CCP9 Conference
&
Community Meeting

Crown Plaza Hotel, Manchester
6-9 September 2022

Programme & Abstracts

Programme

Wednesday 7 September 2022

Time	
12:00	
12:15	
12:30	
12:45	
13:00	*Registration and Lunch*
13:15	
13:30	
13:45	
14:00	Stewart Clark (Durham University & CCP9 Chair)
14:15	
14:30	Chris Hooley (University of St Andrews) invited
14:45	
15:00	Ignacio Martin Alliati (Queen's University Belfast)
15:15	Kemal Atalar (Imperial College London)
15:30	*Coffee*
15:45	
16:00	James Annett (University of Bristol) invited
16:15	
16:30	Wenhan Chen (University of Bristol)
16:45	Ben Hourahine (University of Strathclyde)
17:00	Neil Drummond (Lancaster University)
17:15	Filippo Maria Gambetta (Phasecraft Ltd.)
17:30	*Reception and Posters*
17:45	

Thursday 8 September 2022

Time	
14:00	Juliana Morbec (Keele University) invited
14:15	
14:30	Santanu Saha (University of Oxford)
14:45	Urmimala Dey (Durham University)
15:00	Daniel Murphy (Queen's University Belfast)
15:15	Gavin Woolman (University of Edinburgh)
15:30	*Coffee*
15:45	
16:00	Andrea Droghetti (Trinity College Dublin)
16:15	Volker Heine (University of Cambridge)
16:30	
16:45	
17:00	*Panel Discussion*
17:15	
17:30	
19:30	*Conference dinner*

Thursday 8 September 2022

Time	
9:30	George Booth (King's College London) invited
9:45	
10:00	Matt Hodgson (University of York)
10:15	Alyn James (University of Bristol)
10:30	*Coffee*
10:45	
11:00	Christopher Woodgate (University of Warwick)
11:15	Santosh Kumar Behara (Swansea University)
11:30	Macauley Curtis (University of Bristol)
11:45	Shiyu Deng (University of Cambridge)
12:00	Robert Lawrence (University of York)
12:15	Samuel Magorrian (University of Warwick)
12:30	
12:45	
13:00	*Lunch*
13:15	
13:30	
13:45	

Friday 9 September 2022

Time	
9:30	Albert Bartok-Partay (University of Warwick) invited
9:45	
10:00	Bonan Zhu (University College London)
10:15	Chris-Kriton Skylaris (University of Southampton)
10:30	*Coffee*
10:45	
11:00	
11:15	
11:30	*CCP9 Community Meeting*
11:45	*Stewart Clark*
	Jerome Jackson, Leon Petit, Barry Searle (STFC)
12:00	
12:15	
12:30	*Lunch & Depart*
12:45	

Monolayers, surfaces, and quasi-2D materials: Interplay of band structure, topology, and correlations

Chris Hooley

SUPA, University of St Andrews

In this talk, I will give an overview of some of my group's recent work on 2D materials, quasi-2D materials, and the surface physics of 3D bulk materials, highlighting examples that exhibit interesting topological and/or interaction effects. First, I will introduce a five-orbital symmetry-constrained tight-binding model that we created to describe the surface electronic structure of NbGeSb [1]. This model exhibits Weyl-like points on the edge of the surface Brillouin zone, where the orbital angular momentum rather than the spin has a non-zero winding number. Second, I will discuss the work we have been doing to build a flexible phenomenological tight-binding model of the ruthenates, which has potential applications to the moment-reorientation transition in $Ca_3Ru_2O_7$ [2]. Third, and finally, I will describe our analysis of an extended Hubbard model for monolayer 1T-VSe$_2$ [3], which predicts a purely electronically driven charge-density-wave phase for sufficiently large effective Heisenberg coupling between neighbouring sites. References: [1] I. Marković et al., Nature Communications 10, 5485 (2019). [2] I. Marković et al., Proc. Nat. Acad. Sci. 117, 15524 (2020). [3] M. J. Trott and CAH, Communications Physics 4, 37 (2021).

Floquet formulation of the dynamical Berry-phase approach to non-linear optics in extended systems

Ignacio Martin Alliati

Queen's University Belfast

We present a Floquet scheme for the ab-initio calculation of non-linear optical properties in extended systems. This entails a reformulation of the real-time (RT) approach based on the dynamical Berry-phase polarisation [Attaccalite & Grüning, PRB 88, 1–9 (2013)] and retains the advantage of being non-perturbative in the electric field. Our method applies to periodically-driven Hamiltonians and makes use of this symmetry to turn the time-dependent problem into a self-consistent time-independent eigenvalue problem. We implemented this Floquet scheme at the independent particle level and compared it with the RT approach. Our reformulation reproduces RT-calculated 1st, 2nd and 3rd order susceptibilities for a number of bulk and 2D materials, while reducing the associated computational cost by one or two orders of magnitude.

Electronic structure of twisted bilayer transition metal dichalcogenides

Kemal Atalar

Imperial College London and Phasecraft Ltd.

The discovery of correlated and superconducting states in magic-angle twisted bilayer graphene has generated interest in twisted heterostructures composed of other 2D materials. For example, signatures of superconductivity and exotic optical behaviour have been observed recently in twisted bilayers of transition metal dichalcogenides (TMDs). The theoretical and computational study of these materials using first-principles methods, however, remains challenging due to their large Moiré superlattice sizes at small twist angles. In this work [1], accurate and efficient tight-binding models for predicting and understanding the electronic structure of twisted TMD heterostructures are developed. The first-principles TMD tight-binding model of Fang et al. [2] is extended to twisted and hetero-bilayer structure and additional interlayer interactions between pz and dz^2 orbitals are included. Finally, the band structures and effect of twisting in various Moiré heterostructures of TMDs are demonstrated. References: [1] V. Vitale, K. Atalar, A. Mostofi and J. Lischner, 2D Materials 8, (2021). [2] S. Fang, R. Kuate Defo, S. Shirodkar, S. Lieu, G. Tritsaris and E. Kaxiras, Physical Review B 92, (2015).

Electronic structure and superconductivity

James Annett

University of Bristol

Superconductivity is essentially a correlated quantum state involving pairing of the electrons close to the Fermi surface. Broadly speaking there appear to be two (or perhaps more) classes of materials, depending on whether the dominant pairing interaction arises from electron-phonon coupling or from residual Fermi liquid interactions among the electrons themselves, without major lattice contributions. The most spectacular recent advance in the electron-phonon (BCS type) superconductivity is the achievement of room temperature superconductivity in hydride materials at ultrahigh pressures. On the other hand cuprate 'high temperature' superconductors, iron pnictides and many other 'strongly correlated' materials appear to have unconventional (non-BCS) superconductivity driven by electron-electron interactions. One example of this is the mysterious 1.5 K superconductor Sr_2RuO_4, where the nature and origin of the superconducting state continues to be highly controversial. Sr_2RuO_4 and other materials also appear to show 'time reversal symmetry breaking' which may imply superconductivity with topological character. In this talk I will review recent progress in this diverse field.

