

Book of Abstracts

Game of Materials

Dubrovnik, 2018

| | Tue, Oct 30th | Wed, Oct 31st | Thu, Nov 1st | Fri, Nov 2nd |
|---------------|-------------------|--|--|--|
| 08:00 – 09:30 | | Session I: High throughput | Session V: Transport | Session IX: Machine learning |
| 09:30 - 10:00 | | Coffee break | Coffee break | Coffee break |
| 10:00 – 11:30 | | Session II: Molecules on surfaces | Session VI: 2D materials | Session X: Competition winners |
| 12:00 – 14:00 | | Lunch | Lunch | Lunch |
| 14:00 – 15:30 | | Session III: Magnetism | Session VII: Bio and complex materials | City tour |
| 15:30 – 16:00 | | Coffee break | Coffee break | |
| 16:00 – 17:30 | | Session IV: Theoretical developments | Session VIII: Catalysis | |
| 18:00 – | Registration | Posters | | |
| 19:30 – | | | Conference dinner | |
| 20:00 – | Welcome reception | | | |

| Tuesday, October 30 | |
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| 6:00 pm to 8:00 pm | Registration |
| 8:00 pm | Welcome drinks |
| Wednesday, October 31 | |
| 8:00 am to 8:10 am | Conference opening |
| 8:10 am to 8:40 am | Shyue Ping Ong, Accelerating Materials Science with Automation, Data and Machine Learning |
| 8:40 am to 9:10 am | Rickard Armiento, Materials Design on Three Fronts: Fundamental Theory, Automation, and Artificial Intelligence |
| 9:10 am to 9:40 am | Francesco Ricci High-Throughput ab-initio computing for materials discovery |
| 9:40 am to 10:00 am | Coffee break |
| 10:00 am to 10:30 am | Pavel Jelínek, Molecular systems on surfaces: experiment and theory |
| 10:30 am to 11:00 am | Ikutaro Hamada, Toward predictive density functional theory calculations of surfaces and interfaces |
| 11:00 am to 11:30 am | Nicolae Atodiresei, Hybrid Organic Magnetic Metal Interfaces |
| 12:00 pm to 2:00 pm | Lunch |
| 2:00 pm to 2:30 pm | Bernd Zimmermann, Materials for spin-orbitronics: Predicting and engineering spin-relaxation and Dzyaloshinskii-Moriya interaction by ab initio calculations |
| 2:30 pm to 3:00 pm | Kirill Belashchenko, Spin-memory loss and spin-orbit torques |
| 3:00 pm to 3:30 pm | Igor Lukačević, Perovskite-based transport layer for hybrid perovskite solar cells |
| 3:30 pm to 4:00 pm | Coffee break |

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| 4:00 pm to 4:30 pm | Stefaan Cottenier, To boldly go where no experiment has gone before |
| 4:30 pm to 5:00 pm | Daniel Sánchez Portal, Insights into nanoplasmonics from first-principles time-dependent density functional simulations |
| 5:00 pm to 5:30 pm | Jiří Klimeš, Towards reliable theoretical description of molecular solids |
| 6.00 pm | Poster session with drinks |
| Thursday, November 1 | |
| 8:00 am to 8:30 am | Branislav K Nikolic, Spin-orbit proximity effect in ferromagnetic metals: Fundamentals and spintronic applications |
| 8:30 am to 9:00 am | Thomas Frederiksen, Modelling tools for nanoelectronics |
| 9:00 am to 9:30 am | Federico Grasselli, Charge-transport quantization and gauge-invariance of electrical conductivity in ionic fluids |
| 9:30 am to 10:00 am | Coffee break |
| 10:00 am to 10:30 am | Pablo Ordejón, Charge Density Waves in Transition Metal Dichalcogenides |
| 10:30 am to 11:00 am | Ravindra Pandey, Phosphorene-based 2D Materials |
| 11:00 am to 11:30 am | Roland Gillen, Interlayer excitons in MoSe ₂ /WSe ₂ heterostructures from first principles |
| 12:00 pm to 2:00 pm | Lunch |
| 2:00 pm to 2:30 pm | José Ortega Mateo, Modelling Reactions in Biomolecules |
| 2:30 pm to 3:00 pm | Ali Hassanali, Computational Studies on Deciphering the Many Faces of Liquid Water |
| 3:00 pm to 3:30 pm | Alex Urban, Atoms in Disarray: Simulating Disordered Materials |
| 3:30 pm to 4:00 pm | Coffee break |

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|---------------------------|--|
| 4:00 pm to 4:30 pm | Mark Saeys, Operando computational catalysis – realistic structures, shapes and coverages |
| 4:30 pm to 5:00 pm | Peter Saalfrank, Non-adiabatic molecular dynamics at surfaces |
| 5:00 pm to 5:30 pm | Maria KY Chan, Modeling catalysts - pushing the accuracy frontier and connecting with experiments |
| 7.30 pm | Conference dinner |
| Friday, November 2 | |
| 8:00 am to 8:30 am | Volker Deringer, From Machine-Learning Interatomic Potentials to Materials Chemistry |
| 8:30 am to 9:00 am | Nongnuch Artrith, Development of efficient and accurate machine-learning potentials for the simulation of complex materials |
| 9:00 am to 9:30 am | Joohwi Lee, Efficient algorithm for discovery of crystal structures for oxygen-ion conductors beyond data mining |
| 9:30 am to 10:00 am | Coffee break |
| 10:00 am to 10:30 am | Alessandro Erba, A song of ice and fire: First-principles Modeling of thermal properties of molecular crystals and MOFs |
| 10:30 am to 11:00 am | Atreyi Dasmahapatra Thermoelectric properties of TiNiSn and TaCoSn half-Heusler alloys through ab-initio calculation and experiments |
| 11:00 am to 11:30 am | Dino Novko A first-principles approach to non-equilibrium vibrational dynamics |
| 12:00 pm to 2:00 pm | Lunch |
| 2:00 pm | City tour |

Shyue Ping Ong

University of California San Diego, USA

Accelerating Materials Science with Automation, Data and Machine Learning

As quantum mechanical calculations become increasingly reliable and accessible, the automation of such calculations in high throughput have led to the emergence of vast amounts of computed materials property data over the past decade. Such large databases of computed materials properties have proved invaluable in the screening of vast chemical spaces for novel materials discoveries. In this talk, I will demonstrate how the application of deep learning techniques can enhance the value that can be extracted from large-scale quantum mechanical calculations, from the prediction of entirely novel technological materials, to quantifying fundamental relationships between chemically intuitive descriptors and crystal stability, to accessing time and length scales beyond first principles approaches. I will also provide some perspectives on future challenges and opportunities in the application of deep learning techniques in materials science.

Rickard Armiento

Department of Physics, Chemistry and Biology, Linköping University, Sweden

Materials Design on Three Fronts: Fundamental Theory, Automation, and Artificial Intelligence

The design of new materials with specific properties is at the core of our technological progress. I will present our ongoing efforts in this field, spanning over three connected topical areas: (i) fundamental theory development for improved exchange-correlation functionals in density-functional theory (DFT); (ii) progress on software for high-level automation of materials property calculations and its application to materials design; and (iii) the adoption of methods from big data and machine learning for prediction, data mining, and visual exploration in ways that greatly expand the reach and scope of traditional methods. On the topic of fundamental theory development, I discuss a recent semi-local functional for DFT that better mimics the states (and thus band structure) of higher order methods. I will highlight a few distinct features of the 'high-throughput toolkit', a framework we use for automation, and show recent examples of its application for high-throughput materials design of defects in SiC. On the topic of machine learning, I discuss a model demonstrated to, at the cost of 10k DFT calculations, predict 2M DFT-quality formation energies of substitutions into the elpasolite crystal structure, which have facilitated the identification of 128 new stable elpasolites.

Francesco Ricci

Université Catholique de Louvain, Belgium

High-Throughput ab-initio computing for materials discovery

Nowadays, High-Throughput (HT) ab-initio calculations allow to compute a large quantity of properties for thousands of materials. Many public databases such as Materials Project, AFLOWlib, NOMAD share materials' structures and properties computed within this approach. The availability of these large datasets has been proven effective in (a) discovering general trends and correlations between structure, chemistry and physical properties;(b) in accelerating the experimental discovery of new materials. Also, it opens the way to machine-learning methods that can be trained on these datasets to predict new materials. In this talk I will present how we used HT computing to generate a large dataset of transport properties and to search and design high-performance thermoelectrics, p-type transparent conducting materials, and new electrides.

Pavel Jelínek

Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic

Molecular systems on surfaces: experiment and theory

Complex molecular structures on surfaces have received a lot of attention last years. However, despite recent advances, they are still far from being ready to use in future technological applications, mainly due to lack of our knowledge of such systems and their formation processes. The detailed understanding of underlying chemical and physical process of such systems is not possible without a theoretical insight, often based on total energy density functional theory (DFT) calculations. On the other hand, electron correlations effects in molecular systems are not always properly described within standard DFT formalism or system and related processes are too complex being handled on DFT level. Therefore, a close synergy between experiment and theory is mandatory to understand properly the complex molecular systems. We will discuss several critical examples, where the standard DFT techniques may fail: i) control of molecular spin state via non-covalent interaction; ii) formation of organometallic complexes via on-surface chemistry; and (iii) electron dynamics within a single molecule.

Ikutaro Hamada

Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, Japan

Toward predictive density functional theory calculations of surfaces and interfaces

An accurate description of covalent, ionic, metallic, and van der Waals interactions on the same footing is a prerequisite for designing heterogeneous interfaces, such as organic/metal interfaces and van der Waals heterostructures. However, this task is challenging for density functional theory at the level of local density functional and generalized gradient approximation. Among others, nonlocal van der Waals density functional[1,2] is one of the promising methods to describe different interactions accurately in a seamless fashion. In this talk, after a brief introduction to the van der Waals density functional and its offspring[3], I discuss recent applications of higher accuracy van der Waals density functional to selected problems including surface and interface electronic states[4,5], molecular adsorption[6], and catalytic reaction[7].

