N^5)$, and are difficult to parallelize. We present two low-complexity implementations that have a lower scaling and an almost ideal parallelization efficiency. The key concept of both approaches is to eliminate the summation over all combinations of occupied and unoccupied states, which can be elegantly achieved in the Laplace transformed MP2 formulation. In this way we attain a quartic scaling high performance algorithm, $O(N^4)$, in the plane-wave basis without introducing further approximations [1]. Moreover, using stochastic orbitals [2], a cubic scaling, $O(N^3)$, can be achieved when a fixed absolute error is assumed which turns into a linear scaling, $O(N^1)$, when only a fixed relative error is assumed (e.g. per atom). Analogously, the approaches could allow us to calculate second-order screened exchange as well as particle-hole ladder diagrams with a similar low complexity. Hence, the methods can be considered as a step towards systematically improved correlation energies.

[1] T. Schäfer, B. Ramberger, and G. Kresse, J. Chem. Phys. 146, 104101 (2017).
[2] D. Neuhauser, E. Rabani, and R. Baer, J. Chem. Theory Comput. 9, 24 (2013).

Matthew Evans

 # Crystal structure prediction for next-generation battery anodes
In this work, we perform high-throughput crystal structure prediction on materials that have great promise as alloying anodes for next-generation Li-, Na- and K-ion batteries, namely metal MxPy phosphide alloys. It is hoped that the unmanageable volume expansion that alloying anodes are notorious for can be designed away by rational choice of the metal M. Using ab initio random structure searching [1] and related methods, previous work on phosphorus anodes [2] is extended in an attempt to find such sustainable materials that exhibit manageable volume changes upon cycling. With particular emphasis on the K-Sn-P system, we show how novel ternary phases may contribute to the electrochemistry of the anode.

Ji Chen

Electron correlation in transition metal oxides has resulted in many intriguing phenomena. In this study we use quantum chemical correlation methods in conjunction with cluster embedding schemes to investigate the electronic structure of oxygen deficiency in TiO2 molecules and materials. We present the ground and low lying spin states in various TiO2 molecules and materials, and we discuss the electron correlation in these systems using different electronic structure methods including full configuration interaction quantum Monte Carlo, coupled cluster, multi reference configuration interaction and density functional theory.

Joseph Prentice

Investigating ferroelectric transitions in barium titanate using a vibrational self-consistent field method

Barium titanate is the prototypical ferroelectric ceramic material, but the nature of the transitions between the various ferroelectric phases and the cubic non-ferroelectric phase is still under debate, with both displacive and order-disorder models proposed. The work presented here approaches this topic from a vibrational perspective, using a vibrational self-consistent field (VSCF) method to obtain a description of the vibrational wavefunction of this material from first principles. Our results are in qualitative agreement with experiment, demonstrating the utility of applying the VSCF method to this problem, but further effects must be included to describe these transitions quantitatively.

Lorenzo Monacelli

Self-Consistent-Harmonic-Approximation (SCHA) is a powerful tool to investigate solid systems affected by strong anharmonicities. Recently it has been exploited in many applications, from superconducting hydrates to ferroelectric materials, with astonishing results. However, due to the computational cost of calculating forces on the great number of configurations required, SCHA was limited to high symmetric phases. Here, I show how to improve the method in order to pull down the number of ab-initio calculation needed to achieve the convergence of the algorithm. Thanks to this enhancement, it is possible for the first time to apply SCHA to low symmetric systems, relaxing both all the internal degrees of freedom and the unit cell. This paves the way for the study of anharmonic effects in molecular crystals. I will show SCHA results on the XI phase of ice, and elucidate the role played by anharmonicities in the volume expansion, phonon frequencies and atomic positions. Calculations are carried out both with an empirical Force-Field and through DFT with PBE exchange-correlation functional.

David Muñoz Ramo and John Robertson

Ab initio investigation of tunnelling magnetoresistance effects in the Co(0001)/h-BN/Co(0001) junction
Spin filtering junctions, which involve the tunneling magnetoresistance (TMR) effect in magnetic tunnel junctions (MTJs), hold great promise for future application in various devices like random access memories, sensors and logic circuits. MTJs are junctions consisting of two ferromagnetic electrodes separated by a nonmagnetic insulating spacer. The relative magnetization orientation of the electrodes determines the tunnelling current across the MTJ and leads to a large difference in resistance in the junction, which constitutes the TMR effect. The most well known example is the Fe/MgO/Fe MTJ, but other junctions with spacers like Al_2O_3 and ferromagnetic electrodes including metals like Co, or complex Heusler alloys have been investigated as well. More recently, 2D materials

like graphene or hexagonal boron nitride (h-BN) have been considered as spacers. The use of these materials for MTJs offers several advantages: sharp interfaces with the electrodes thanks to the absence of covalent bonds in that space, thermal stability and excellent control of the thickness. The use of these materials as spacers raises questions about the mechanisms that govern the appearance of the TMR effect in the corresponding heterojunctions, which are linked to the electronic structure of these 2D systems.