Local electron correlation effects on the Fermiology of the weak itinerant ferromagnet ZrZn$_2$

Wenhan Chen

University of Bristol

The weak itinerant ferromagnet ZrZn$_2$ has been shown to host various phenomena such as quantum criticality [1-3]. Previously, it was considered an example of a ferromagnetic superconductor [4], but this was later shown not to be the case [1]. The thermodynamic, magnetic and transport properties strongly support the existence of van-Hove singularities accompanied by a Lifshitz transition around the L high symmetry point in the Brillouin zone [5, 7]. The paramagnetic Fermi surface measured by positron annihilation [6] has features which are not predicted by full potential augmented plane-wave with local orbitals (APW+lo) basis density functional theory (DFT) calculations. Recently, it was shown that the inclusion of dynamical mean field theory with DFT (i.e., the DFT+DMFT method) results in the Fermiology notably changing [8]. Here, in-depth analysis of the predicted Fermiology of paramagnetic ZrZn$_2$ using both DFT and DFT+DMFT methods, along with directly comparing these to the positron experimental data, will be discussed. The DFT+DMFT results clearly provide better agreement with the experiment as well as predicting key features not present in the DFT, such as the extra Fermi surface neck at L. These results emphasise that positrons are a powerful tool for probing the Fermi surface and are sensitive to the effects of electron correlation. References: [1] E. A. Yelland, Phys. Rev. B 72, 184436 (2005). [2] M. Sutherland, Phys. Rev. B 85, 035118 (2012)[3] R. P. Smith, Nature 455, 1220 (2008) [4] C. Pfleiderer, Nature 412 660 (2001) [5] Y. Yamaji, Journal of the Physical Society of Japan 81, 07306 (2012) [6] Z. Major, Phys. Rev. Lett. 92, 107003 (2004). [7] N.Kabeya, Journal of the Physical Society of Japan 81, 073706 (2012)[8] - S. L. Skornyakov, Phys. Rev. B 102, 085101 (2020)

Coupling external Machine learning to DFTB+

Ben Hourahine

University of Strathclyde

Machine learning (ML) driven electronic structure has the potential to radically improve both model accuracy and the speed of development for new chemical, condensed matter and materials simulations. Both density functionals and atomistic classical models have shown substantial, but sometimes controversial, improvements and gains performance based on ML models. In the semi-empirical world, several approaches have reached chemical accuracy, as compared to reference DFT thermochemical results, or spectroscopic accuracy with respect to post-DFT data. However, much of the work in this area has been 'single shot,' in the sense that it often results in proof of principle calculations, being more for the expert than for use by the general physical science audience. In part this is due to a lack of connection with more usual frameworks for methods like general DFT or quantum chemical codes (and their existing user-base). In this contribution, I will discuss work towards general tools for connecting a broad range of atomistic and electronic structure ML (and other) models to an existing framework. Here, long range interactions (electrostatics, dispersion, solvation, etc.) are treated using the conventional tools of a general semi-empirical electronic structure code (DFTB+), which also performs tasks such as the solution of the Hamiltonian (perhaps on GPUs or with massive parallelism), property calculations and geometry optimisation or dynamics. The role of the ML side is to generate one or both of the short-range part of the quantum-mechanical Hamiltonian and total energy contributions (with the option of Delta learning against other models). Interfacing between the two parts of the calculation relies on a general purpose application programming interface, flexibly enabling replacement options for the ML model when stored as an external library that follows the API.

Phase diagram and quasiparticle effective mass of the three-dimensional homogeneous electron gas

Neil Drummond

Lancaster University

A homogeneous plasma of electrons is the simplest and best known model in condensed matter physics; yet the Coulomb repulsion between electrons causes this system to exhibit nontrivial quantum phase behaviour, including spontaneous breaking of translational symmetry (Wigner crystallisation) and possible magnetic phase transitions. Furthermore, the Coulomb interactions between electrons modify the electronic dispersion relation and hence the quasiparticle effective mass of the electron gas in a manner whose density dependence is poorly understood. In addition to its intrinsic interest, the homogeneous electron gas has long served as a testbed for the development of theoretical methods in condensed matter physics. In this talk I will summarise recent and ongoing work on quantum Monte Carlo (QMC) simulations of the three-dimensional homogeneous electron gas, discussing revisions to the zero-temperature phase diagram and the density-dependence of the quasiparticle effective mass. Furthermore, I will compare QMC methods based on "traditional" Slater-Jastrow-backflow trial wave functions with QMC methods based on fermionic neural network wave functions in studies of phase transitions in the homogeneous electron gas.

Towards near-term quantum simulation of materials

Filippo Maria Gambetta

Phasecraft Ltd.

Simulation of materials is considered one of the most promising applications of quantum computers. On near-term hardware, the limiting constraint on such simulations is the requisite circuit depth and qubit numbers. The core of many quantum simulation algorithms, including time-dynamics and the variational quantum eigensolver under the Hamiltonian variational ansatz, is a layer of unitary evolutions by each local term in the Hamiltonian. In this work, we develop a new quantum algorithm design for materials modelling which dramatically reduces the estimated cost of material simulations using this subroutine — improving circuit depths by as many as 5 orders of magnitude. To achieve this, we develop a full stack compiler to translate a density functional theory description of a target material into an efficient quantum circuit by exploiting the locality of materials Hamiltonians in the Wannier single-particle electron basis to design custom fermionic encodings and fermionic swap networks that minimize the cost of executing the requisite interactions. This design generates quantum circuits whose depth is independent of the system's size. We also discuss an efficient measurement protocol to extract information about the system and its static and dynamic properties. We present numerical results for different materials spanning a wide structural and technological range. Our results demonstrate a reduction of many orders of magnitude in circuit depth and qubit numbers over standard prior methods that do not consider the structure of the Hamiltonian and show that realistic materials simulation may be feasible on quantum computers without necessarily requiring fully scalable, fault-tolerant quantum computers.

What is the chance of a rigorous 'post-DFT' future for materials science?

George Booth

King's College London

We know of many ways to solve quantum interacting problems (which is what materials science is), without resorting to empirical exchange-correlation functionals of DFT. If used, these would enable us to systematically improve the quality of those results to exactness – critical for allowing validation and internal checks on the quality of results. However, we are still using DFT, which we know will fail in many situations. The problem obviously is the scaling of these truly ab initio approaches which generally precludes their application to bulk systems. We will describe a framework whereby we exploit the locality of the interactions in a solid, and the correlations between the electrons which results, in order to develop a rigorous scheme to bypass this high scaling in a systematically improvable manner. The result is a practical embedding approach for entirely ab initio simulations on realistic materials with no more than DFT scaling. References: Nusspickel, Booth, Physical Review X, 12, 011046 (2022)

Should discontinuities in the Kohn-Sham potential be avoided or exploited?

Matt Hodgson

The University of York

Kohn-Sham density functional theory (DFT) is the most popular method for calculating the ground-state electronic properties of materials owing to its unprecedented balance of accuracy and computational efficiency. However, Kohn-Sham DFT is notoriously unreliable for calculating electron excitation energies and modelling molecules with strong electron localisation. In this talk, I discuss how, in principle, the fully non-interacting Kohn-Sham system can be used to obtain exact many-body excitation energies and bonding energy curves via the infamous discontinuous behaviour of the Kohn-Sham potential. I introduce recently proposed approaches which approximate this non-analytic behaviour and some which avoid discontinuities all together.

Electron momentum density calculations for strongly correlated materials

Alyn James

University of Bristol

Fermi surfaces can be measured using various techniques ranging from angle-resolved photoemission spectroscopy (ARPES), quantum oscillations, and Compton scattering, each having their own advantages and disadvantages. Compton scattering probes the bulk ground-state wave function [1,2] by measuring the doubly projected electron momentum density (i.e., the so-called Compton profile) which can be used to determine the Fermi surface of metals, such as high entropy alloys [3], which is inaccessible by other techniques. Density functional theory (DFT) has been used to predict the (projected) electron momentum density for comparison with the experiment to gain insight into the electronic structure. These predictions are often adequate for weakly correlated materials, but due to improvements in experimental resolution and statistical precision as well as probing materials in which the electron correlation effects are significant, the widely used approximations to the exchange-correlation functional used in DFT are no longer sufficient. The inclusion of local electron correlations from dynamical mean field theory with DFT (the so-called DFT+DMFT method [4]) is one way forward in improving the description of electron correlations within materials, especially where these types of correlations are important. Here, the recently developed technique of calculating the DFT+DMFT electron momentum density [5] will be discussed alongside comparisons to experimental data. References: [1] B. Barbiellini, Journal of Physics: Conference Series 443, 012009 (2013). [2] S. B. Dugdale, Low Temperature Physics 40, 328 (2014). [3] H. C. Robarts et al., Phys. Rev. Lett. 124, 046402 (2020). [4] K. Held, Advances in physics 56, 829 (2007). [5] A. D. N. James et al., Phys. Rev. B 103, 115144 (2021).