References

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Nicolae Atodiresei

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Hybrid Organic Magnetic Metal Interfaces

The density functional theory provides a framework with predictive power that can be used to describe organic-metal hybrid systems in a realistic manner. In this respect, *ab initio* studies elucidate how the subtle interplay between the electrostatic, the weak van der Waals and the strong chemical interactions determine the geometric, electronic and magnetic structure of hybrid organic-metal interfaces. More precisely, the interaction between the π -like electronic cloud of organic materials with the magnetic states of a metal influences the (i) spin-polarization, (ii) magnetic exchange coupling, (iii) magnetic moments and (iv) their orientation at the hybrid interfaces. In this talk I will briefly summarize how first-principles calculations (i) provide the basic insights needed to interpret surface-science experiments and (ii) are a key tool to design novel materials with tailored properties that can be integrated in carbon-based spintronic devices.

References

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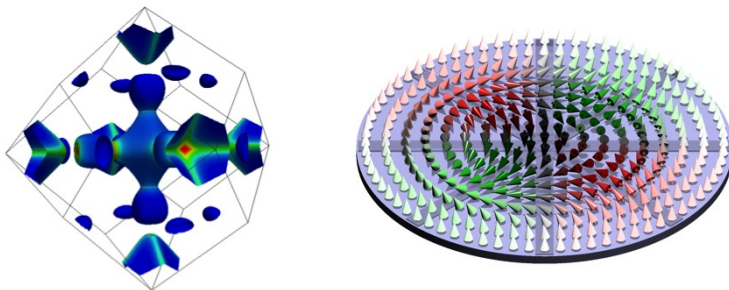
Bernd Zimmermann

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Materials for spin-orbitronics: Predicting and engineering spin-relaxation and Dzyaloshinskii-Moriya interaction by ab initio calculations

The spin-orbit interaction (SOI) is at the core of spintronics 4.0—often referred to as spin orbitronics—and gives rise to completely new physical effects. The vision is to exploit SOI for the all-electric manipulation of spin currents and magnetization textures, which finally may allow for devices with ultra-low power consumption and unforeseen computational efficiency. Novel properties come about due to the presence of defects, at an interface or surface of thin films or by breaking the structure-inversion symmetry, which together with the relative sensitive SOI ultimately enable the tuning of material properties towards applications.

By means of density-functional theory investigations, we show that exploiting anisotropy effects in transition-metal compounds presents an ideal way to tune spin-orbit effects, *e.g.*, to suppress spin relaxation by orders of magnitude [1–3]. In a non-magnetic thin film, the anisotropy of the “Elliot-Yafet” spin-mixing parameter may be controlled by the film thickness and tuned to match experimental needs [4]. Interfacing with a magnetic layer, the chiral Dzyaloshinskii-Moriya interaction emerges [5], which can lead to the stabilization of chiral magnetic textures [5] or single magnetic solitons, such as antiskyrmions [6], and may be tuned by choosing different material combinations [7]. Finally, we explore the influence of disorder on magnetic properties within the Korringa-Kohn-Rostoker method, which utilizes the realistic Coherent Potential Approximation and reveal a rather peculiar stability of DMI against intermixing at the prominent Co/Pt interface [8].



Left: Spin hot-spots on the Fermi surface of tungsten.

Right: Antiskyrmions stabilized by anisotropic Dzyaloshinskii-Moriya interaction in 2Fe/W(110).

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Kirill Belashchenko

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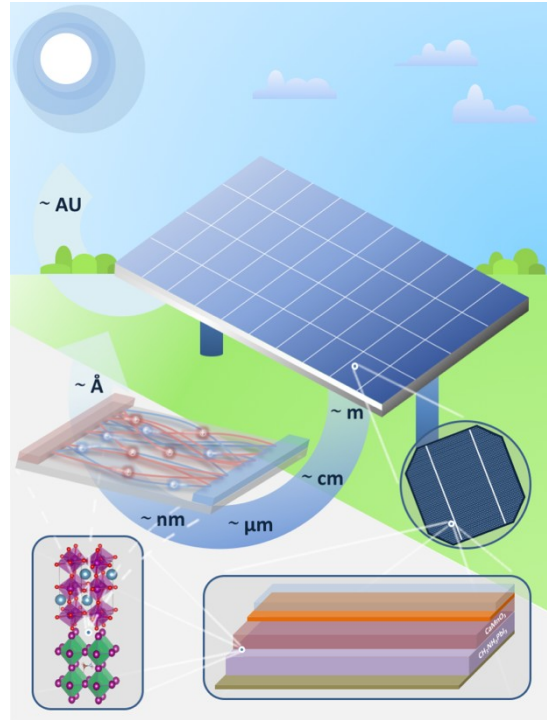
Spin-memory loss and spin-orbit torques

Igor Lukačević

Physics Department, Josip Juraj Strossmayer University of Osijek, Croatia

Perovskite-based transport layer for hybrid perovskite solar cells

The detailed analyses of interface properties and device performance of inorganic perovskite CaMnO_3 -based buffer layer hybrid perovskite solar cell have been undertaken. Analyses are based on both *ab initio* simulations and macroscopic Poisson model. A thorough study of electronic and optical properties and interface charge dynamics revealed that CaMnO_3 presents a better candidate for the electron transport material in thin film hole transporting material free hybrid perovskite solar cells with the planar architecture than the most common anatase TiO_2 . This result is founded on the more appropriate band gap and better band alignment with the hybrid perovskite, leading to the faster charge carrier mobility, improved charge transfer and reduced exciton recombination. The results of theoretical simulations are justified by the solar cell model, which explored the basic cell characteristics and parameters: open circuit voltage, short circuit current, fill factor and efficiency, as the functions of cell performance factors, like defect density, diffusion length, absorber layer thickness and band offset. Our model suggests an unoptimized device with a photo-conversion efficiency of almost 10% for the low defect concentrations under 10^{15} . With efficiency in the upper range for HTM free perovskite solar cells, we propose that the CaMnO_3 -based solar cell poses as an improvement upon the up to now most frequently used ones and provides an important step toward their commercialisation.



References

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Stefaan Cottenier

Center for Molecular Modeling, Ghent University, Belgium

“to boldly go where no experiment has gone before”

The goal of this conference was described as “to show what is possible to do with DFT and computational methods in materials science/physics”. The title of this talk sketches one of the possible answers: if experiments are too hard, too expensive, too dangerous or even just impossible to perform, then a computational approach can be an alternative. This will be illustrated by two case studies where computational materials science contributes to either the understanding of the inner core of planet Earth (too hard for experiments only) or to the design of fusion reactors (too dangerous for experiments). Furthermore, I’ll take the occasion to report on the development and adoption of www.compmatphys.org, a free self-paced online course on applied DFT.

Daniel Sánchez-Portal

Centro de Física de Materiales CSIC-UPV/EHU and DIPC, San Sebastián, Spain

Insights into nanoplasmonics from first-principles time-dependent density functional simulations

Our optimal implementation of time-dependent density functional theory within linear response allows computing the optical properties of systems with several thousands of atoms [1,2]. We applied this method to study the dependence of the near-field enhancement and localization on the structural details of the plasmonic nano-gaps [3,4], the different size dispersion of the plasmon resonance of silver and sodium nanoparticles and how this behaviour correlates with the

presence of 4d electrons in the Ag case [2], and more recently to describe valence EELS [5]. In this talk I will concentrate mostly in the correlation between transport properties across sub-nanometric metallic gaps and the optical response of the system. In Ref. [6] we presented a study of the simultaneous evolution of the structure and the optical response of a plasmonic junction as the particles forming the cavity approach and retract. Atomic reorganizations are responsible for a large hysteresis of the plasmonic response of the system, which shows a jump-to-contact instability during the approach process and the formation of an atom-sized neck across the junction during retraction. Our calculations show that, due to the conductance quantization in metal nanocontacts, small reconfigurations play a crucial role in determining the optical response. We observe abrupt changes in the intensity and spectral position of the plasmon resonances, and find a one-to-one correspondence between these jumps and those of the quantized transport as the neck cross-section diminishes. These results point out to a connection between transport and optics at the atomic scale at the frontier of current optoelectronics. The author acknowledges financial support from FP7 FET-ICT project No. 610446 project, MINECO (Grant No. MAT2013-46593-C6-2-P), the Basque Dep. de Educación and the UPV/EHU (Grant No. IT-756-13).

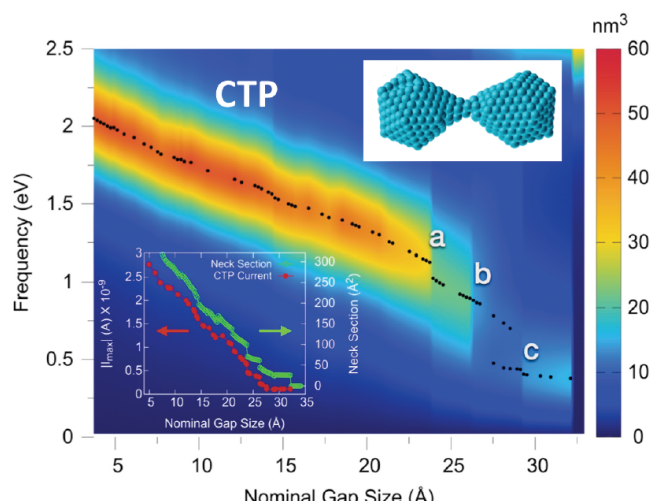


Figure 1: There is a one-to-one correspondence between the jumps in the current flowing through the metal neck, its cross-section and the far-field optical response at the frequency of the so-called charge transfer plasmon (CTP).

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Jiří Klimeš

Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Towards reliable theoretical description of molecular solids

Molecular crystals are materials important both in nature and industries. From methane clathrates at the bottom of the sea, over pharmaceuticals in pills, to carbon dioxide ice caps on Mars. For example, even at the same conditions, many pharmaceuticals can exist in different crystal structures, called polymorphs. One of these polymorphs is the most stable, but the others are usually very close in energy. If we want to reliably predict the energy ordering of different structures from simulation, we clearly need methods which are accurate enough. However, accuracy is not the only thing to consider. The results of the simulations depend on numerical parameters, such as the basis set size. If we want to benefit from the use of a highly accurate method, we need to converge the desired property with respect to the parameters, that is, the precision needs to be high as well. Doing calculations precisely is important if we want to understand how accurate a given method, such as some density functional theory (DFT) functional, is. Unfortunately, obtaining tightly converged results can increase the computational requirements substantially and can be even impossible for methods based on perturbation theory. I will show several examples to illustrate some of these issues. First, I will discuss the application of the random phase approximation (RPA) scheme and second-order Moller-Plesset perturbation theory (MP2) to molecular solids. The RPA is the least demanding correlated method available within periodic boundary conditions and, together with the so-called singles corrections, achieves an accuracy that surpasses state-of-the-art DFT functionals [1,2]. However, as correlated schemes, both MP2 and RPA suffer from slow convergence with respect to the basis-set size, or with the simulation cell volume if periodic boundary conditions are used. Nevertheless, converged results can be obtained. This allows us to understand the precision of an alternative scheme for calculating lattice energies of solids, the many-body expansion. Second, I will show that weak intermolecular interactions are very suitable to study and understand the precision of computational set-up. Moreover, I will give an example where such test identified a difference in implementation of a widely used DFT functional.