In this work, we study the Co/h-BN/Co magnetic tunnel junction by means of density functional theory calculations. We obtain the electronic structure of the heterojunction and calculate the tunnelling transmission coefficients and related magnetoresistance properties. Our calculations find that the valence band of h-BN is located about 1.7 eV below the Fermi level of the junction. As a result, we find a sharp increase in the tunneling magnetoresistance around that energy that mostly increases with the thickness of the h-BN layer. The sharpness of the TMR peak is related to changes in the complex band structure of h-BN at the edges of the Brillouin zone. Different configurations of h-BN over the Co (0001) surface yield slightly similar TMR peaks with one exception; in this particular case, a severe misalignment of the h-BN and Co (0001) surfaces induces a large TMR decrease, which becomes almost half of the value found for the most stable configuration.

Jacek Golebiowski

QM/MM hybrid simulations of critical failure at the interface in CNT/polymer nanocomposites

Functionalized carbon nanotube (CNT)/polymer composites have received significant interest as promising structural materials with applications in the most demanding areas of industry such as aerospace and ballistic protection. Developing a fundamental understanding of failure mechanisms at the CNT/polymer interface is essential to making better materials suited to a broader range of applications.

From a computational perspective, the problem is challenging because it is inherently multi-scale: the bond-breaking processes that occur at the polymer-CNT attachment and initiate failure involve quantum mechanical phenomena, yet the mechanisms by which external stresses are transferred through the disordered polymer occur on length and time-scales far in excess of anything that can be simulated quantum mechanically.

We address this issue by using a QM/MM hybrid approach where classical molecular dynamics (MM) is used to simulate the majority of the system, while regions of particular interest are investigated using quantum mechanical (QM) methods, taking advantage of their accuracy and transferability. The QM regions are selected automatically “on the fly” [1] as the hybrid simulation proceeds. We use this approach to investigate critical failure at a CNT-polymer interface, showing that it leads to qualitatively different results compared to a fully classical, forcefield-based approach.

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Bartomeu Monserrat and David Vanderbilt

Temperature effects in spin-orbit physics from first principles

The spin-orbit interaction drives a number of physical phenomena, including the band inversion in topological insulators and the spin splitting of electronic bands in inversion asymmetric crystals. In this work, we study the effects of finite temperature on such spin-orbit physics, including both thermal expansion and electron-phonon coupling effects [1]. First, we describe the temperature dependence of the inverted gap in topological insulators. We find that increasing temperature reduces the topological gap in the Bi_2Se_3 family of materials, and we predict a temperature-induced topological phase transition in Sb_2Se_3 [2]. Second, we study the temperature dependence of the spin splitting of electronic bands in both inversion symmetric and asymmetric crystals. We predict a dynamical spin splitting in centrosymmetric crystals and characterise the associated phenomenology in the cubic perovskite $CsPbCl_3$ [3]. In inversion asymmetric crystals, exemplified by the bismuth tellurohalides, we find that increasing temperature suppresses the static spin splitting arising from the Rashba effect [4].

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Fangyuan Gu

Simulation study of photo-induced phase transitions and coherent optical phonon generation in $BaTiO_3$

The effects of above band gap ultrafast optical excitation on the structural properties and lattice dynamics of the prototypical perovskite multiferroic, $BaTiO_3$, are investigated using a constrained density functional method (É. D. Murray et. al. PRB 72, 060301 (2005), P. Tangney and S. Fahy, PRB 65, 054302 (2002)). We calculated the dependences of phonon frequencies and structural stability on excited carrier density. Our work shows a reduction in 10odelling due to electrons being returned by O anions to Ti cations. At moderate excitation levels, this causes a decrease in polarization, a softening of several long wavelength optical phonons, and a lowering of local barriers to ferroelectric domain reversal. This indicates that a transient photo-induced lowering of both the coercive field and the phase transition temperature is possible. We suggest that pump probe spectroscopy could be used to induce a purely-displacive transition to a higher symmetry phase at low temperature and/or to generate and study the decay of coherent optical phonons. Our findings may also provide guidance to the design of optically controlled devices.

Eszter Székely

Development of Force Fields for Small Molecules

Machine Learning (ML) is applied to develop an accurate atomistic, quantum mechanical model for methane-water systems with the aim of modelling clathrates. Preliminary results for the interactions of water molecules are discussed. The final goal of the force field to be developed is to model the methane-water systems accurately. These systems are interesting both in industrial and environmental chemistry.

Wednesday 10th January 2018

Verena A. Neufeld and Alex J. W. Thom

Stochastic Coupled Cluster: Development and Excited States

We develop stochastic coupled cluster techniques and apply them to systems such as the uniform electron gas achieving high truncation levels. We have also started working on excited states stochastic coupled cluster.

The coupled cluster Monte Carlo (CCMC) algorithm we are using has been introduced in Ref. [4] based on the algorithm of full configuration interaction quantum Monte Carlo (FCIQMC) [2]. It is a stochastic sampling version of coupled cluster theory (see review [1]). New stochastic coupled cluster results on the 14 electron gas using up to coupled cluster up to quintuples (CCSDTQ5) have shown the need to go beyond coupled cluster singles and doubles (CCSD) (and possibly CCSDT) for good accuracy in the finite uniform electron gas [3].