Short-range order in refractory high-entropy alloys: First principles theory and atomistic modelling

Christopher Woodgate

University of Warwick

Short-Range order (SRO) can be either beneficial or detrimental to the properties of novel high-entropy alloys. An understanding of phase behaviour and underlying physical mechanisms driving ordering is therefore essential. We present results from an all-electron, first principles, Landau-type theory which enables us to obtain SRO directly, and also to obtain parameters suitable for atomistic modelling to understand incipient order in these materials. Following successful earlier work on the Ni-based high-entropy alloys[1], I will present new results on the refractory-based high-entropy alloys, which are being studied as candidate materials for components in fusion reactors, due to their exceptional strength, high melting points, and high levels of resistance to radiation. We present a complete description of SRO in the five-component VNbMoTaW and its derivatives. Further, we elucidate the origins of this order and describe the underlying physical mechanisms by which it is driven.1. C. D. Woodgate, J. B. Staunton, "Compositional Phase Stability in medium-entropy and high-entropy Cantor-Wu alloys from an ab initio all-electron Laundau-type theory and atomistic modelling", Phys. Rev. B, 105, 115124 (2022).

Strain-induced effects in the electronic and optical properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$: An ab-initio study

Santosh Kumar Behara

Swansea University

Sodium bismuth titanate (Na$_{0.5}$Bi$_{0.5}$TiO$_3$-NBT), a mixed A-site perovskite, has been studied primarily due to its promise as a good replacement for lead-based ferroelectric. The ground-state properties of NBT are studied using first-principles calculations based on density functional theory (DFT). The electronic band structure reveals that the direct and indirect band gaps are rather close (within 0.07 eV of each other). This has implications for resolving the existing variance in reports regarding the nature of the band gap in NBT. We also report hydrostatic strain-induced ($\varepsilon = -0.02$ (compression) to 0.02 (tension)) band gap variation and demonstrate electron/hole effective mass (m_e^*/m_h^*) tunability in NBT. Importantly in compression, NBT has both direct and indirect band gaps that are rather close; but in tension, it is clearly an indirect band gap system. We identify conditions ($\varepsilon = 0, -0.01$) wherein $m_e^* > m_h^*$; this is known to be a predictive measure for transparent p-type conducting oxides. For all the optical constants, we find a significant blue shift in their spectra under compressive strains and a nominal red shift in their values under tensile strains. Our results offer pointers that can make NBT relevant for light harvesting, charge separation, and charge storage applications.

Effect of hopping anisotropy on the critical temperature of unconventional, superconducting pairing states

Macauley Curtis

University of Bristol

Varying of hopping anisotropy, strain is mimicked through a controlled topological transition through the Liftshitz point in 2D showing a strain tuned critical temperature dependence. The maximum of T$_c$ is at the topological transition, which coincides with the point at which the Van Hove Singularity due to the Lifshitz transition coincides with the Fermi energy. This process is presented systematically for a range of possible pairing symmetries for the material Sr$_2$RuO$_4$. In comparison with experimental evidence, either a $d + id$, or $d + ig$ pairing symmetry can accurately capture the physics of Sr$_2$RuO$_4$ under uniaxial strain.

Evolution of structural, magnetic and electronic properties with pressure in TMPX3 van-der-Waals compounds

Shiyu Deng

University of Cambridge

Control of dimensionality in condensed matter continues to reveal novel quantum phenomena and effects. TMPX3 (e.g. FePS$_3$) have proven to be ideal examples where structural, magnetic and electronic properties evolve into novel states when their dimensionality is tuned with pressure. At ambient pressure, they are two-dimensional van-der-Waals antiferromagnets, and Mott or charge-transfer insulators. Our recent studies [1-4] have reported dimensionality crossover related pressure-induced insulator-to-metal transitions and novel magnetic phases. There are also reports of superconductivity in a related member of this family of compounds [5]. To further understand the structure and physical property evolution with pressure, we have performed a random structure search using first-principles calculations at high pressures and DFT+U studies to elucidate relationship between structural transitions, magnetism and electronic properties. Our computational explorations into pressure tuned TMPX3 are expected to guide the discovery of novel phases and superconductivity in these van-der-Waals systems. References: [1] C. R. S. Haines, et al., Phys. Rev. Lett. 121, 266801 (2018). [2] M. J. Coak, et al., J. Phys. Condens. Matter 32, 124003 (2020). [3] M. J. Coak, et al., Phys. Rev. X 11, 011024 (2021). [4] D. M. Jarvis, et al., arXiv preprint arXiv:2203.07015 (2022). [5] Y. Wang, et al., Nat. Commun. 9, 1914 (2018).

Atomistic control of magnetic anisotropy

Robert Lawrence

University of York

Magnetocystalline Anisotropy is the energetic barrier to the reorientation of spin lattices within a magnetic crystal. For exchange-bias devices, antiferromagnetic (AFM) materials are often used to 'pin' a ferromangetic layer, making evaluating the anisotropy of the AFM material key to understanding the performance of the whole device.In this talk, we will discuss the use of first-principles density functional theory (DFT) simulations of the magnetocrystalline anisotropy of equiatomic FCT PtMn performed using the CASTEP code to evaluate the total anisotropy of our example antiferromagnetic system. The use of theoretical techniques to model the anisotropy enables fine control of the structures under investigation, ensuring that any changes to the anisotropy originate in the expected changes. Furthermore, the full angular dependence of the barrier can be extracted, and we find that the phi- (azimuthal) dependence is very weak in comparison to the theta (polar) dependence, explaining why uniaxial models can provide a good approximation for these types of systems.Finally, we investigate further effects beyond a simple infinite bulk crystal that can be used to control the anisotropy of the system. Our simulations indicate that whilst applied biaxial compressive strain increases the anisotropy, applied tensile biaxial strain can cause the easy and hard magnetic axes of the crystal to swap, thereby providing a potential mechanism for strain control of exchange bias devices through strain engineering techniques.

Band alignment and interlayer hybridisation in transition metal dichalcogenide/hexagonal boron nitride heterostructures

Samuel Magorrian

University of Warwick

In van der Waals heterostructures, the relative alignment of bands between layers, and the resulting band hybridisation, are key factors in determining a range of electronic properties. We examine these effects for heterostructures of transition metal dichalcogenides (TMDs) and hexagonal boron nitride (hBN), an ubiquitous combination given the role of hBN as an encapsulating material. By comparing results of linear-scaling density functional calculations with experimental angle-resolved photoemission spectroscopy (ARPES) results, we explore the hybridisation between the valence states of the TMD and hBN layers, and show that it introduces avoided crossings between the TMD and hBN bands, with umklapp processes opening 'ghost' avoided crossings in individual bands. Comparison between DFT and ARPES spectra for the MoSe2/hBN heterostructure shows that the valence bands of MoSe2 and hBN are significantly further separated in energy in experiment as compared to DFT. We then show that a novel scissor operator can be applied to the hBN valence states in the DFT calculations, to correct the band alignment and enable quantitative comparison to ARPES, explaining avoided crossings and other features of band visibility in the ARPES spectra.