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Branislav K Nikolić

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Spin-orbit proximity effect in ferromagnetic metals: Fundamentals and spintronic applications

The control of recently observed spintronic effects in topological-insulator/ferromagnetic-metal (TI/FM) heterostructures is thwarted by the lack of understanding of band structure and spin texture around their interfaces. This talk will discuss our recently developed approach [1] to this problem where we combine density functional theory (DFT) with Green's function techniques to obtain the spectral function at any plane passing through atoms of TI (such as Bi₂Se₃) and FM (such as Co) or normal metal (such as Cu) layers comprising the interface. In contrast to widely assumed but thinly tested Dirac cone gapped by the proximity exchange field spectral function, we find that the Rashba ferromagnetic model describes the spectral function on the surface of Bi₂Se₃ in contact with Co near the Fermi level, where circular and snowflake-like constant energy contours coexist around which spin locks to momentum. The remnant of the Dirac cone is hybridized with evanescent wave functions injected by metallic layers and pushed, due to charge transfer from Co or Cu layers, few tenths of eV below the Fermi level for both Bi₂Se₃/Co and Bi₂Se₃/Cu interfaces while hosting distorted helical spin texture wounding around a single circle. These features explain recent observation of sensitivity of spin-to-charge conversion signal at TI/Cu interface to tuning of the Fermi level. Crucially for experiments on spin-orbit torque in TI/FM heterostructures [3], few monolayers of Co adjacent to Bi₂Se₃ host spectral functions very different from the bulk metal, as well as in-plane spin textures (despite Co magnetization being out of plane) due to proximity spin-orbit coupling in Co induced by Bi₂Se₃. I will also discuss spectral functions and spin texture at heavy-metal/FM (such as Ta/Co and Pt/Co) [2] and Weyl-semimetal/FM interfaces, as well as how DFT Hamiltonian of these heterostructures can be combined with Keldysh Green's functions to compute field-like and antidamping-like components of spin-orbit torque [3,5,6] or spin memory loss [2] at interfaces from first principles.

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Thomas Frederiksen

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Modeling tools for nanoelectronics

In this talk I will introduce the so-called DFT+NEGF method for simulations of electron transport in nanoscale junctions. This method is based on the nonequilibrium Green's function (NEGF) technique that allows to describe open quantum systems and to compute transport properties, in combination with density functional theory (DFT) to provide realistic atomistic and electronic descriptions of nanoscale devices. More specifically, I will provide an overview of the TranSIESTA [1] and Inelastica [2] DFT+NEGF codes, and describe some of our recent applications of these, e.g., the proposal of an electron beam splitter realized with crossed graphene nanoribbons [3] and a study to understand inelastic electron tunneling spectroscopy (IETS) experiments of graphene/SiC samples [4].

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Federico Grasselli

Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy

Charge-transport quantization and gauge-invariance of electrical conductivity in ionic fluids

Charge transport is observed in electronically insulating fluids, such as molten salts, where the ionic diffusion leads to a non-vanishing static electrical conductivity even in the absence of conducting electrons. Standard tools to study the electric transport in such systems are provided by molecular dynamics (MD): according to the Green-Kubo theory of linear response[1], the electrical conductivity can be extracted from the time-correlation function of electric currents in equilibrium MD simulations.

Despite the apparent simplicity of a naive classical description - where ions transport an integer, time independent, charge - in a first-principle framework the instantaneous electric currents are obtained from the Born effective charge tensors, which are real, tensor, and time-dependent quantities: a computationally time-consuming and conceptually abstruse task.

Interestingly enough, if we aim at the static electrical conductivity, the same results are exactly obtained if the Born tensors are replaced by the integer oxidation numbers of the atoms[2].

We discuss how a recently-formulated gauge-invariance principle of transport coefficients[3], together with arguments from charge-transport quantization[4], can be employed to understand the latter unexpected coincidence, providing an alternative method to compute first-principle electrical conductivity of ionic fluids[5]. Examples and numerical experiments are given for the case of molten potassium chloride.

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Pablo Ordejón

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Charge Density Waves in Transition Metal Dichalcogenides

I will present some of our recent work [1-5] on the understanding of the electronic properties of layered materials and their 2D relatives by means of first principles electronic structure calculations. In particular, the presentation will focus on the correlation between the crystal structure and the electronic properties, with special emphasis on the structural instabilities which have an electronic origin. This will be done in connection with recent experimental studies that have been able to demonstrate the presence of charge density waves (CDW) in several 2D single-layer materials like NbSe₂ and TiSe₂ and TiTe₂. For NbSe₂, we have focused on the nature and atomic displacements associated with the CDW. The evolution of the CDW with external electrostatic doping, which has been achieved experimentally using field effect transistor setups, will be analysed for the case of TiSe₂ [4]. For the case of TiTe₂, we focus on the recently observed CDW in the single layer, which is not present in the bulk material [5].

Work supported by European Union H2020-EINFRA-5-2015 MaX Center of Excellence (Grant No.824143) and Spanish MINECO (Grant No. FIS2015-64886-C5-3-P). ICN2 is funded by the Severo Ochoa Centers of Excellence Program under Grant SEV-2013-0295 and the CERCA Program/Generalitat de Catalunya. Funding from Generalitat de Catalunya (Grant 2017SGR1506) is also acknowledged.

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Phosphorene-based 2D Materials

In this talk, we will report the results of density functional theory calculations on phosphorene-based 2D materials including hybrid allotropes and extrinsic point defects of phosphorene, and phosphorene oxide. We will show that the electronic properties of phosphorene can be modified by the adatom functionalization. Additionally, the oxygen absorption may not degrade the phosphorene, and degree of the functionalization of phosphorene determines the electronic properties. This is reaffirmed by dependence of the diode-like asymmetric current-voltage response on the degree of stoichiometry for the phosphorene oxide.

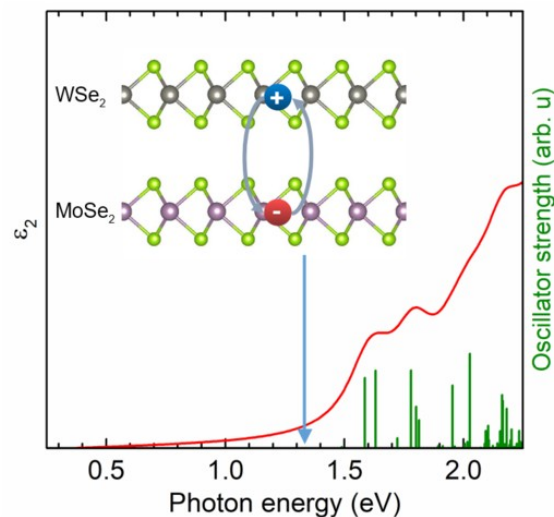
In collaboration with Gaoxue Wang and Shashi Karna.

Roland Gillen

Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Interlayer excitons in MoSe₂/WSe₂ heterostructures from first principles

Novel two-dimensional materials from the group of layered transition metal dichalcogenides (TMDC) have recently attracted scientific interest for their unusual physical properties, such as their strong optical response. Two possible ways to tailor the electronic and optical properties are (i) the combination of different TMDCs to form lateral and stacked heterostructures and (ii) creation of alloys containing different metal or chalcogen atoms. Recent experiments have found the occurrence of additional photoluminescence signals that have been attributed to long-lived interlayer excitons in stacked heterostructures, with spatial separation of electrons and holes across the layers, possibly allowing for exploitation in solar cells. We computed the theoretical absorption spectra of bilayer MoSe₂-WSe₂ heterostructures by solution of the excitonic Bethe-Salpeter equation with GW quasiparticle corrections [1] and inclusion of spin-orbit-coupling for three different stacking orders. Our calculations strongly suggest two qualitatively different contributions to the observed additional photoluminescence peaks: We find two spin-orbit split Rydberg series of low oscillation strength below the absorption onset of the monolayer materials, which arise from momentum-direct and spatially indirect excitations at the K point of the hexagonal Brillouin zone with a binding energy on the order of 250 meV. Additionally, our calculations firmly establish that the fundamental band gap of MoSe₂-WSe₂ heterostructures is indirect and has a distinct interlayer nature, possibly giving rise to a momentum- and spatially indirect contribution [2]. These results confirm the recent experimental observation of a doublet nature of the interlayer photoluminescence [3]. We further show that the local stacking order leads to small variations in the hybridization between the MoSe₂ and WSe₂ bands and has a decisive effect on the polarization dependence of the interlayer excitonic absorption [2]. Our results motivate detailed studies of electron-phonon coupling effects and exciton dynamics in TMDC heterostructures by time-resolved optical experiments and *ab initio* methods.



MoSe₂/WSe₂ heterostructures exhibit interlayer excitons below the absorption onset of the monolayer materials.

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Modelling Reactions in Biomolecules

Biomolecules are the most complex materials that exist. Moreover, at room temperature they are highly dynamic structures. Therefore, the theoretical/computational analysis of enzymatic or photochemical reactions in biomolecules is a very challenging problem that usually involves the exploration of a large conformational space. Recently we have developed a quantum mechanics / molecular mechanics (QM/MM) method for the simulation of reactions in biomolecules: *Fireball / Amber* [1]. This technique presents a very appealing balance between accuracy and computational efficiency. In this talk the application of this technique will be illustrated by means of three examples: (I) an enzymatic reaction (enzyme: triosephosphate isomerase) [2]; (II) proton transfer reactions in DNA [3]; and (III) a photochemical reaction in DNA [4].