We are now working on improving the *spawn* step in the algorithm where we connect different determinants and we will show some comparisons of different algorithms for the *spawn* step. We will also describe the algorithm for excited states stochastic coupled cluster.

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Vincent E. Sacksteder and K. Refson

Calculations of charge and spin susceptibilities and quasiparticle energy shifts within the CASTEP plane-wave DFT code.

CASTEP is a pseudopotential based plane wave code which scales to the largest supercomputers and offers a wide feature set, including ultrasoft pseudopotentials, hybrid functionals, DFT+U, noncollinear magnetism, NMR chemical shifts, excited state calculations, and structure searching and optimization. Within CASTEP we have implemented calculation of the charge and spin susceptibility tensor, which describes the system’s response to a perturbing charge or spin. The susceptibility can be measured experimentally, for instance in neutron scattering experiments observing magnons.

Within the RPA approximation, the susceptibility contains the physics of screening by particle-hole pairs, and therefore can be used to improve on LDA, GGA, or hybrid functional calculations. We present corrections to the Kohn-Sham energies obtained by using the susceptibility tensor to screen Hartree-Fock exchange. In the static limit this is the SEX part of the COHSEX approximation, and if instead the dynamic susceptibility is used one obtains the GW approximation.

We have implemented three ways of calculating the susceptibility: finite differences, the space-time method, and a density functional perturbation theory method incorporating a Sternheimer solver. The latter method's memory and CPU consumption scales linearly with the plane wave basis size, allowing thorough exploration of convergence with basis size, not only of the susceptibility itself, but of the SEX and GW quasiparticle shifts. This scaling also allows the susceptibility to be used as an alternative to traditional Pulay and Broyden forms of density mixing, with a similar computational cost. We emphasize that our calculations are heavily parallelized, in exactly the same way as a standard DFT ground state calculation.

This work will also allow first principles calculations of the screened potential, exchange coupling strengths, the KKR interaction, the Dzyaloshinskii-Moriya interaction, ionization potentials vs. electron affinities, and the Hubbard U used DFT+U and in DMFT.

Vincent E. Sacksteder

Transport in strongly correlated materials and in topological insulators

We report new theoretical results on the linear magnetoresistance seen in many materials including strongly correlated bad metals. We also report detailed predictions for transport experiments in topological insulators in the ballistic, diffusive, and perfectly conducting channel regimes.

Martin Schlegel

Making Existing Classical Forcefields More Reliable

Reliable forcefields are important for large-scale atomistic calculations. Even though they can reproduce the behaviour of materials over certain regimes of pressure, temperature or alloy composition, many classical forcefields fail to fully reproduce the experimental phase diagrams in wider regimes of interest. Using nested sampling [1-3] to sample the phase space of atomic systems, we have calculated phase diagrams for several forcefields found in the literature. Now, we aim to improve these forcefields by fitting them to experimental phase diagrams – potentially by first fitting to the DFT energies of representative sampled structures. In addition, we are exploring which other techniques for phase diagram calculation may aid in this process.

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Geneviève Dusson and Eric Cancès

Discretization error cancellation in electronic structure calculation: toward a quantitative study

In this poster, we present a study on discretization error cancellation, investigating the claim that energy differences are better approximated than energies themselves in quantum chemistry and first-principle simulation for condensed matter physics and materials science. We first report numerical simulations performed with Abinit on two simple chemical systems, the hydrogen molecule on the one hand, and a system consisting of two oxygen atoms and four hydrogen atoms on the other hand. We observe that errors on energy differences are indeed significantly smaller than errors on energies, but that these two quantities asymptotically converge at the same rate when the energy cut-off goes to infinity. We then analyze a simple one-dimensional periodic Schrödinger equation with Dirac potentials, for which analytic solutions are available. This allows us to explain the discretization error cancellation phenomenon on this test case with quantitative mathematical arguments.

Volker Deringer

From machine-learning potentials to materials chemistry

"Learning" from ab initio data, a novel class of interatomic potentials finds increasing use for materials modelling. With this poster I will present results enabled by such a potential that we developed recently, namely, a Gaussian approximation potential (GAP) model for liquid and amorphous carbon [PRB 95, 094203 (2017)]. First, we performed simulations of tetrahedral amorphous carbon (ta-C) surfaces, including their reconstruction and "graphitisation". Second, we showed how a GAP can be used for random structure searching, and so identified several hitherto unknown carbon allotropes. Our finger exercises hint towards long-term perspectives for the use of GAPs and other machine-learning-based potentials in materials chemistry.

Sanghamitra Mukhopadhyay

First principles modelling of neutron spectroscopy of hydrogen bonded organic ferroelectrics

Hydrogen bonded organic ferroelectrics are important both for fundamental chemical interests as well as for technological applications [1-2]. Neutron spectroscopy is used to understand these hydrogen bonded materials experimentally [3]. The static lattice dynamics are not often suitable to analyse these spectroscopic results, specially, where complex picosecond order dynamics are involved. In this work I will present our work on modelling of neutron spectroscopic results using first principles lattice and molecular dynamics.