Quantum simulations of materials for renewable and sustainable energy

Juliana Morbec

Keele University

The increasing demand for energy and the impact that conventional energy technologies (mostly based on fossil fuel) has on the environment have led to an urgent need for the development of efficient ways of capturing, storing and transforming energy in a more renewable and sustainable way. In this talk I will discuss how high-performance computer simulations combined with state-of-the-art first-principles methods can be used to predict and design materials for renewable energy applications. In the first part of the talk, I will present a study of the electronic, optical and transport properties of transition metal nitrides (Ta_3N_5) [1,2] and oxides ($BiVO_4$) [3] for solar water splitting. The second part will focus on the investigation of heterostructures formed by organic molecules and two-dimensional materials for wearable and portable photovoltaic devices [4]. References: [1] Juliana M. Morbec, Ieva Narkeviciute, Thomas F. Jaramillo, and Giulia Galli. Phys. Rev. B 90, 155204 (2014). [2] Juliana M. Morbec and Giulia Galli. Phys. Rev. B 93, 035201 (2016). [3] Gokul V. Govindaraju, Juliana M. Morbec, Giulia Galli, and Kyoung-Shin Choi. J. Phys. Chem. C 122, 19416 (2018). [4] Edward Black, Peter Kratzer and Juliana M. Morbec, submitted (2022).

Computational design of green ternary semiconductors for optoelectronic applications

Santanu Saha,* Anna Tippett and Marina R. Filip

University of Oxford

Lead based halide perovskites are the new emerging champions of optoelectronic materials. This is due to their promising electronic and optical properties for applications such as solar cells, LEDs etc. However, lead toxicity and stability are some of the key issues affecting commercial deployment. A wide range of theoretical and experimental investigations have been focused on understanding and mitigation of these issues. In parallel, these activities have rejuvenated interest in the search of novel green materials, which are made of abundant and environmentally friendly chemical elements [1]. High-throughput computational screening plays a key role in this context. We approach this material design problem by first searching structural templates incorporating elements of interest (Cu and Zn here) [2].Our screening procedure identifies a new family of ternary halide semiconductors with several promising Cu and Zn based compounds. Among our list of hypothesised stable/metastable compounds, only a relatively small fraction ($\sim$25%) has been synthesised prior to our work, validating our promising methodology [3]. At the same time, we find a large number of promising candidates for optoelectronic applications. Our material design framework is adaptable to any family and significantly widens the search pool for optoelectronic materials.
References: [1] M. Filip, and F. Giustino, J. Phys. Chem. 120(1), 2015. [2] A. Jain et al. APL Materials 1, 011002 (2013)[3] R. Roccanova et al. ACS Materials Lett. 1, 4, 459-465 (2019)

First-principles study of structure-property correlations in filled tetragonal tungsten bronze $Sr_4Na_2Nb_{10}O_{30}$

Urmimala Dey

Durham University

While the structure-property correlations are well studied in perovskites, interplay of polar and structural instabilities in tetragonal tungsten bronze (TTB) oxides have received comparatively little attention due to their complex crystal structures. In contrast to perovskites, the corner-sharing BO6 octahedra in TTBs give rise to three different A-sites and two inequivalent B-sites with the general formula $(A1)_2(A2)_4(A3)_4(B1)_2(B2)_8O_{30}$. The high temperature aristotype TTB unit cell is tetragonal; however, structural distortions and polar instabilities generally result in lower symmetry structures at low temperature. The Ni-based electrodes used in modern manufacturing industries are thermodynamically incompatible with Bi and Pb-based oxides and therefore, motivated by the need to discover new type-II high temperature dielectrics, attention is shifted to filled $Sr_4Na_2Nb_{10}O_{30}$ (SNN) which has a high curie temperature and large dielectric constant over a wide temperature range. The crystal structure of SNN is debatable and there is a number of contradictory reports on the room temperature crystal structure of SNN. In the present work, we start with the aristotype $P4/mbm$ unit cell of SNN and condense in various unstable phonon modes to study the temperature-dependent structural evolution of SNN by means of density functional theory (DFT) and group-theoretical approach. The PBEsol version of general gradient approximation (GGA) is considered as the exchange-correlation functional in our calculations, which is generally used to accurately describe the equilibrium properties of bulk solids. We aim to predict the interplay between various lattice degrees of freedom and identify the low symmetry structures of SNN, which will be scrutinised in the on-going electron microscopy and X-ray diffraction experiments.

Bringing ab-initio design into the lab: Temperature dependence of plasmonic materials

Daniel Murphy

Queen's University Belfast

As part of the next generation of hard drive technologies for Seagate Technologies, heat assisted magnetic recording (HAMR) relies on the novel combination of plasmonics and material design. The material choice of the near field transducer (NFT) as part of HAMR is critical to the efficiency and effectiveness of future hard drive technologies. The NFT is subjected to intense environmental conditions, high temperature and strain. Previously, the choice of material was dictated by experimental testing, which can be expensive and time consuming. This project aims to use state of the art ab-inito techniques to discover new materials for plasmonic applications. Using density functional theory, many-body perturbation theory and including electron-phonon interactions, the effect of temperature the plasmonic performance will be evaluated through a range of temperatures in a fully ab-inito way.

Detectability of core-level crossing and electronic topological transformations: The case of osmium

Gavin Woolman

University of Edinburgh

Osmium, the least compressible metal, has recently been observed to undergo abrupt changes in the c/a ratio at extreme pressures. These are claimed to provide evidence for two unusual electronic behaviors: a crossing of the semicore 4f and 5p levels, and an electronic topological transition. We demonstrate that these two electronic phenomena are readily reproduced and understood in density functional theory, but that neither perturbs the trend in c/a ratio against pressure. Hence the observed anomalies in c/a must have another cause. Osmium is also notable for its high yield stress: the c/a anomalies lie well within the differential strains which osmium can support. We propose that observed c/a changes can arise from mechanical yield of crystallites with strong preferred orientation under high deviatoric stress in the experimental data. We discuss what evidence remains for the more general hypothesis that core-level overlap under pressure can have measurable effects on the crystal structure in any material.

Exploring electron correlation at transition metal interfaces and in spintronic devices

Andrea Droghetti

Trinity College Dublin

Density functional theory is the most popular method to study ferromagnetic transition metals. However, it is often insufficient for describing correlation effects in magnetic thin film heterostructures, which are the material platforms of spintronic devices. This work presents a computational approach, which combines Density Functional and Dynamical Mean Field Theory, for transition metal thin films, using a multi-orbital perturbative solver for the many-body problem[1]. Calculations accurately describe the 3d-state spin splitting and the appearance of satellite features. Furthermore, when combined with quantum transport schemes [2], the method allows for the simulations of the correlated transport properties of spin-valve devices [3] and to estimate the effect of correlations on the giant (or tunnelling) magnetoresistance. References: [1] A. Droghetti, M.M. Radonjić, A. Halder, I. Rungger, and L. Chioncel, Phys. Rev. B 105, 115129 (2022). [2] A Droghetti, I Rungger, Phys. Rev. B 95, 085131 (2017). [3] A. Droghetti, M.M. Radonjić, L. Chioncel, I. Rungger, arXiv:2201.13118

Understanding the peculiarities of metallic bonding

Volker Heine

University of Cambridge

The inter-atomic bonds in metals are basically (I) strong covalent bonds, but (II) metals are malleable and ductile, with the bonding structure re-arranging rather easily. Also (III) metals usually have a closely packed crystal structure, and (IV) often have phase transitions between them at rather modest temperatures or pressures.(V) The formation energy of an atomic vacancy is only about *half* of what one might expect from counting the net number of broken bonds. (VI) Metals tend to speed up and change chemical reactions (catalysis) at their surfaces. All the above can be found and explained in a simple model, but treated rigorously quantum mechanically, for a metal of one type of electron (e.g. atomic s-electrons or d-electrons) only, the latter being quite a good approximation for the transition metals. A short quantum mechanical argument shows the energy to be proportional to the *square root* of the coordination number C of near neighbours, which then gives properties II to VI.