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Ali Hassanali

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Computational Studies on Deciphering the Many Faces of Liquid Water

Despite long study many questions still remain regarding the physical and chemical properties of liquid water and how it changes in the proximity of interfaces. In this talk, I will highlight our work in using atomistic simulations to study both bulk liquid water as well as water near interfaces such as biomolecules, the surface of water and the oil-water interface. I will try to illustrate using various examples that a treatment of both electronic and nuclear degrees of freedom are needed for a complete molecular description of water - examples will include, studying the importance of charge transfer in bulk water at the air-water interface, describing the complexity of water networks around biomolecules, and finally density fluctuations in water and their role in creating inhomogeneities in the liquid. Some perspectives on open problems and challenges will also be highlighted.

Alexander Urban

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Atoms in Disarray: Simulating Disordered Materials

Substitutional disorder is a common phenomenon in inorganic solids in which multiple species occupy equivalent lattice sites in a crystal. Such disorder can have a profound impact on phase stability, ionic transport, the electronic structure, and other materials properties. For computation, disorder poses a challenge as the statistical description of disorder calls for extensive configurational sampling. Small defect concentrations may additionally require structure models with large numbers of atoms.

Here, I will recap some of the techniques available for the modeling of disordered crystals based on first principles. I will show how relatively simple approaches can enable significant insight into the inner workings of disordered energy materials.

Mark Saeys

Laboratory for Chemical Technology, Ghent University, Belgium

Operando computational catalysis – realistic structures, shapes and coverages

The structure and coverage of catalysts under reaction conditions often differs dramatically from the ideal models often used in computational catalysis. By incorporating effects of pressure and temperature in our simulations, we describe how ideal surfaces undergo a massive reconstruction to form active sites under reaction conditions, and how some particles change shape, while others don't. In combination with operando microscopy, the dynamics of catalyst systems is finally revealed. While catalyst surfaces are often highly covered by reactants and reaction intermediates, many computational models still use ideal clean surfaces. For Fischer-Tropsch synthesis and for ketone hydrogenation, we find that coverage effects change both the activity and the selectivity of the kinetic model and are hence critical ingredients in next generation computational models.

Peter Saalfrank

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Non-adiabatic molecular dynamics at surfaces

Non-adiabatic effects, i.e., the violation of the Born-Oppenheimer approximation due to strong electron-nuclear coupling, are ubiquitous in the dynamics of molecules near solid surfaces. Nonadiabatic effects are particularly important in substrate-mediated or direct surface photochemistry and femtochemistry, but also for processes considered as proceeding typically in the electronic ground state, in particular at metal surfaces: The electron-mediated vibrational relaxation of adsorbed or scattering, vibrationally excited molecules is an example, the occurrence of “chemicurrents” and exoelectron emission another.

Fully quantum, multi-dimensional dynamical approaches to treat non-Born-Oppenheimer dynamics are unfeasible in most cases and / or rely on far-going model assumptions. Recent years have seen the emergence of powerful tools based on classical dynamics, however, which are feasible but nevertheless account for non-adiabatic effects. One such approach is (Langevin) Molecular Dynamics with Electronic Friction (MDEF), either on precomputed potential energy surfaces or “on the fly”. When coupled with Density Functional Theory (DFT) for forces and the Local Density Friction Approximation (LDFA), this method, allows for parameter-free, multi-dimensional molecular dynamics accounting for non-adiabaticity in an approximate, indirect way. A more direct approach to classical non-adiabatic dynamics is so-called “surface hopping”, i.e. classical dynamics on multiple, non-Born-Oppenheimer coupled potential energy surfaces.

In the present contribution, we illustrate the methodologies for both approaches, MDEF and “surface hopping”, and apply them to selected problems of surface science. MDEF is applied to femtosecond-laser induced, associative desorption of oxygen molecules from an Ag(110) surface [1] or molecular hydrogen from Ru(0001) [2,3], and to femtosecond-laser induced processes in CO/Ru(0001) [4] and CO/Cu(100). Surface hopping is realized within a semiempirical electronic structure method (AM1/CI), and applied to the photoisomerization of azobenzene molecules on solid substrates [5,6].

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Maria KY Chan

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Modeling catalysts - pushing the accuracy frontier and connecting with experiments

The effective prediction of catalytic processes hinges on (1) accurate determination of the catalyst structure, and (2) accurate computation of adsorption energies of reacting molecules on catalyst surfaces. In this talk, we will discuss advances in (1) integrating experiments and computational data via machine learning and (2) the use of quantum Monte Carlo (QMC) that allows us to advance predictive catalysis modeling on these two fronts. In particular, I will discuss an automated framework for the determination of precious metal nanocatalyst structure using a combination of density functional theory calculations and x-ray pair distribution function data, and the use of QMC to investigate adsorption of CO on transition metal oxide surfaces.

Volker L. Deringer

Department of Engineering, University of Cambridge, UK

From Machine-Learning Interatomic Potentials to Materials Chemistry

Understanding the links between atomic structure, chemical bonding, and macroscopic properties in materials is a formidable task. Quantum-mechanical atomistic simulations, prominently based on density-functional theory (DFT), have played important roles in this – but they are computationally expensive, and can describe complex materials only in small model systems. Novel interatomic potentials based on machine learning (ML) have recently garnered a lot of attention in the computational materials-science community: they achieve close-to DFT accuracy but at only a fraction of the cost.

In this talk, I will argue that ML-based interatomic potentials are particularly useful for studying materials with complex structures, such as amorphous (non-crystalline) solids. I will first describe an ML potential for amorphous carbon [1] using the Gaussian Approximation Potential (GAP) framework [2], with a special view on what is needed to validate ML potentials for the amorphous state. I will then present an application to porous and partly "graphitized" carbon structures, which are relevant for applications in batteries and supercapacitors [3]; this includes a new ML strategy for simulating the movement of Li ions in such materials [4]. Finally, I will present recent work on amorphous silicon (*a*-Si), another prototypical non-crystalline material, where ML-driven simulations allowed us to unlock long simulation times and accurate atomistic structures [5], again making steps toward the routine and realistic atomic-scale modelling and understanding of the amorphous state.

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Nongnuch Artrith

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Development of efficient and accurate machine-learning potentials for the simulation of complex materials

Many complex materials for energy applications such as heterogeneous catalysts and battery cathode materials have compositions with multiple chemical species and properties that are determined by complex structural features. This complexity makes them challenging to model directly with first principles methods. As an alternative, machine-learning techniques can be used to interpolate first principles calculations. Such machine-learning potentials (MLPs) enable linear-scaling atomistic simulations with an accuracy that is close to the reference method at a fraction of the computational cost. Here, I will give an overview of recent applications of MLPs based on artificial neural networks (ANNs) [1] to the modeling of challenging materials classes, e.g., nanoalloys in solution [2], oxide nanoparticles [3], and amorphous alloys [4].

The original multi-species ANN potential formalism [5] scales quadratically with the number of chemical species. This has previously prevented the modeling of compositions with more than a few elements. To overcome this limitation, we have recently developed an alternative mathematically simple and computationally efficient descriptor with a complexity that is independent of the number of chemical species [6,7]. The new methodology has been implemented in our free and open source atomic energy network (aenet) package (<http://ann.atomistic.net>) [7]. This development creates new opportunities for the modeling of complex materials for example in the field of catalysis and materials for energy applications.

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Joohwi Lee

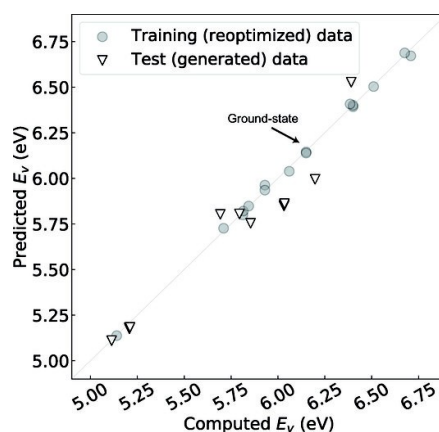
Toyota Central R&D Laboratories, Inc.

Efficient algorithm for discovery of crystal structures for oxygen-ion conductors beyond data mining

Materials discovery based on first principles calculations have been widely used to develop better functional materials for the applications with advantage of its accuracy and efficiency. Machine learning techniques have been often applied to the crystal structure database in order to screen pre-existing materials having new functional properties. However, to find a new functional material beyond pre-existing database, one needs to develop a clever and efficient way to construct adequate crystal structures with optimum functional property.

For discovery of fast oxygen-ion conductors, it is important to find crystal structures with a low formation energy (E_v) and a migration-barrier energy (E_m) with respect to an oxygen vacancy. The E_v and E_m are strongly correlated so we employed E_v as a descriptor for searching good oxygen-ion conductors. For the zirconium dioxide (ZrO_2) system, we used two efficient ways of crystal structure generation [1]; firstly, we reoptimized the crystal structures of various metal-dioxides in database with total substitutions of Zr for metals (reoptimized- ZrO_2), then, we directly generated the crystal structures (generated- ZrO_2) using evolutionary algorithm [2]. As a fitness value for the evolutionary algorithm, we employed the predicted E_v estimated by the linearized ridge regression based on eleven descriptors that can be obtained at the density-functional-theory level. As the training data of the regression model, the computed E_v values of reoptimized- ZrO_2 were used. The evolutionary algorithm tries to construct the crystal structure with low E_v for thirty cycles. The optimizations of crystal structures of reoptimized- ZrO_2 and generated- ZrO_2 , and computations of the E_v value were performed by first-principles calculations.

As figure 1 shows, the prediction error between predicted and computed E_v for the fourteen generated- ZrO_2 is small as 0.16 eV. The lowest E_v between generated- ZrO_2 is ~ 1 eV lower than that of the ground-state ZrO_2 . In addition, these crystal structures with low E_v are confirmed to have also low E_m . This suggests that a direct generation of the crystal structures with high oxygen-ion conductivity (considering low E_v and E_m) is successfully done on the basis of a combination of evolutionary algorithm, regression method, and first-principles calculations. We expect that this method can be applicable to other oxide systems in finding crystal structures with other optimum functional property.



Caption: Relationship between the predicted and computed eV of crystal structures of ZrO_2 .