We employed state-of-the-art calculations based on plane wave pseudo potential density functional theory to predict the structure of a number of organic molecular crystals, showed room temperature ferroelectricities as high as 30μC/cm^2 [2]. Comparing with in-house neutron diffractions we showed that application of Van-der Walls potentials were essential to predict the structure of these type of materials [4]. Inelastic neutron scattering (INS) spectrum was used to understand the nature of hydrogen bonds in these materials [5]. The quasielastic neutron spectrum (QENS) were calculated by analysing the trajectory of the molecular dynamical simulations and also compared with experiments [4]. Berry phase method was employed to calculate the spontaneous ferroelectric polarisations [5].

The motion of hydrogens was predicted from calculated of anisotrotropic displacement parameters (ADP) and compared with temperature dependent INS spectrum [5]. Two types of hydrogen bonds were identified from their distinctly different normal mode frequencies and compared well with INS spectrum [3-4]. From the correlation of temperature dependent ferroelectric polarisation along with ADP and temperature dependent crystalline structures of these materials, it was shown that the in-plane strains on hydrogen bonds were responsible for high ferroelectric polarisation of these organic solids.

We will discuss the modelling of neutron spectrum for understanding the motions of hydrogen ions. Further, the calculated Born effective charge tensors and polarisations obtained from Berry phase methods are analysed to understand the nature of dynamic charges and the origin of room temperature ferroelecticity.

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Stela Makri, James Kermode and Christoph Ortner

A Preconditioning scheme for Minimum Energy Path finding methods.

In transition state theory, the study of thermally activated transitions between energy minima relies on finding transition paths connecting the minima of a free energy landscape. These provide information about the energy barrier and reaction rates of the system without the need to go through long and expensive simulations. Current techniques use the principle of steepest descent minimisation which is slow for ill-conditioned potentials. To reduce the condition number of a potential and improve the convergence speed and robustness of these methods we propose a preconditioning scheme. The key assumption is that the cost of constructing a preconditioner is much smaller than the cost of computing the potential; for density functional theory the cost of single point evaluations is much more expensive than the computation of a preconditioner and thus the proposed approach improves computing times significantly. We have developed a local preconditioning scheme, where locality refers to the preconditioner acting as a coordinate transformation of the individual images along the path, and a global preconditioning scheme is currently in development, in which the entire path is preconditioned as one entity.

Punit Patel and James Kermode

Modelling Chemomechanical Materials Failure Processes in SiC and Diamond

Atomistic simulations of crack propagation are key to understanding the behaviour of materials. Cracks involve strong coupling across the scales, with bond breaking on the quantum scale driven by long range stress fields. Current QM methods have limited simulation sizes in comparison to the sizes required to adequately capture elastic effects. This limitation can be overcome by combining a QM description of the critical part of the system with a classical interatomic model sufficient to reproduce the elastic response [1]. This relies on insensitivity of QM forces to moving atoms far away, i.e. strong force locality. The overall goal is to further coarse grain to the continuum scale while maintaining the overall fracture dynamics.

Applications in covalently bonded single crystals to complex alloys are underway. Screened classical potentials [2] predict a brittle response in both silicon carbide (SiC) and diamond, giving confidence in their applicability. DFT SiC surface energy calculations produced predictions in good agreement with experiment [3]. Extension of multiscale approach to SiC and diamond, includes computing energy barriers for crack extension bridging DFT and long time scale MD.

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Valerio Vitale, Arash Mostofi, Jonathan Yates and Michael C. Payne

*Automation of Maximally Localised Wannier Functions for high throughput calculations via the selected column of the density matrix algorithm (**SCDM-k**) in WANNIER90*

Wannier90 [1] is a post-processing tool for the computation of the Maximally Localised Wannier Functions [2,3,4] (MLWFs). It requires the Bloch states from an electronic structure calculation in input and returns the MLWFs in output, from which many electronic, magnetic and transport properties can be computed [4]. The Souza-Marzari-Vanderbilt (SVM) algorithm [3], implemented in Wannier90, minimizes the total spread $\Omega = \Sigma_n[(r^2)_n - (\bar{r})_n^2]$, in a given subspace selected via projection. This results in a multi-objective nonconvex optimization procedure whose solution can depend sensitively on the initial guess (projections). This is particularly true in the case of entangled bands (entangled manifold), whereas for isolated bands the algorithm is quite robust (insensitive to the initial guess). In the former case, the choice of a good initial guess is crucial, but far from trivial in complex materials. Thence, in this framework, automation of WFs is hindered by the hard step of choosing a set of initial localized functions with the correct symmetries and centers to use as initial guess for the optimization. The SCDM-k method proposed by Damle and Lin [5,6], removes the need for an initial guess altogether. At each k-point, the sought N Wannier functions, are obtained from the columns of the density matrix $P_{\underline{k}} = \Sigma_n \left|\psi_{n\underline{k}}\right\rangle f(\epsilon_{n\underline{k}}) \left\langle\psi_{n\underline{k}}\right|$, exploiting two important properties: gauge-invariance and nearsightedness of the kernel in real space $P_{\underline{k}}(\bar{r}, \bar{r}')$. The algorithm employs a QR factorization with column pivoting [7] (QRCP) of the density matrix, to select a set *C* of *N* points in real space $C = \{\bar{r}_i\}_{i=1}^N$, such as $\left\{P_{\underline{k}}(\bar{r}, \bar{r}_i)\right\}_{i=1}^N$ are the "most representative" columns of $P_{\underline{k}}(\bar{r}, \bar{r}')$, which are localized by construction. However, this is often impractical since $P_{\underline{k}}$ is prohibitively expensive even to construct and store in memory. The QRCP is performed on the matrix $f\left(\epsilon_{\underline{k}}\right) \Psi_{\underline{k}}^\dagger$ instead, where $P_{\underline{k}} = \Psi_{\underline{k}} f\left(\epsilon_{\underline{k}}\right) \Psi_{\underline{k}}^\dagger$. Only two parameters are required to define the matrix function $f\left(\epsilon_{\underline{k}}\right)$ which can be choose euristically. We have implemented this method in quantum espresso and combined with Wannier90 to generate MLWFs. We have tested the method on a variety of solid-state systems, exploiting the AiiDA [8] workflow and databases.