Regularising a meta-generalised gradient approximation functional, and applications in materials science

Albert Bartok-Partay

University of Warwick

The regularised SCAN functional and follow up work has improved the applicability of the functional in condensed matter calculations. I'll present our efforts to develop a smoother version of SCAN, and the resulting improvements and shortcomings. I'll show applications for organic crystals and solid state NMR.

First-principles exploration of earth-abundant cathode materials for Li-ion batteries

Bonan Zhu

University College London

The transition towards a carbon-neutral society relies on cost-effective and scalable energy storage systems, to which the currently leading answer is the Li-ion battery technology. Historically, the identification of new cathode materials has led to significant advances in Li-ion batteries, and today cathode materials still underpin the overall performance and production costs. Accurate first-principles calculations, coupled with the database-based big-data approach, have led to advances and predictions into new materials in the past. The scarcity of data among the underexplored chemical spaces, however, has limited the ability of such approaches to computationally predict truly new materials. To overcome this, we apply ab initio random structure searching (AIRSS) to explore new cathode material focusing on systems consisting of earth-abundant elements. The polyanionic cathode $LiFePO_4$ can be rediscovered computationally with high efficiency by exploiting the rigid PO_4 units. In the search of $LiFeSO_4F$, a previously reported material, a new polymorph is found combining the high voltage and good ionic conductivity of the two existing polymorphs. Anti-perovskite structured Li_2FeSO is a promising low-cost cathode material, yet it is the only experimentally reported Li-Fe oxysulphides so far. We performed an unbiased search targeting the Li-Fe-S-O chemical and discovered a few new stable and metastable oxysulphides. Further calculations suggest that two of the new phases could offer increased energy densities compared to $LiFePO_4$.

Supporting research communities with large-scale DFT in the next decade and beyond with ONETEP

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First-principles quantum-mechanical simulations based on density-functional theory (DFT), are today used hand in hand with experiment to design new materials. Conventional DFT has a computational effort which increases with the cube of the number of atoms and this limits the practical size of calculations. ONETEP [1] is a world-leading UK-developed software package which uses a linear-scaling framework to enable calculations on much larger scales, offering unmatched capabilities for constructing and simulating more realistic models of materials and including their environment in multiscale simulations. ONETEP is an academic community code which emerged from CCP9, and in 2016 became the flagship project of CCP9 and free to UK academics. As with all software, ONETEP needs to be continuously evolved and updated in order to stay at the cutting edge. This is particularly challenging for a large collaborative academic project that has evolved over two decades. Furthermore, a range of developments, such as excited states, electrochemistry, embedding and wavefunction methods, have required pervasive changes. In this talk I will summarise some recent applications of ONETEP to technologically important cases and present the new EPSRC software for research communities project for the code whose main aims are to re-engineer the code and to support and train the rapidly-expanding communities within solid-state materials and biochemistry that deploy first-principles quantum simulations based on large-scale DFT.

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Poster Contributions

A DFT investigation into copper-based ternary semiconductors in the presence of point defects

Christopher Dickens

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Copper-based ternary semiconductors ($CuInS_2$, $CuFeS_2$, $CuAlS_2$) have a wide range of potential uses making them a key area of research, particularly in the field of photovoltaics, where the possibility to have some control over optical properties, with small shifts in particle size, for these semiconductors can be exploited. Most photovoltaics at the moment are still based on silicon which is a relatively expensive material whilst the basic precursors in these ternary semiconductors are much cheaper due to their relatively high earth abundance. $CuFeS_2$ in particular also poses a key interest due to the debate about the potential narrow intermediate band seen in its electronic structure. We investigate if this intermediate band could also emerge when doping other semiconductors with Iron. When working on materials their properties can be altered by structural defects so it is vital to consider such defects. Although this is even more important when dealing with the nanoscale as even a small imperfection in crystal structure can have large changes on the exhibited characteristics. Therefore, we have investigated which defects are most likely to form in various conditions such as those typically used in the synthesis of colloidal nanocrystals. It is also possible that defects do not form in a solitary regime but instead prefer to cluster, which is why a series of neutral charge clusters were also considered alongside their isolated charged counterparts. The work has primarily been done within the CP2K DFT framework using both PBE and a range of hybrid functionals to search for patterns in defect formation and determine which are both likely to occur and significantly change the exhibited optical properties of the material. In the future, this work will be expanded by considering alternative ternary semiconductors and potential dopants or defect pathways that could lead to more favourable defect formations.

A molecular dynamic study on rheological properties of lubricants under operational conditions

Davide Sarpa

University of Southampton

Classical simulations can greatly enhance our understanding of the microscopic behaviour of lubricants, leading to better design of future lubricants. Viscosity is the dynamic property of interest, being the fundamental property of lubrication and friction reduction. We present the results of simple yet realistic bulk lubricant systems simulations at different operational conditions, using non equilibrium molecular dynamics. We focus on the industrially relevant mixture of two synthetic diesters, di(2-ethylhexyl)sebacate (DEHS) and di(2-ethylhexyl) adipate(DEHA) for the bulk simulations. Our approach finds reasonable agreement with experimental data and provides a methodology to simulate and predict viscosity behaviour for other lubricants and surfaces at a range of pressures and temperatures.

Arrays of optical tweezers and dressed Rydberg atoms for quantum simulators of complex multi-band Hamiltonians

James Hague

The Open University

We calculate Hubbard parameters for arrays of optical tweezers, and discuss how dressed Rydberg atoms (DRAs) in such arrays can be used to make quantum simulators for electron-phonon interaction and multi band effects. Arrays of optical tweezers are highly flexible: both depth and shape of individual lattice sites can be controlled dynamically. Our goals are to understand how (1) Hubbard parameters differ between arrays of optical tweezers and standard optical lattices (2) quantum simulators can be used to emulate quantum materials in the weak- and intermediate-coupling regimes where multiple bands interact and the basis is not localised and (3) quantum simulators built from arrays of optical tweezers can be used for other key interactions such as electron-phonon coupling. We determine expressions for the hopping and Hubbard U of arrays of optical tweezers finding that strongly correlated systems with arbitrary structures can be simulated, including those with multiple-site basis and impurities [1]. We consider experimental parameters for quantum simulation of Hubbard models with an arbitrary basis. Finally, we discuss the onset of charge transfer insulating states in ionic Hubbard models. We then describe a quantum simulator for the Hubbard-Holstein model (HHM), comprising two DRA species held in a monolayer by independent arrays of optical tweezers, predicting that boson-mediated preformed pairing and Berezinskii-Kosterlitz-Thouless (BKT) transition temperatures are experimentally accessible [2,3]. We discuss phonon-mediated pairing and condensation. Finally, as proof of concept, density-functional calculations are made for the bandstructure for a 'graphene' quantum simulator made from arrays of optical tweezers [4].[1] Phys. Rev. A. 104, 053321 (2021). J.P.Hague, L. Petit and C. MacCormick. [2] Phys. Rev. A, 102, 033333 (2020). J. P. Hague P. E. Kornilovitch and C. MacCormick[3] PRL 109, 223001 (2012). J. P. Hague and C. MacCormick.[4] Phys. Rev. A, 95, 033636 (2017). J.P. Hague and C. MacCormick.