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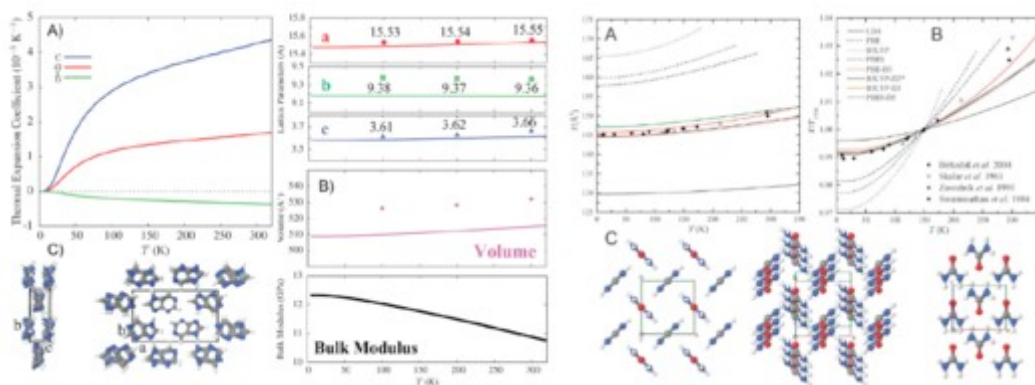
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A Song of Ice and Fire: First-principles Modeling of Thermal Properties of Molecular Crystals and MOFs

Quantum-mechanical calculations based on the density functional theory (DFT) represent an effective mean to the determination and rationalization of many advanced properties of materials. The inclusion of thermal effects on computed condensed matter properties would allow to significantly extend their use towards a broader range of applications and of classes of materials and yet constitutes a formidable challenge to state-of-the-art methodologies. Indeed, while the opening of a new age of molecular *ab initio* quantum-chemistry has recently been declared (“*In the fourth age we are able to incorporate into our quantum chemical treatment the motion of nuclei [...] and compute accurate, temperature-dependent, effective properties, thus closing the gap between measurements and electronic structure computations*”) [1], we are still far from having general-purpose, robust and efficient implementations of thermal effects in a solid state context. This is particularly so when the limitations of the harmonic approximation (HA) have to be overcome: null thermal expansion, elastic response independent of temperature, equality of constant-pressure and constant-volume thermodynamic functions, infinite thermal conductivity as well as phonon lifetimes, etc. This is particularly relevant to the study of molecular crystals and metal-organic frameworks (MOFs) of pharmaceutical and catalytic interest. Owing to their weakly-bound, soft chemical nature, these materials are indeed significantly affected by temperature even at ambient conditions. A proper account of thermal effects on these materials often requires to go beyond the harmonic approximation. In this contribution, I discuss some of the methodologies that I have implemented in recent years into the public CRYSTAL program in order to include thermal effects (beyond the harmonic approximation) on computed structural, mechanical, thermodynamic, electronic properties of solids [2]. Examples will be given on the application of these methods to several molecular crystals and MOFs [3].



Caption: Anisotropic thermal structural properties of two molecular crystals: purine and urea.

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Thermoelectric properties of TiNiSn and TaCoSn half-Heusler alloys through ab-initio calculation and experiments

Keywords: thermoelectric materials, half-Heusler alloys, ab-initio, Seebeck coefficient, power factor

Thermoelectric materials are novel materials that convert waste heat directly to electricity. These materials pave a way to reduce greenhouse gas emissions and promote sustainable development. Half-Heusler alloys, with chemical composition as XYZ where X, Y = transition/Nobel/rare-earth element and Z = main group element, are classic examples of thermoelectric materials with potential applications in spintronics, solar cells and data storage

In this work, we used the CRYSTAL code to study thermoelectric properties of half-Heusler alloys, in particular, TiNiSn and TaCoSn. We compared our results to experimental results obtained in an independent parallel investigation. Experimental thermoelectric characterization was performed on single phase TiNiSn half-Heusler alloys prepared by arc melting followed by suitable annealing.

The CRYSTAL program [1,2,3] is a powerful computational tool for the *ab initio* study of crystalline solids, that is hereby applied to the simulation of transport properties of alloys. Thanks to the use of a local (Gaussian) basis set, the band velocities are easily and accurately obtained as analytical derivatives of electronic bands [3], within small computational costs, and the possibility of using hybrid functionals (such as PBE0) can be used routinely.

Electrical conductivity and Seebeck coefficient were computed as a function of the charge carrier concentration at different temperatures. We also compute the power factor as a function of temperature.

In addition, we computed the carrier concentration and compared it with experimental values obtained by measurement of the Hall effect between 4 K and 400 K. In the same temperature range, electrical conductivity and Seebeck coefficient were measured for a complete comparison with the computed thermoelectric properties.

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Dino Novko

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A first-principles approach to non-equilibrium vibrational dynamics

Pump-probe vibrational spectroscopy is one of the most valuable experimental tools for studying photo-induced ultrafast phonon or nuclear dynamics. Here I present a theoretical framework based in first principles that is able to simulate non-equilibrium dynamics of phonons in metallic systems. The main relaxation mechanism in this approach is coupling between hot electrons and system phonons (i.e., nonadiabatic coupling under non-thermal condition). Using this universal theory I study two different examples: laser-excited non-equilibrium (i) motion of molecular overlayer of CO on the Cu(100) [1,2] and (ii) dynamics of E_{2g} phonon mode in MgB₂ superconductor [3].

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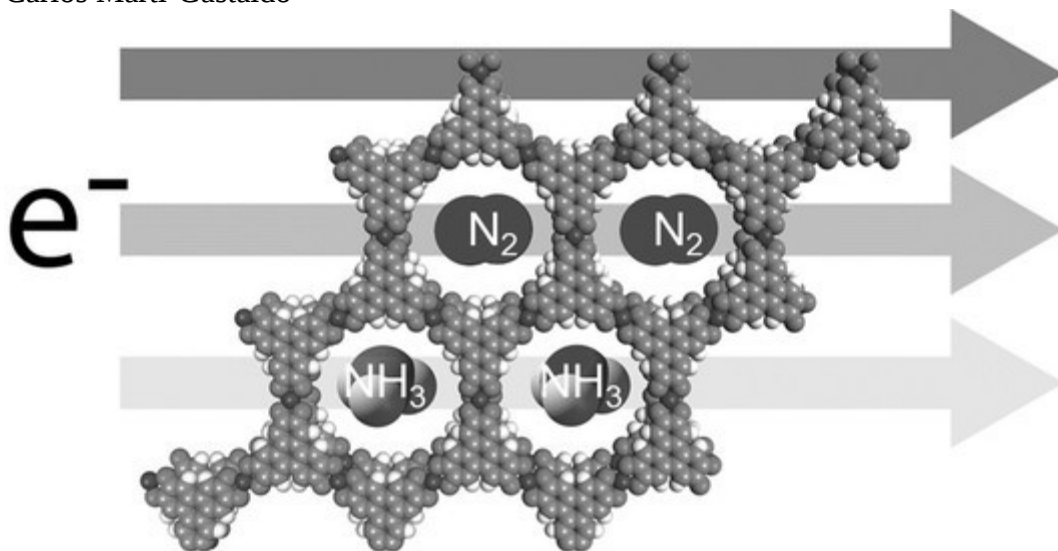
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Guest-modulation of semiconducting behaviour in two-dimensional Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) are porous coordination polymers built from the interlinking of metal clusters and organic linkers. MOFs have already demonstrated great potential in gas storage, separations, sensing and catalysis. Nowadays there is an increasing interest in developing an advanced generation of electronic and optoelectronic devices that make use of electrically active MOFs to exploit combination of electrical conductivity and porosity[1]. An excellent example of the functionalities accessible by combining porosity and electrical conductivity in a solid device is the recent development of chemiresistive sensors capable of transducing the presence of specific guests into an electrical response with good selectivity and sensitivity[2]. These works experimentally confirm that there is a direct dependence of the electrical response with MOF/guest interactions that can be also modified for different metal nodes. However, further information that helps to unveil the exact mechanism controlling this phenomenon is still missing. By combining experimental data with computational modelling, we describe a possible origin for the underlying mechanism of this phenomenon in ultrathin films of Cu-CAT-1. Our results suggest that changes to the electrical conductivity in ultrathin films are controlled by the ability of the guest to coordinate to the open metal sites in the 2D MOF layer. Molecules capable of stronger interaction like NH₃ or H₂O can induce a change in the coordination geometry that has a direct impact over the electronic structure of the solid and its electrical response[3].

In collaboration with: Garin Escorcia-Ariza, Víctor Rubio-Giménez, Marta Galbiati, Sergio Tatay, Carlos Martí-Gastaldo



Caption: Understanding of electrical response with MOF/guest interaction phenomenon in ultrathin films of Cu-CAT-1, which was possible through synergy between experiment and simulation.

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Mihovil Bosnar

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Efficient spin gating with van der Waals heterostructures

We consider a possibility of operation of a device by which spin polarization of the current passing through it can be modified significantly using small electric fields, that is by which spin currents can be efficiently gated. Such a device could potentially find place as a building block for high performance spintronic devices [1]. The core of device would be an interface between a ferromagnetic metal (e.g. cobalt) and graphene. The small density of states (DOS) of graphene near the Fermi level and its two-dimensional nature would cause a significant shift in DOS at the Fermi level, and hence conductivity, in response to even the small gate electric fields, while the magnetic proximity effect would ensure that the shift is spin dependent.

We find, however, that graphene and cobalt bind chemically and thus convenient electronic structure of graphene is lost, making the desired response to the electric field absent [1]. To preserve graphene's electronic structure, as well as keep the desired spin dependent response, we find it sufficient to add an additional layer of two-dimensional insulator, such as hexagonal boron nitride, between the metal and graphene [1] to which graphene would bind by van der Waals force. Still, because of the strong doping of graphene because of the chemical potential equilibration, the shift in the spin components of DOS at small external fields in such a metal - van der Waals heterostructure interface is not large enough for gating to be efficient. To counteract this unwanted doping we added a platinum layer to the structure, in two different configurations. The effect of the platinum layer seems favorable for intended application in both of them. The open questions are the effect of the gate field on the structures with platinum, as well as more detailed calculation of conductivity in all proposed structures.