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Brahim Marfoua, Hamza Lidjici, Brahim Lagoun, Ali Benghia and Souraya Goumri-Said

p-n type Mg_2X(X=Si,Sn) an ab-initio *prediction of structural, electronic and transport properties*

The semiconductors with the formula Mg2X (X= Si and Sn), have attract attention as potential high-performance thermoelectric materials for their electronic and thermoelectric properties, they have extensively investigated. They are an indirect band gap semiconductor. We carried in this work an ab initio study based on the density functional theory to calculate structural, electronic properties of Mg2X(X=Si and Sn). The FP-LAPW method was used with TB-mBJ exchange-correlation. The transport properties of *p-n* type Mg2X(X=Si,Sn) like electrical conductivity (σ), Seebeck coefficient (S), power factor (S2.σ) and electronic thermal conductivity (Ke), have been obtained by solving the linearized Boltzmann, our results are in good agreement with experiment and other theoretical results.

Georg Schusteritsch and Chris J. Pickard

Predicting the structure of interfaces and extended defects using the Ab Initio Random Structure Searching method

First-principles structure prediction of bulk materials is now routinely performed, however the field of predicting the atomic structure of interfaces and extended defects from first-principles is still in its infancy. A detailed understanding of and ability to predict the atomic structure of interfaces is however of crucial importance for many technologies. Interfaces are very hard to predict due to the complicated geometries, crystal orientations and possible non-stoichiometric conditions involved and provide a major challenge to structure prediction. We present here the ab initio random structure searching (AIRSS) method and how it can be used to predict the structure of interfaces. Our method relies on generating random structures in the vicinity of the interface and relaxing them within the framework of density functional theory. The method is simple, requiring only a small set of parameters, and can be efficiently run on modern parallel computer architectures. Examples of several grain boundary defects in technologically important materials will be presented, including grain boundaries in 2D materials (graphene), as well as much more complex 3D systems such as grain boundary interfaces in transition metal oxides ($SrTiO_3$ and TiO_2). Direct comparison to experimental results will be made.

Thomas Durrant, Samuel Murphy, Mathew Watkins and Alexander Schluger

Electrostatics of charge corrections for charged defects in periodic boundary conditions

Using recent advances in the numerical solution of the Poisson equation, we develop a new charge correction method for defects in semiconductors, calculated using periodic density functional theory (DFT). Rather than using a simple electrostatic model, we construct defect charge models directly, using electronic density differences from DFT calculations. Even with these electrostatic corrections, an additional potential alignment procedure is still required to account for the modification to the average potential due to the removal (or addition) of ions. We demonstrate that this effect is rooted in the electrostatics of isolated atoms and show how this can be approximated. Our results corroborate the simple Lany-Zunger method for cubic supercells, and show a general approach that can be applied to more complex situations, such as materials with anisotropic dielectrics or simulation cells that contain multiple interfaces. We demonstrate how correction models for surface defect calculations can be systematically constructed.

Himadri Barman

Two relaxation rates in the Hubbard-Falicov-Kimball Model

In a typical Fermi liquid (FL) metal both resistivity and cotangent of Hall angle measurements show quadratic low temperature dependence, reflecting a single relaxation rate for two kinds of transport. However, a breakdown of this fundamental feature was noticed first in the normal phase of two-dimensional cuprate superconductors and later in other correlated metal oxides in three dimension, as the resistivity there exhibits non-Fermi liquid (NFL) temperature dependence. Motivated by these experiments, we theoretically investigate the emergence of this "two relaxation rates" scenario in the Hubbard-Falicov-Kimball model (HFKM) using the dynamical mean-field theory (DMFT). Our results show that NFL-like relaxation rate in resistivity arises when the Falicov-Kimball interaction exceeds a critical value and reasonable agreements with experiments on doped vanadium sesquioxide materials. We justify our findings form the perspective of Anderson's spin-charge separation phenomenon after employing a bosonization method applied earlier by Schotte and Schotte in the context of the famous x-ray edge problem.

Reference : https:// arxiv.org/abs/1611.07594 .