Charge transport through single-molecule bilayer- graphene junctions with atomic thickness

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Lancaster University

The van der Waals interactions (vdW) between pi-conjugated molecules offer new opportunities for fabricating heterojunction-based devices and investigating charge transport in heterojunctions with atomic thickness. In this work, we fabricate sandwiched single-molecule bilayer-graphene junctions via vdW interactions and characterise their electrical transport properties by employing the cross-plane break junction (XPBJ) technique. The experimental results show that the cross-plane charge transport through single-molecule junctions is determined by the size and layer number of molecular graphene in these junctions. Density functional theory (DFT) calculations reveal that the charge transport through molecular graphene in these molecular junctions is sensitive to the angles between the graphene flake and peripheral mesityl groups, and those rotated groups can be used to tune the electrical conductance. This study provides new insight into cross-plane charge transport in atomically thin junctions and highlights the role of through-space interactions in vdW heterojunctions at the molecular scale.

Chiral valley phonons and flat phonon bands in Moiré materials

Indrajit Maity

Imperial College London

A chiral object is not the same as its mirror image. The chirality of quasiparticles is a critical concept behind many modern developments in condensed matter physics. Some recent examples include Klein tunnelling and the chiral magnetic effect due to chiral Fermions. Using detailed atomistic simulations we show that multiple phonon modes in twisted bilayers of WSe_2 can be chiral [1]. We demonstrate distinct chiral behaviour of the K/K′valley phonons for twist angles near 0 and 60 degrees. Furthermore, we observe the flattening of bands near the phononic bandgap edges in this system. Our findings, which are more generally applicable to Moiré systems created from 2D materials that break inversion symmetry, have important implications for understanding electron-phonon and exciton-phonon scattering and for designing phononic crystals. [1] I. Maity, A. A. Mostofi, J. Lischner, Phys. Rev. B 105, L041408 (2022).

Computational studies on an Ag_5 atomic quantum cluster deposited on TiO_2 surfaces

Moteb Alotaibi

Lancaster University

Electronic structure investigation of endohedral metallofullerenes (EMFs)

Ali Ismael

Lancaster University

Electronic structure, magnetism and superconductivity in FeSe(S,Te) iron based superconductors

Abyay Ghosh

Queen's University Belfast

Iron based superconductors have been a matter of great interest to the condensed matter physics community since its discovery in 2008 due to their complex phase diagram consisting magnetism, superconductivity and quantum critical phase like nematicity. We have explored these phenomena in the simplest possible iron based chalcogenide superconductor FeSe and FeSe(S,Te) with our Density Functional Theory (DFT) based electronic structure, lattice dynamics and magnetic calculations.

Electronic structure of endohedral metallofullerenes (EMFs

Ibrahim Ghanim Alsaadi

Lancaster University

Electrostatic Fermi level tuning in large-scale self-assembled monolayers of oligo(phenylene-ethynylene) derivatives

Hanan Althobaiti

Lancaster University

Understanding and controlling the orbital alignment of molecules placed between electrodes is essential in the design of practically-applicable molecular and nanoscale electronic devices. The orbital alignment is determined both by the molecular backbone structure and the molecule-electrode interface. In this work, we demonstrate a way of tuning the orbital alignment in large-scale self-assembled monolayers (SAMs), with single-layer graphene (SLG) as a top electrode and gold as a bottom electrode. The SAMs are formed from oligo(phenylene-ethynylene) (OPE)-based molecular wires with different anchor groups (thiolate, pyridyl and thiomethyl) that determine the molecule-electrode contacts. Control of orbital alignment in the junction was achieved by using an ionic liquid as a top gate. The zero-bias orbital alignment of different molecules was signalled by a shift in conductance minimum vs. gate voltage for molecules with different anchoring groups. Molecules with the same backbone, but different contacts, were shown experimentally to have conductances that differ by a factor of 5 near zero bias. Theoretical calculations using density functional theory support the trends observed in the experimental data. This work sheds light on how to control electron transport within the HOMO-LUMO energy gap in molecular junctions and will be applicable in scaling up molecular electronic systems for future device applications.

First principles study of ferroic complex oxide interfaces

Alex Lione

Durham University

Interfaces between materials, such as metals and dielectrics, have led to the discovery of many well-known electronic components such as the Capacitor, Diode, and MOSFET, which are the building blocks of the technology used in our day-to-day lives. This project aims to study interfaces between complex oxides for possible next generation electronic devices, such as ferroelectric memristors. For this purpose we will be focusing on the epitaxial interface between an incipient ferroelectric ($SrTiO_3$) and a material that undergoes metal to insulator transitions ($NdNiO_3$). I will present preliminary results of first principles calculations based on Density Functional Theory on the effect of epitaxial strain of these two perovskite materials. Other interfacial effects, beyond epitaxial strain, will be considered in the future. We find that the paraelectric-ferroelectric and metal-insulator transitions can be finely tuned via epitaxial strain, and discuss structural insights into the competing phases.

Gap energy from step structure in the analytically inverted non-additive kinetic potential functional vNAD

Mojdeh Banafsheh

University of Geneva and University of California

The exact properties of the exchange-correlation (xc) functional are essential for improving the approximations made within density functional theory. Features such as step structure in the xc potential are required for yielding an accurate density and gap energy. vNAD is bifunctional of pair of electron densities ρA and ρB, used in embedding and partition DFT. Using our exact analytical inversion procedure to generate reference vNAD for weakly overlapping ρA and ρB (M. Banafsheh, T. A.Wesolowski, Int. J. Quant. Chem. 118 (2018): e25410). We show that the step structure of v_{xc} associated with molecular dissociation also appears in vNAD, even with local and semi-local functionals, despite the fact that these functionals do not show steps in the xc potential. We discuss the accuracy of the E_g calculated from steps in vNAD and compare to E_g from LDA, PBE, EXX-KLI, and from both Kohn-Sham eigenvalues and ΔSCF.

Giant Stark effect in two-dimensional Hittorf's phosphorene

Ju Zhou

Queen's University Belfast

The electric field tunable band gap and optical properties in low-dimensional materials (quantum-confined Stark effect) are very useful in applications of optoelectronics. In this work, based on the many-body perturbation method, we investigate the evolution of the quasiparticle electronic structure, exciton, and optical properties of two-dimensional (2D) Hittorf's phosphorene under an out-of-plane electric field. Compared to other 2D monolayers, the relatively large thickness of Hittorf's phosphorene leads to a significant reduction in the quasiparticle band gap when an electric field is applied along the quantum confinement direction. The unique bilayer structure, on the other hand, guarantees a well spatial separation of photon-excited electron-hole pairs and, consequently, reduced exciton binding energy under an out-of-plane electric field. These combined effects lead to an almost fixed exciton energy and optical absorption edge at low applied electric fields. However, when the field is larger than 0.1 V/Å, substantial reductions in the exciton energy and optical absorption edge are identified. For the higher-order exciton states, the involvement of more complex band-to-band electron-hole pair formation results in a non-monotonic electric field dependence. The effective optical modulation accompanied with these giant Stark effects shows potential applications of Hittorf's phosphorene in 2D optoelectronic devices.