In collaboration with: Ivor Lončarić, Predrag Lazić

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Theory of phonon-assisted luminescence in solids: application to hexagonal boron nitride

Common wisdom dictates that only direct band gap materials are good light emitters, while indirect band gap materials such as silicon are poor light emitters. It therefore came as a surprise when it was discovered that hexagonal boron nitride (h-BN), despite being an indirect band gap material, is a very efficient light emitter [1]. This original observation has motivated a large body of literature attempting to explain the microscopic origin of this unconventional phenomenon [2], but so far no satisfactory solution to this problem has been provided. In this work we propose a new theory of phonon-assisted luminescence in solids, and present its first implementation in an ab initio context. Equipped with this new theory, we are able to calculate fully from first principles the finite temperature luminescence of h-BN, and demonstrate that the strong emission observed experimentally arises from the interaction between lattice vibrations (phonons) and electron-hole pairs (excitons). Our work not only rationalises the microscopic origin of efficient light emission in an indirect band gap material, but also provides a full theory of exciton-phonon coupling, that we expect will be widely applicable in many areas of condensed matter physics. Of particular interest will be the areas of 2-dimensional materials in which exciton binding energies are large, and also applications in solar cells, LEDs, and related optoelectronic devices which rely on efficient luminescence for their operation.

In collaboration with: Bartomeu Monserrat, Claudio Attaccalite

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On Optimizing Gaussian Basis sets for Crystalline Solids

CRYSTAL is a well known ab initio code for solid-state quantum-mechanical simulations; one of its peculiar aspects, is that it is based on Gaussian type functions[1]. Although the local nature of the basis allows an accurate description of the electronic distribution in periodic systems, allowing for the easy and relatively cheap use of hybrid functionals, the calibration-optimization of exponents and coefficients for each atomic species is quite often not straightforward. Despite recent attempts, standardized and well-assessed libraries of basis sets are not available for solids as they are for molecules. One reason for that, is the wide chemical diversity of different solids, where the same atomic species can be present as an ion, a covalently bonded atom, or involved in a metallic bond. For all of these reasons optimization of a basis set can be system specific and is, nowadays, often left in the hands of the user. In this view we have developed a novel method to optimize the basis sets, that we call BDIIS (Basis set Direct Inversion of Iterative Subspace). The method is an application of the well known DIIS algorithm[2] to the optimization of basis sets, in the spirit of its geometry-optimization variant (GDIIS)[3]. The DIIS method is today a standard tool in quantum chemistry and provides a significant acceleration of the SCF (self-consistent field) convergence rate. The method involves the construction of a suitable error vector at each iteration and its minimization implicates the SCF convergence. In a similar manner, BDIIS requires the construction of an error vector that in this case instead of being related to SCF parameters, is based on previous values of both exponents and coefficients. A double-sided numerical derivatives are used as gradients and they are scaled by a suitable scale factor obtained by a line search method. We implemented the BDIIS algorithm in the CRYSTAL code[1] and in this contribution details of the method and first results will be presented.

In collaboration with: Lorenzo Maschio

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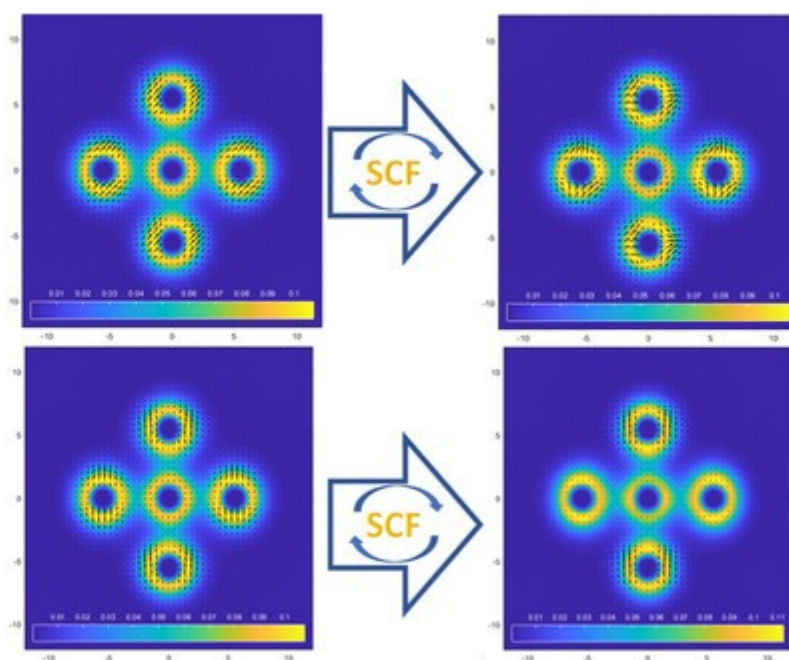
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Self-consistent treatment of spin-orbit coupling for two-component Hartree-Fock and DFT calculations with the CRYSTAL code: lessons learned on molecules

The CRYSTAL [1] code for quantum-mechanical simulations of periodic systems is based on a linear-combination of atomic-orbitals (LCAO) framework. Crystalline orbitals are expressed as a linear-combination of Bloch functions that are in turn defined using a basis-set of solid-spherical Gaussian-type functions (GTF). The use of the GTF basis-sets has advantages and disadvantages over other approaches, such as plane-wave basis sets. Some of the advantages are the following i) a greater chemical intuition of the results of the calculation; ii) a more direct transferability of molecular quantum-chemical methods; iii) the possibility of modeling real 0D, 1D, 2D systems without fictitious structural repetitions along non-periodic directions; iv) a natural description and greater efficiency in calculating local properties; v) a greater ease in the efficient evaluation of non-local Fock exchange series that is beneficial to the inclusion of a portion of Fock exchange in hybrid functionals of the density functional theory (DFT), as well as for Hartree-Fock (HF) based (or wavefunction based) methods. The code was first made public in 1988 and has undergone major public releases every 3-4 years, up to CRYSTAL17. [1] During these decades, the code has been used for non-relativistic all-electron calculations, as well as scalar-relativistic (i.e. without spin-orbit) calculations using scalar-relativistic effective-core (or pseudo) potentials (ECP). Here we generalize the CRYSTAL code to perform fully relativistic calculations, using spin-orbit (SO) ECPs with a two-component relativistic self-consistent-field (SCF) procedure for HF and DFT calculations. One of the consequences of the SO effects is the emergence of non-collinear magnetic structures. The treatment of the SO ECPs follows a theory initially formulated for molecules by Ermler and co-workers. [2] Initial results are presented on molecular systems. In particular, we discuss algorithmic and theoretical considerations for the treatment of non-collinear magnetism in the DFT, for which numerical instability challenges and concerns on its proper theoretical formulation have been acknowledged before. [3] We find that problems related to numerical instabilities and proper invariance properties can both be rectified by either using a modified set of density and magnetization variables in the definition of the functional or by including a fraction of Fock exchange in its definition. We also discuss the development of tools for the definition of a non-collinear magnetic starting guess, which can be indispensable for convergence to the proper magnetic structure. As an example of the effect of the starting guess on the converged magnetic structure, in Figure (a) we show the magnetization field before and after the SCF for two different starting guesses on an Fe_3 cluster. In this case, convergence to the lower energy structure (top right panel) is clearly only achieved using the uppermost non-collinear starting guess.



Caption: Magnetization and total density distributions for an I_5^+ cluster. The coloured contours represent the total density (or particle number density), while the arrow direction and length represent the magnetization direction and magnitude. All quantities are plotted in atomic units. The left-most panels are plotted after the first diagonalization of the SCF, while the right-most panels are plotted at convergence of the SCF. The lower energy magnetic structure (top-right panel) is only obtained using the starting guess from the top-left panel.

In collaboration with: Alessandro Erba, Jean-Pierre Flament

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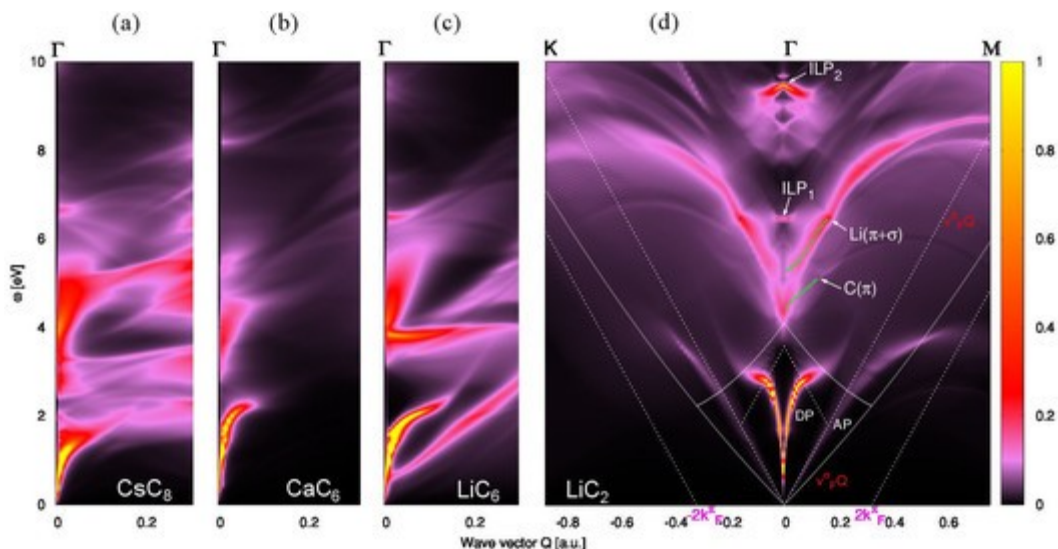
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Electronic excitations in alkali-intercalated graphene

Pristine graphene supports only interband plasmons, and the dominant modes are π and high energy $\pi + \sigma$ plasmons [1]. The doping causes the appearance of the “tunable” Dirac plasmon in the graphene. However, for experimentally feasible dopings it is usually very weak and broad. Therefore, nowadays graphene is being intercalated with various alkali and alkali earth metals, with very different motives. One is to explore the possible superconductivity of such compounds, another is to restore the original properties of free-standing graphene which has been modified by the presence of a substrate (in which case low coverage is preferred), and the third one is to modify the plasmonic properties of the graphene. This last feature is the most interesting from our point of view and we therefore present it in detail, focusing especially on the lithium intercalated graphene. The intercalated alkali metal donates electrons to the graphene causing the electronic doping of the graphene π band, in a way that the metallic (parabolic) σ band remains partially filled. This results in the formation of two quasi two-dimensional plasmas and also adds new bands to the graphene band structure, opening possibilities for the intraband and interband electronic transitions not possible in the pristine or doped graphene. For example, most of these systems support not one, but two intraband plasmons [2], acoustic and Dirac, with frequencies up to 4eV, as well as various interband modes which occur at higher frequencies, and can be intra-layer and inter-layer [3], as can be seen in Fig.1. Because of the heavy doping, the Dirac plasmon is very strong, while the interband and especially the inter-layer modes can be optically active in the visible and UV frequency region and therefore interesting for optical applications. In addition to that, some of these modes can be manipulated, and even switched on and off, by doping. We present how the choice of the intercalated metal and the coverage, i.e. the intensity of the electronic doping influences the spectra and tunes the intensities of the plasmon modes.