Max Veit

Machine learning potentials for liquid hydrocarbons

We explore the use of exceptionally accurate, systematic approximations to the quantum mechanical potential energy surface of hydrocarbon liquids in order to make accurate predictions of their macroscopic properties, such as density and viscosity, across a wide range of temperatures and pressures. The intramolecular component of a hydrocarbon potential was created with this approach in [M. D. Veit, M.Phil. thesis, University of Cambridge (2015)] using the GAP machine learning model [A. Bartók, M. Payne, R. Kondor, and G. Csányi, Phys. Rev. Lett. 104, 136403 (2010)]. Now, various models for the intermolecular interactions are explored, including a GAP model fit using the methane dimer prototype system. The most accurate potential is a GAP using a full-dimensional descriptor of the dimer, fit to coupled-cluster energies of a methane dimer database. This potential can be used to simulate bulk methane at the quantum chemical level, but at the expense of neglecting three-body or higher terms. Another approach, fitting directly to bulk methane DFT calculations and adding a dispersion correction, is also explored. The performance of these models is tested using MD simulations and it is found, at least for the bulk fit potentials, that their predictions become more accurate as they get closer to the true potential energy surface. This result validates the approach, paving the way for bulk simulations of larger hydrocarbons and arbitrary mixtures with quantum mechanical accuracy.

Bonan Zhu, Georg Schusteritsch, Chris J. Pickard, Judith L. MacManus-Driscoll

Interfaces in vertically aligned nanocomposites for enhanced ionic conduction - A computational study
Vertically aligned nanocomposites films consist of two phases that are structurally and compositionally different. The unique column-matrix structure of these films was found to induce magnetoelectric coupling, resistive switching and enhanced ionic conduction. Understanding the vertical interface structure is crucial to explain the existence of these novel properties. Ab-initio random structure searching (AIRSS) is a method that have been used to successfully predict crystal structures of bulk materials, defects, and grain boundaries. In this work, we present an approach using random structural searching (RSS) with empirical pair-potentials to find the low energy interface structure between SrTiO3-Sm doped CeO2 VAN films that are found to have enhanced ionic conductivity and resistive switching properties. We show that both AIRSS and RSS with empirical pair-potentials can reproduce the stable bulk structures. To search for low energy interface structures, we randomised only the interfacial layers in a simulation cell with two identical interfaces related by mirror symmetry. A few low energy structures with different symmetries have been discovered. Their stabilities were tested by further randomising the surrounding bulk regions. First-principles calculations were used to validate the energy ordering of the empirical potentials and no major reversal has been found. Oxygen formation energies at the interface were calculated using first-principles methods and were found to vary significantly among different sites. Further investigation is underway to reveal the origin of previously observed properties. This work opens a new way to computationally resolve atomic structure of heterogeneous interfaces and hence allow first-principles calculations to be used for explaining and predicting interface induced novel phenomena.

Robert Charlton

Implicit and explicit host effects on excitons in pentacene derivatives
An ab initio study of the effects of implicit and explicit hosts on the excited state properties of pentacene and its nitrogen-based derivatives has been performed using ground state density functional theory (DFT), time-dependent DFT (TDDFT) and SCF. We observe a significant solvatachromic redshift in the excitation energy of the lowest singlet state (S1) of pentacene from inclusion in a p-terphenyl host compared to vacuum; it amounts to -65 meV for an explicit host consisting of six nearest neighbour p-terphenyls and -78 meV with a conductor-like polarisable continuum model (CPCM). Comparison is made between the excitonic properties of pentacene and four of its nitrogen-based analogues, 1,8-, 2,9-, 5,12-, and 6,13-diazapentacene with the latter found to be the most distinct due to local distortions in the ground state electronic structure. We observe that a CPCM is insufficient to fully understand the impact of the host, requiring the use of explicit treatments. We find that the use of semi-local exchange-correlation functionals for explicit hosts can result in spurious charge-transfer interactions which can distort the excitation spectrum, requiring the use of range-separated hybrid functionals for singlet excited states.

Andrea Zen, Jan Gerit Brandenburg, Jiri Klimes, Alexandre Tkatchenko, Dario Alfe and Angelos Michaelides

Fast and accurate quantum Monte Carlo for molecular crystals
Computer simulation plays a central role in modern day materials science. The utility of a given computational approach depends largely on the balance it provides between accuracy and computational cost. Molecular crystals are a class of materials of great technological importance which are challenging for even the most sophisticated ab initio electronic structure theories to accurately describe. This is partly because they are held together by a balance of weak intermolecular forces but also because the primitive cells of molecular crystals are often substantially larger than those of atomic solids. Here, we demonstrate that diffusion quantum Monte Carlo (DMC) delivers sub-chemical accuracy for a diverse set of molecular crystals at a surprisingly moderate computational cost. As such, we anticipate that DMC can play an important role in understanding and predicting the properties of a large number of molecular crystals, including those built from relatively large molecules which are far beyond reach of other high accuracy methods.