Halogen incorporation into calcium carbonate: Computational chemistry insights and geochemical implications

Xiaolei Feng

University of Cambridge

Incorporation of halogens, as trace elements, into biomineral-related materials has been investigated by ab initio computational methods, and the geochemical implications explored. Trace element incorporation into the three polymorphs of calcium carbonates – calcite, aragonite and vaterite – is considered. Iodine is most easily accommodated as iodate (IO_3) replacing carbonate. Local strain fields around the iodate solute atom show aragonite displays the greatest degree of local structural distortion while vaterite is relatively unaffected. The energy penalty for iodate incorporation is least in vaterite and greatest in aragonite, implying that iodine will display partitioning between calcium carbonate polymorphs in the order vaterite aragonite calcite. This suggests that iodine is incorporated as iodate within biogenic carbonates, important in the application of I/Ca data in palaeoproxy studies of ocean oxygenation. The presence of vaterite in any biocalcification process, be it as an end-product or a precursor, should be taken into account when applying I/Ca geochemical proxies. Fluorine incorporation into crystalline $CaCO_3$ has also been explored. Different mechanisms have been considered, and the two most stable involve replacing one oxygen atom within the carbonate group to form a (CO_2F) group alongside a substitution involving replacement of the CO_3 group by two fluorine ions to form a CaF_2 defect. These mechanisms contrast with those of iodine incorporation into calcium carbonates. The substitution of CO_3 by F_2 is most favourable and fluorine is preferentially incorporated into the three polymorphs of calcium carbonate in the order vaterite > aragonite > calcite. These results explain previously-reported preponderance of fluorine in aragonite corals, and lend support to the use of F/Ca as a proxy for ocean pCO_2. The results serve as a set of key illustrative studies that demonstrate the power of predictive geochemical (in particular mineralogical structure prediction) approaches.

Highly conductive single-molecule junctions with double n-heterocyclic carbene anchors

Maryam Alshahrani

Lancaster University

Hybrid QM/MM investigation of metal atom adsorption on defective and doped diamond surfaces

Shayantan Chaudhuri

University of Warwick

Polycrystalline boron-doped diamond is widely used as a working electrode material in electrochemistry, and its properties such as a high stability make it an appealing support material for nanostructures for (electro)catalytic applications. Experiments have shown that electrodeposition can lead to the creation of stable small nanoclusters and even single metal adatoms on diamond. We investigate the structural stability and reactivity of single atoms on diamond as predicted by conventional exchange-correlation functionals. As hybrid functionals are computationally intractable for large-scale periodic surface structures, we use the quantum mechanics/molecular mechanics (QM/MM) methodology to compare different exchange-correlation functionals on equal footing. We investigate the adsorption energy of metal single atoms on an oxygen-terminated diamond (110) surface and explore the effect on adsorption after introducing defects and dopants into the substrate. Our work forms the foundations for wider efforts to model hybrid organic-inorganic interfaces, which can be facilitated by QM/MM approaches.

Investigating the quasi-liquid layer on ice surfaces: a comparison of order parameters

Jihong Shi

King's College London

Understanding QLLs at the molecular level is necessary to unravel the mechanisms of ice crystal formation. Computational studies of the QLLs heavily rely on the accuracy of the methods employed for identifying the local molecular environment and arrangements, discriminating between solid-like and liquid-like water molecules. Here we compare the results obtained using different order parameters to characterise the QLLs on hexagonal ice (Ih) and cubic ice (Ic) model surfaces investigated with molecular dynamics (MD) simulations in a range of temperatures. For the classification task, in addition to the traditional Steinhardt order parameters in different flavours, we select an entropy fingerprint and a deep learning neural network approach (DeepIce), which are conceptually different methodologies.

Linear-scaling density functional theory meets swarm intelligence to solve problems in catalysis.

Loukas Kollias

University of Southampton

Authors: Loukas Kollias, Vassiliki-Alexandra Glezakou, Roger Rousseau, Chris-Kriton Skylaris.Abstract: The Linear-Scaling Density Functional Theory code ONETEP can perform calculations on systems with thousands of atoms. Swarm Intelligence describes decentralised and self-organised groups and how they reach the optimal solution to a problem. In this work, we follow the behaviour of bees in a colony to find nectar of "increasing quality" as a means to search for molecular structures of "decreasing total energy" relevant to a process of interest in catalysis. More elaborately, we use the Artificial Bee Colony algorithm as it is implemented in the Northwest Potential Energy surface Search engine (NWPEsSe) code. Different bee roles are described by relevant mathematical expressions in a way to find local minima of decreasing total energy. NWPEsSe searches for structures in an iterative fashion given certain geometrical features, e.g., the relative orientation or distance between two or more sets of molecules, that are set to describe configurations relevant to a process of interest, such as a chemical reaction. Every candidate structure is communicated from NWPEsSe to ONETEP, then it is relaxed in ONETEP and communicated back with its optimised atomic coordinates and total energy to NWPEsSe. This way we build a set of structures and energies that is being advised at every iteration to generate the next candidate structure. The interface between the two codes allows for the evaluation of numerous local minima related to a catalytic process, hence understanding the configurations and energetics of the most favourable structures. In this work, we present developments on the interface between the two codes, while focusing on systems describing adsorption of gaseous molecules on metal catalysts.

Localised soft vibrational modes and coherent structural phase transformations in rutile TiO$_2$ nanoparticles under negative pressure

Kang Wang

Imperial College London

We study the effect of size on the vibrational modes and frequencies of nanoparticles, by applying a newly developed, robust, and efficient first-principles-based method that we present in outline. We focus on rutile TiO$_2$, a technologically important material whose bulk exhibits a softening of a transverse acoustic mode close to q=(1/2,1/2,1/4), which becomes unstable with the application of negative pressure. We demonstrate that, under these conditions, nanoparticles above a critical size exhibit unstable localised modes and we calculate their characteristic localization length and decomposition with respect to bulk phonons. We propose that such localised soft modes could initiate coherent structural phase transformations in small nanoparticles above a critical size.

Nonuniform grids for Brillouin zone integration and interpolation

Siyu Chen

University of Cambridge

We present two developments for the numerical integration of a function over the Brillouin zone. First, we introduce a nonuniform grid, which we refer to as the Farey grid, that generalises regular grids. Second, we introduce symmetry-adapted Voronoi tessellation, a general technique to assign weights to the points in an arbitrary grid. Combining these two developments, we propose a strategy to perform Brillouin zone integration and interpolation that provides a significant computational advantage compared to the usual approach based on regular uniform grids. We demonstrate our methodology in the context of first principles calculations with the study of Kohn anomalies in the phonon dispersions of graphene and MgB_2, and in the evaluation of the electron-phonon driven renormalization of the band gaps of diamond and bismuthene. In the phonon calculations, we find speedups by a factor of 3 to 4 when using density functional perturbation theory, and by a factor of 6 to 7 when using finite differences in conjunction with supercells. As a result, the computational expense between density functional perturbation theory and finite differences becomes comparable. For electron-phonon coupling calculations we find even larger speedups. Finally, we also demonstrate that the Farey grid can be expressed as a combination of the widely used regular grids, which should facilitate the adoption of this methodology.

Once-in-a-lifetime - using ab initio calculations to analyse experimental positron annihilation measurements

Massimiliano Favaro-Bedford

University of Bristol

In condensed matter physics, positrons are used in the two-dimensional angular correlation of electron-positron annihilation radiation (2D-ACAR) technique to probe a material's electronic properties, such as half-metallicity [1,2]. A 2D-ACAR experiment measures the electron-positron momentum distribution which can be used in to infer the Fermi surface [3]. In these experiments, the positron's sensitivity to its electronic environment and the subsequent influence this has on the measured momentum distribution can also provide a deeper understanding of the positron's interactions within the metal. Beta-plus decay is a weak process and thus violates parity [4]. This results in the positron having its spin preferentially in the direction of propagation. This is maintained throughout the subsequent thermalisation in a sample prior to annihilation. This technique of investigating the momentum-space spin properties of the bulk sample is known as spin-polarised ACAR [5]. The subject of this work is to utilise theoretical density functional theory (DFT) calculations with experimental spin-polarised ACAR data for different metals allowing us to extract properties of, not only the metal, but also the source and the positron itself. References: [1] K. E. H. M. Hanssen and P. E. Mijnarends, Phys. Rev. B 34, 5009 (1986). [2] S. DeBenedetti et al, Phys. Rev. 77, 205 (1950).[3] S. B. Dugdale, Low Temperature Physics 40, 328 (2014).[4] P. W. Zitzewitz et al, Phys. Rev. Lett. 43, 1281 (1979).[5] P Genoud et al, J. Phys.: Condens. Matter 3, 4201 (1991).