Caption: The intensities of the electronic excitations in CsC8, CaC6, LiC6 and LiC2 monolayers.

In collaboration with Leonardo Marušić.

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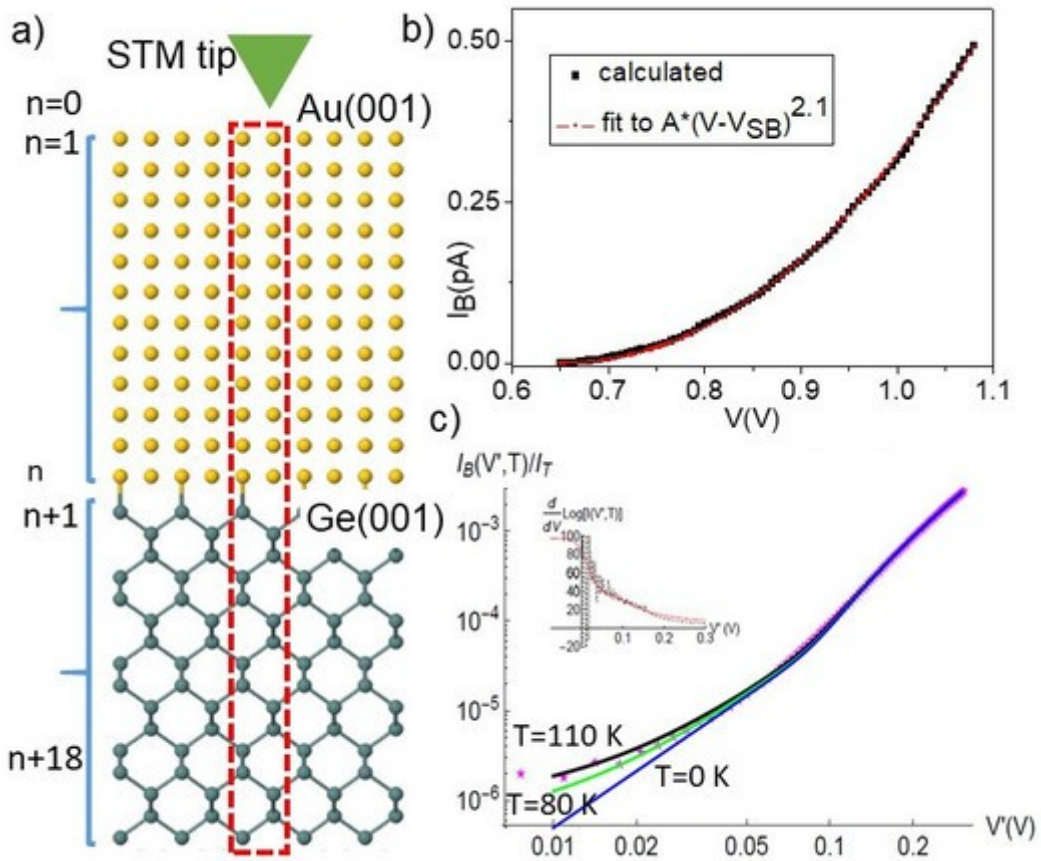
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Modelling the electronic transport in a Ballistic Electron Emission Microscope using ab initio calculations

A new theoretical model for the simulation of the electronic current in a Ballistic Electron Emission Microscope (BEEM) fully based on ab initio data is presented. Based on the Scanning Tunneling Microscope (STM), BEEM measures the electronic current collected after a metal-semiconductor interface placed far away from the metallic surface. This technique allows the study of the corresponding Schottky barrier formed in such interface. The previous proposed models took into consideration only a semi-infinite metallic part joined to the semiconductor by a semiclassical approach, while the revised method has been generalized to make accessible the analysis of new interesting and promising systems in spintronics, including ferromagnetic thin films or (mono)layers of organic molecules. Our new layer-by-layer procedure allows the simulation of both large and thin metallic regions using the Keldysh Green function formalism [1]. The atomic and charge redistribution at the interfacial structure is taken into account through its relaxation with the Density Functional Theory (DFT) FIREBALL code [2]. In a final step, a semi-infinite semiconductor is connected creating a realistic interface. As a first result, we should highlight that the three parts of the problem (metal, interface and semiconductor) can be simulated using an accurate ab initio parametrization. As a proof of concept, we have applied our new developed methodology to analyze the well-known Au(111)/Si(111) interface and the recently measured Au(100)/Ge(100) interface (see the scheme in Figure 1a) [3]). Our theoretical calculations can reproduce the experimental results for both cases. On the later metal-semiconductor interface, our theoretical results can fit, without using adjustable parameters, to new precise Ultra-High Vacuum, low-Temperature experimental measurements performed by A. Gerbi and R. Buzio from CNR-Spin in Genova. Although for a voltage (V) close to the Schottky barrier (V_{SB}) temperature effects become significant, we show that at $T = 0$ K the theoretical current follows, in the Au/Ge interface, closely the law $(V-V_{SB})^{2.1}$ (see Figure 1b). The inclusion of the temperature effect leads us to identify two slightly different values for the Schottky barrier located at 0.67 and 0.75 eV that we associate to different patches forming the interface. As Figure 1c) shows, a very good fit is obtained for $T=110$ K close to the experimental temperature ($T=80$ K).



Caption: a) Ball-stick model of the Au(100)/Ge(100) interface (the red square shows the unit cell used), b) fit of the theoretical BEEM current to $(V-V_{SB})^n$, c) best fit to experimental values (stars), assuming $n=2.1$ and two VSB for $T = 110$ K, 80 K and 0 K.

In collaboration with P. de Andrés and F. Flores.

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Color properties of materials: a multi-scale computational approach for anthocyanins dyes in solution

Anthocyanins are among the most abundant natural pigments, which, depending on the chemical environment (such as acidity and copigmentation), give rise to a variety of colors and shades in the red-purple-blue gamut. In spite of the ubiquity and potential applications of anthocyanins, the mechanisms underlying their exceptional photophysical versatility are not yet fully understood.

In this work we introduce a new multiscale modeling protocol to study the optical properties of complex molecular species in solution and apply it to the photophysics of anthocyanins in a broad pH range (1-9). Our protocol is based on enhanced sampling from classical force-fields based molecular dynamics (MD), advanced statistical analysis to identify the relevant molecular conformers, ab-initio MD in explicit solvent to accurately sample thermal fluctuations within individual conformers, and time-dependent density-functional theory to compute absorption spectra on selected molecular frames [1].

Our simulations reveal that the broad range of colors expressed by anthocyanins crucially depend on a subtle combination of different structural and electronic traits, as determined by thermal fluctuations and/or molecular distortions impacting on the electronic conjugation. This finding allowed us to rationalize the spectroscopic behaviour of anthocyanins in terms of factors such as the overall molecular charge (modulated by pH) affecting the relative character and energy of frontier orbitals; the bond-order between the aromatic moieties of the chromophore as coupled to the corresponding dihedral angle; the fluctuations of other slow degrees of freedom and the role of the solvent [1].

In collaboration with Mariami Rusishvili, Sara Laporte, Alessandra Magistrato and Stefano Baroni.

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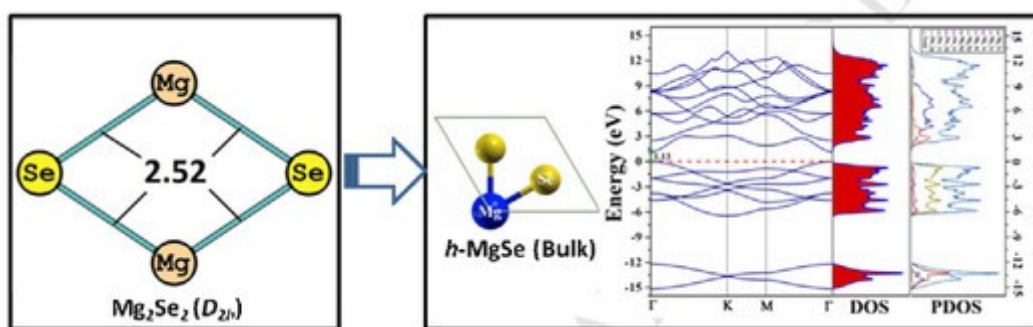
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2D and bulk h-MgSe materials from MgmSen (m, n = 1 - 3) clusters: Density functional investigation

An investigation in detail on the structure, electronic and thermodynamic properties for a series of group II and VI Combined hybrid alloy clusters, viz, MgmSen (m, n = 1 - 3) is performed, under density functional theory (DFT). The geometries of all clusters have been optimized by employing a very popular and reliable exchange-correlation functional, viz, Becke's parameter exchange with Lee-Yang-Parr correlation functional (B3LYP). The influence of adding of group II and/or group VI elements on the electronic properties is also addressed in the present work. A sincere effort has been tendered to identify any potential cluster motif from the considered series for utilizing as the building block for prospective metal-insulator-semiconductor (MIS) materials at the bulk scale. Accordingly, with an achievement of exceptionally stable rhombus shaped and D_{2h} symmetric Mg₂Se₂, we have investigated structure and electronic properties of 2D hexagonal magnesium selenide (2D h-MgSe) as well as hexagonal magnesium selenide at bulk scale (bulk h-MgSe). It is evident from the present study that although 2D planar h-MgSe reveals as an insulator with the direct band gap 4.20 eV whereas bulk h-MgSe come out to be a semiconductor material with direct band gap as 1.13 eV. The bulk h-MgSe phase is reported to be an exceptionally stable semiconductor in the magnesium selenide family.