Robert Baldock

Calculating Multicomponent Phase Diagrams with Nested Sampling
The automated calculation of complete phase diagrams, directly from a first-principles or empirical potential energy function, is one of the outstanding challenges in computational materials science. Here, we show how nested sampling, a Bayesian Markov chain Monte Carlo algorithm, can be transformed into a powerful tool for exactly this task. This poster introduces a new nested sampling algorithm, which enables the one-shot calculation of composition-temperature phase diagrams for multicomponent systems, including systems that exhibit a miscibility gap whereby the material separates into domains of different composition. I will showcase the efficacy of the approach by presenting the binary phase diagrams of a Lennard-Jones alloy (continuous atomistic state space) and $Ga_xIn_{1-x}P$ as described using a lattice model (discrete atomistic state space).

Martik Aghajanian

Theory of Bound Impurity States in Monolayer Transition-Metal Dichalcogenides
Semiconducting monolayer transition-metal dichalcogenides (TMDCs) are two-dimensional (2D) materials that exhibit direct band gaps, favourable for nanoelectronic applications such as field-effect transistors. We discuss the behaviour of single-particle bound states in molybdenum disulphide (MoS_2) with a charged impurity atom adsorbed to its surface. The bound states associated with shallow defect potentials extend over tens of nanometers or more because of weak screening in 2D materials. These long-range screened potentials are difficult to fully capture with conventional DFT supercells. To understand the behaviour of TMDCs with impurities, we employ tight-binding models for systems with 10^3-10^4 atoms, including the static screening of impurity charges through the random phase approximation, obtained through first-principles calculations. We have studied spatial densities of bound impurity states and the local density of states near impurity ions. We find localized Rydberg states near the band edges, with a significant asymmetry between donor and acceptor states, which is related to specific features of the MoS2 band structure. We also predict signatures of these defect states that can be measured in scanning tunnelling experiments.

Note regarding posters:

Since the last day of the workshop is very short, we ask the authors of the posters displayed on Wednesday 10th January to take their posters down at 3.30pm on that day, and the authors of the "Thursday" posters can start displaying their work on the 10th from 3.30pm onwards.

Conference Dinner

Wednesday 10th January 2018

Wild Mushroom Risotto

with Parmesan Shavings, Micro Basil and Truffle Oil

~

Venison Fillet

Pan Fried Loin of Suffolk Venison

Served on a Chestnut and Potato Rosti with a Port Wine Jus

or

Beetroot and Blue Cheese Pancake

With Fried Vegetables and Crispy Beetroot and Beetroot Puree (Veg)