Quantum interference-controlled conductance enhancement in stacked graphene like dimers

Bader Alharbi

Arabic

Stacking interactions are of significant importance in the fields of chemistry, biology and material optoelectronics because they determine the efficiency of charge transfer between molecules and their quantum states. Previous studies have proven that when two monomers are π-stacked in series to form a dimer, the electrical conductance of the dimer is significantly lower than that of the monomer. Here, we present a strong opposite case that when two anthanthrene monomers are π–stacked to form a dimer in a scanning tunnelling microscopic break junction, the conductance increases by as much as 25 in comparison with a monomer, which originates from a room-temperature quantum interference. Remarkably, both theory and experiment consistently reveal that this effect can be reversed by changing the connectivity of external electrodes to the monomer core. These results demonstrate that synthetic control of connectivity to molecular cores can be combined with stacking interactions between their π systems to modify and optimise charge transfer between molecules, opening up a wide variety of potential applications ranging from organic optoelectronics and photovoltaics to nanoelectronics and single-molecule electronics.

Quantum interference dependence on molecular configurations for cross-conjugated systems in single-molecule junctions

Iain Grace

Lancaster University

We report a combined experimental and computational study of seven cross-conjugated enediyne derivatives functionalised with a pendant group (diphenyl, 9-fluorenyl, 9-thioxanthene or cyclohexyl) at the central alkene site, and with thiomethyl (SMe) or thioacetate, as protected thiol, (SAc) groups as anchors. Measurements of the conductance (G) and Seebeck coefficient (S) of gold | single-molecule | gold junctions were obtained using a modified scanning tunnelling microscopy-break junction (STM-BJ) technique. It is shown that most of the molecules give multiple conductance plateaus ascribed to different molecular configurations inside the junction. The higher conductance plateaus are consistent with the aryl pendant units interacting with one of the gold electrodes, thereby circumventing transmission of electrons through the enediyne system; the lower conductance plateaus are consistent with anchoring of both of the terminal SMe or S units to the electrodes. Most of the compounds show a positive value of S in the range 3.7–12.7 μV/K indicating electronic transport through the HOMO, while one of them presents a negative value of S (-6.2 μV/K) indicating a predominance of the LUMO in the electronic transport. Theoretical calculations using density functional theory show a destructive quantum interference (DQI) feature in the gap between the highest occupied and lowest unoccupied molecular orbitals (the HOMO-LUMO gap) for the lower conductance plateaus, supporting the trends observed in the experimental data.

Searching for high thermoelectric performance molecular junctions

Bashayr Alanazi

Lancaster University

Simulations of liquid-liquid phase transitions in supercritical fluids

Ian Morrison

University of Salford

A combination of neutron diffraction, Raman spectroscopy and ab initio molecular dynamics is used to investigate supercritical phase transitions in Ethane and Nitrogen. For Ethane we have observe a transition between rigid and nonrigid liquid states in liquid ethane at ca2 50 MPa. For N_2 we observe a narrow transition from gas-like to rigid liquid-like behaviour at ca1 50 MPa. Our findings allow us to reliably characterise the Frenkel line using both diffraction and spectroscopy methods, backed up by simulation, for the same substance. We clearly lay out what parameters change, and what parameters do not change, when the Frenkel line is crossed.

Structural, electronic and mechanical properties of Re doped FeMnP$_{0.67}$A$_{0.33}$ (A=Ga and Ge): A DFT study

Gabriel Chirchir

Egerton University

The structural, electronic and mechanical properties of Re doped FeMnP$_{0.67}$A$_{0.33}$ (A= Ga and Ge) were examined by use of density functional theory (DFT) within the generalised gradient approximations as demonstrated in Quantum ESPRESSO code. The optimised structural parameters as well as derived lattice parameters are inconsistent with other computational and achievable experimental results. The computed independent elastic constants confirm the mechanical stability of the investigated materials. The computed Poisson's and Pugh's ratios as well as Cauchy pressure, verify that FeMn$_{0.67}$Re$_{0.33}$P$_{0.67}$Ga$_{0.33}$ is the most ductile among the studied compounds. The calculated values of bulk modulus, shear modulus and Young's modulus confirm high values of bond strength, hardness and stiffness of the investigated materials respectively. Therefore, the four compounds considered may be appropriate for industrial applications. The results report that FeMn$_{0.67}$Re$_{0.33}$P$_{0.67}$Ga$_{0.33}$ compound is more ductile and mechanically stable compared to other investigated compounds. This is the first qualitative computational prediction of the elastic properties of FeMnP$_{0.67}$Ge$_{0.33}$, FeMnP$_{0.67}$Ga$_{0.33}$, FeMn$_{0.67}$Re$_{0.33}$P$_{0.67}$Ge$_{0.33}$ and FeMn$_{0.67}$Re$_{0.33}$P$_{0.67}$Ga$_{0.33}$ compounds and this awaits experimental ratification. The calculated electronic density of states confirms that the Re-2p states are located in the conduction band (CB) in the unit cell while Re-3d dominate the CB in the supercell. Results from the doped compounds could not be compared with experimental or computational findings because to the best of our knowledge, this has not been done.

Surface modification of TiO$_2$ with Cu5 atomic cluster in the presence of silicates

Fatimah Alhawiti

Lancaster University

The effect of vibrations on the Seebeck coefficient (S) in molecular junction

Wafa Al Malki

Lancaster University

At the molecular level, a great deal of attention has been devoted to quantum interference QI effects due to their potential to control the charge transport through molecular materials at the phase-coherent scale. The Seebeck effect is particularly appealing for technical applications since it leads to direct heat-to-electricity conversion, and therefore QI effects can be exploited to enhance the thermoelectric performance of single molecules and molecular films. Towards this aim, we have investigated theoretically the vibrational effect of different side groups attached to the central core of fluorene-biphenyl unit which binds to gold via pyridyl anchor group. We propose that the Seebeck coefficient can be controlled because of the combined effect of QI and vibrations. The main result has shown that meta-connected compounds are sensitive to this fluctuations compared to para due to the presence of the dip transmission.

Theory of molecular-scale electron and phonon transport

Bandar Alsuwayni

University of Lancaster

The role of the anchor group in controlling the thermoelectric behaviour of molecules

Angham Alahdal

Lancaster University

This study aims to investigate the role that anchor groups play in thermoelectric behaviour, we've chosen to study seven anchor groups by comparing these anchors to see if they influence the behaviour of quantum interference. We've tested the connectivity of these molecules to different cores and different configurations We want to know what controls the quantum interference and we want to see what is the sort of best behaviour or what controls the resulting Seebeck coefficient from the parameters. Here, we used the density functional theory DFT to obtain the main field Hamiltonian then we calculated the transmission coefficient $T(E)$ and the Seebeck coefficient $S(E)$ of the electrons with energy E passing from one electrode to the other using Gollum code. Our findings indicate that the expected behaviour para versus meta connectivity is different due to the different configurations. We also find that for the para connectivity, the linear & the nonlinear configuration are always going to give the same sort of conductance. Finally, the anchor groups control the position of the Fermi energy. This study indicates that in the future the configuration of the single-molecule electronic should be considered for designing better materials.

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