Caption: Cluster unit cell and its bulk form

In collaboration with Debesh R. Roy.

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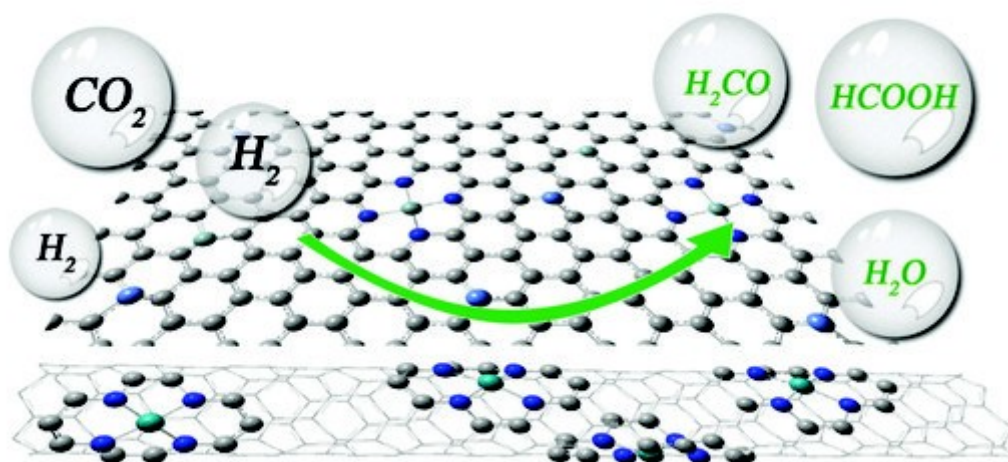
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RuN4 embedded graphene and carbon nanotube for CO₂ hydrogenation

Unraveling mechanisms of CO₂ hydrogenation to value-added chemicals such as formic acid is of importance in the context of renewable energy storage [1,2]. We use density functional theory (DFT) calculations to study the catalytic activity of RuN₄-graphene (RuN₄-G) and RuN₄-carbon nanotube (RuN₄-CNT) as well as the effects of Ru-doping on the adsorption of reactants, activation barriers, and thermodynamic properties toward the hydrogenation of CO₂. Based on the adsorption energies, we predict that in presence of CO₂ and H₂ reactants, all active surface sites are quickly covered by H₂ molecules. Both direct and indirect hydrogenation mechanisms for conversion of CO₂ to formic acid on both RuN₄-G and RuN₄-CNT are found to be possible. The indirect hydrogenation mechanism results in the formation of formic acid (HCOOH), as well as two other by-products, viz. formaldehyde (H₂CO) and water (H₂O). In the direct hydrogenation mechanism, the formic acid will be dominantly produced. We find that direct and indirect hydrogenation of CO₂ are showing a lower activation barrier on RuN₄-G and RuN₄-CNT, respectively, while the thermodynamic properties are better in the case of RuN₄-CNT than in the case of RuN₄-G. Generally, we suggest that RuN₄-CNT can efficiently catalyze the CO₂ hydrogenation reaction since the reaction proceeds spontaneously and with low energy barrier. Our results provide new insights into the nature of CO₂ conversion and may serve as guidance for fabricating effective and costless graphene-based catalysts.



Caption: CO₂ hydrogenation catalyzed by RuN₄-doped graphene and carbon nanotube

In collaboration with Erik Neyts.

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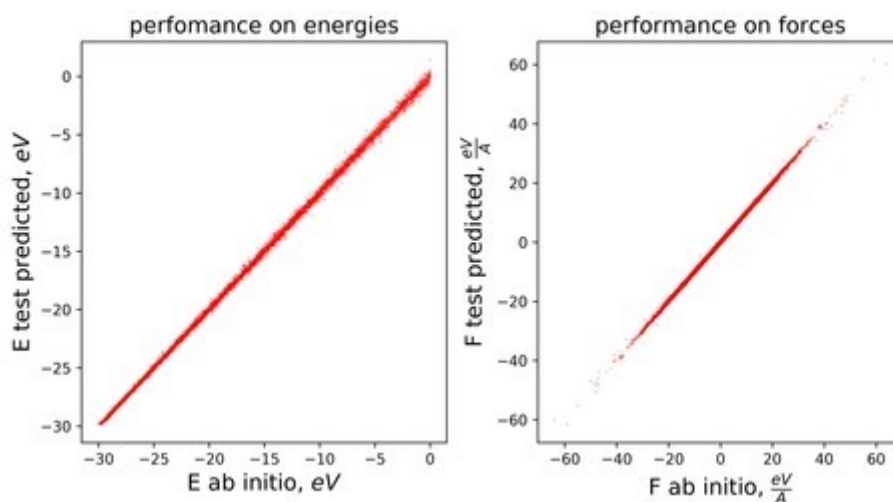
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Fast general two- and three-body potential

In computational chemistry the majority of calculations are performed within Born-Oppenheimer approximation and the concept of potential energy surface (PES) is introduced as the functional dependence of the potential energy on atomic positions. The PES can be calculated very accurately by performing ab initio electronic structure calculations, but such calculations are computationally very demanding. So there exist two possible ways to get around this problem - empirical interatomic potentials and machine learning potentials. The former are very fast, but have limited accuracy. The later represent the compromise between ab initio calculations and empirical interatomic potentials.

In this talk I will present a recently developed fast general two- and three-body potential, which is as fast as empirical interatomic potentials and has competitive accuracy with machine learning potentials for some systems. In our potential we use two- and three-body interactions, which led to the energy being expressed as sum of energy contributions related to pairs and triples of the atoms. Any pairwise and three-body energy contributions can be approximated arbitrarily close not affecting the evaluation time. After fitting is done, the complexity of predicting both energies and forces is $O(1)$ for every considered pair and triple. Additionally the fitting procedure is very simple and comes down to solving a linear regression problem.



Caption: Performance on aluminum

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Phase transitions of Sb₂Se₃, Sb₂S₃ and Bi₂S₃ under compression

Sesquichalcogenides are compounds with A₂X₃ stoichiometry (where A is a trivalent cation and X=S,Se,Te) which have gained major interest because of their many interesting applications. Moreover, high-pressure effects have greatly been considered in the last few years since the discovery of the topological insulating [1] tetradymite (R-3m phase) Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ compounds. In fact, focus lies in the possibility of bridging the properties between topological insulators and high-performance thermoelectrics [2] and several studies have centred their attention on the understanding of pressure-induced electronic topological transitions and topological-insulator of sesquichalcogenides [3]. Our interest lies on the R-3m phase of three structures, namely Sb₂Se₃, Sb₂S₃ and Bi₂S₃, at which a topological insulating phase transition can be induced. It is well known that these three structures are dynamically and mechanically stable at the Pnma phase, however questions remain as to whether these systems can (co)exist at the R-3m phase. Theoretical and experimental studies have indeed suggested that pressure can induce a topological phase transition of the Sb₂Se₃ structure. These observations have also been confirmed by ab-initio studies to which it has been concluded that van der Waals interactions are essential in defining the topological properties of quantum materials.

In this work we will provide a theoretical description of the structural and phonon properties of the three systems under applied pressure, and infer about the mechanical and dynamical stability of the R-3m phase.

In collaboration with A. Muñoz, P. Rodríguez-Hernández, J. A. Sans, F. J. Manjón.

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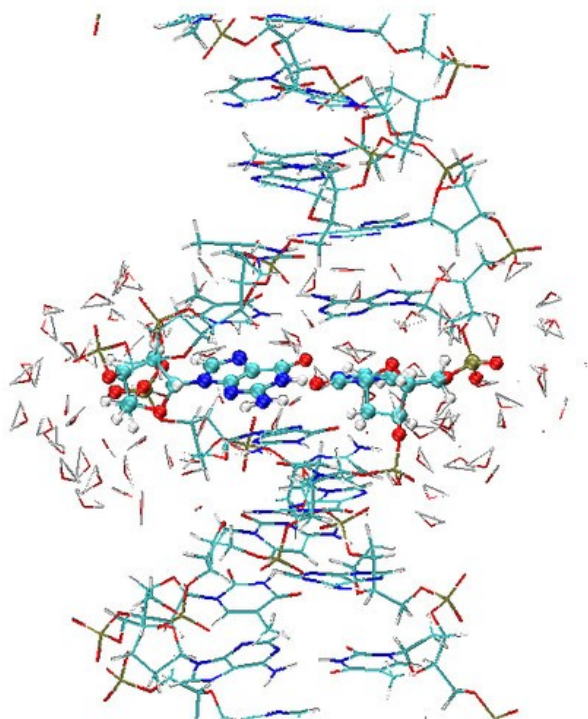
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QM/MM Free Energy Calculations of a Proton Transfer Reaction in Guanine-Cytosine

Proton transfer reactions in DNA yield the so-called rare tautomers, which are known to be a possible source of spontaneous mutations through the alteration of the canonical complementarity A/T-G/C. In this work, we make a dynamical study of tautomerization of a guanine-cytosine pair embedded in a realistic biomolecular environment using an efficient QM/MM technique [1] based on the combination of local orbital DFT (Fireball) and Amber.

We have studied the reaction mechanism, charge profiles, electronic structure and Free Energy profiles of the proton transfer reaction and we compare our results with what is known in gas phase and in static studies. We find that the environment has a crucial role in making the mutagenic rare tautomer unstable, thus ruling out proton transfer as a source of spontaneous mutations.



Caption: A snapshot of the system is shown with the QM region highlighted. Only a few of the water molecules are shown, for clarity.

In collaboration with Jesús I. Mendieta-Moreno, Daniel G. Trabada, Jesús Mendieta, José Ortega.

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Ivor Lončarić

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Thermosalient (jumping) crystals

Thermosalient materials when heated or cooled are characterized by a fast and energetic phase transition in which crystals experience macroscopic change in dimensions and jump to distances much larger than their own dimension. Since the first systematic study [1], there has been a rising interest for these interesting, and potentially useful, actuating materials. As an example, N-2-propylidene-4-hydroxybenzohydrazide shows irreversible thermosalient phase transition from Form I to Form II and reversible thermosalient phase transition from Form II to Form III. We combine experiments and first-principles electronic structure calculations to elucidate this interesting and technologically useful phenomenon[2].

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