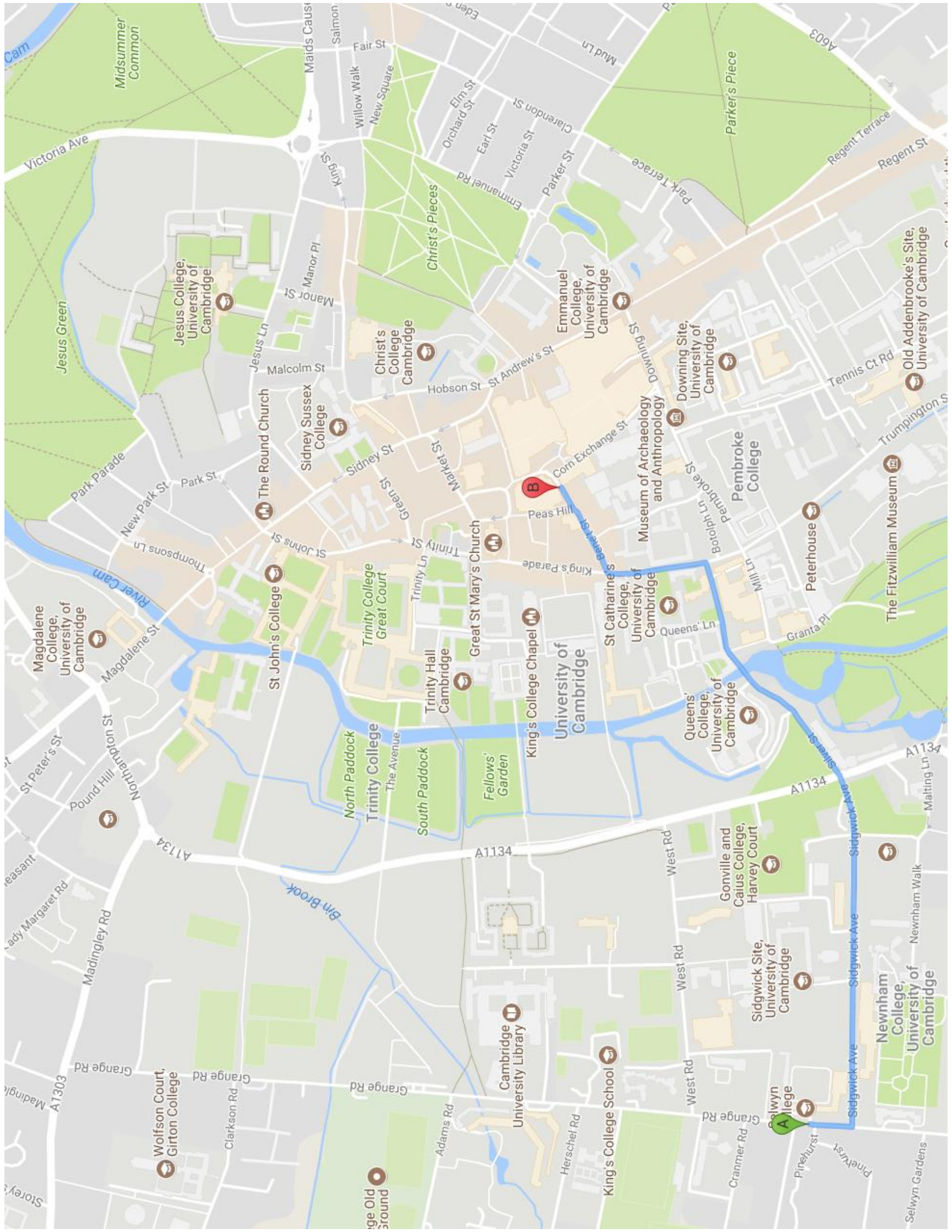
~

Chestnut Pudding

With Toffee and Whiskey Sauce

Each course will be adapted to accommodate the participants' dietary requirements.

Walking directions to Cambridge City Centre



With thanks to our sponsors:

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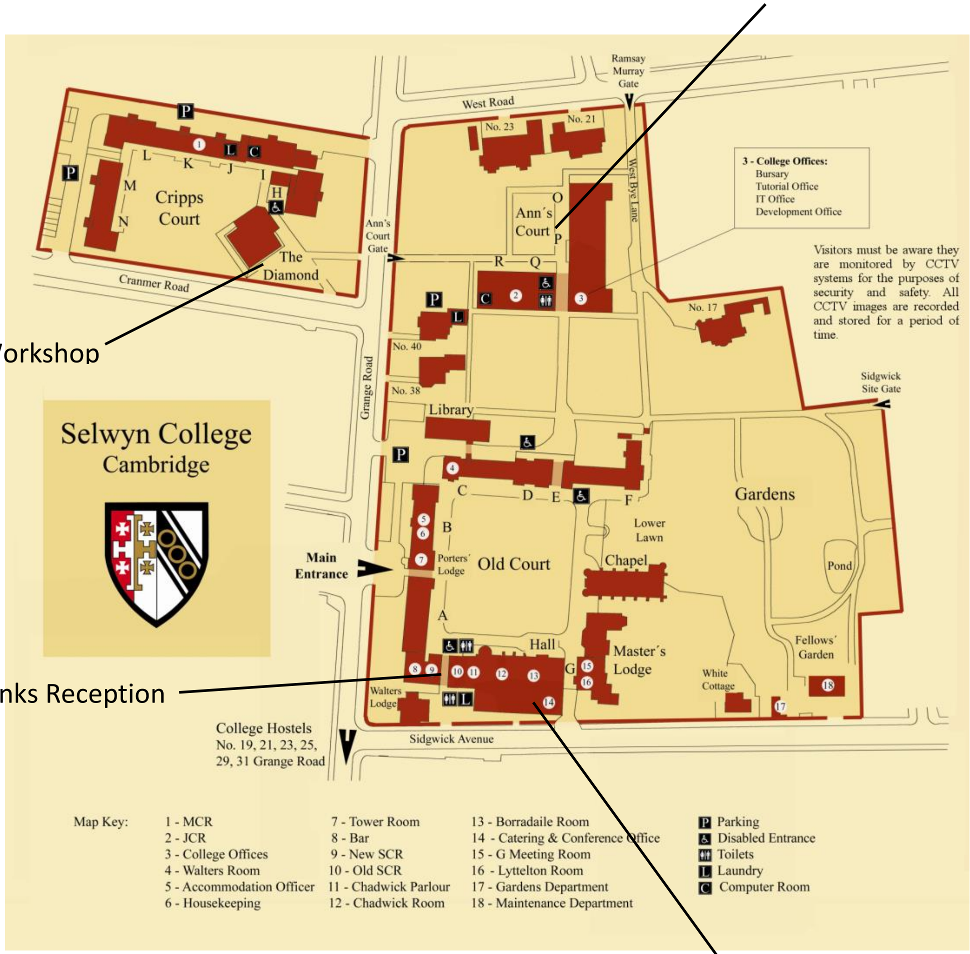
Plan of Selwyn College

Accommodation

Workshop

Drinks Reception

Lunch and Dinner



3 - College Offices:
Bursary
Tutorial Office
IT Office
Development Office

Visitors must be aware they are monitored by CCTV systems for the purposes of security and safety. All CCTV images are recorded and stored for a period of time.

Map Key:

1 - MCR	7 - Tower Room	13 - Borradaile Room	P Parking
2 - JCR	8 - Bar	14 - Catering & Conference Office	♿ Disabled Entrance
3 - College Offices	9 - New SCR	15 - G Meeting Room	🚻 Toilets
4 - Walters Room	10 - Old SCR	16 - Lyttelton Room	L Laundry
5 - Accommodation Officer	11 - Chadwick Parlour	17 - Gardens Department	C Computer Room
6 - Housekeeping	12 - Chadwick Room	18 - Maintenance Department	