Hands-on Workshop Density-Functional Theory and Beyond

First-Principles Simulations of Molecules and Materials

Report

Held at the Harnack-Haus of the Max Planck Society
Berlin, Germany, July 13 - July 23, 2015

Organizers:
Carsten Baldauf, Volker Blum, and Matthias Scheffler

Contents

1 Report

The ten-day school on “Density-Functional Theory and Beyond” was held from July 13 to 23, 2015. 113 participants (speakers, tutors, and regular participants, predominantly graduate students and early-stage postdocs) met at Harnack House in Berlin to learn and discuss about electronic-structure theory, from the basics to advanced topics. Its broad scope and the combination of lectures and practical session are hallmarks of this series of events and makes it attractive to the international community, which resulted in about two-times more applications for participations than we were able to accept. The 70 students were instructed in 26 lectures that were given by internationally-renowned scientists. Besides the lectures, practical sessions in front of computers were mainly conducted by the 19 tutors from Fritz Haber Institute (Berlin, Germany), Duke University (Durham, NC, USA), and Aalto University (Helsinki, Finland). The main computational workhorse for the afternoon sessions was the FHI-aims all-electron code. The overall workshop, however, is not designed to teach a single code, but rather to introduce scientific concepts and workflows. The program is designed to give an overview of as wide a range of approaches as possible, including leading representatives of other codes and methods like, for example, Christoph Friedrich (FZ Jülich) who contributes to `FLEUR` and `FLEUR-SPEX`, Pavel Hobza (IOCB Prague) who develops improved semi-empirical methods and represents the idea of high-level benchmarking in quantum chemistry, Chris Pickard (UC London) who is one of the main developeres of `CASTEP`, and Markus Reiher (ETH Zurich) who contributes to `MOLCAS` and develops vibrational spectroscopy approaches like `AKIRA` and `MOVIPAC`. We did aim to promote the whole field of electronic-structure theory for materials and molecules by connecting aspects of practical usage to the broader methods and concepts of current research and development. In the following we give an overview on the range of topics:

- *The basic concepts and formalisms of DFT* were introduced in presentations by Matthias Scheffler and John Perdew. Advanced developments beyond standard DFT were introduced by Adrienn Ruzsinszky. Methods to treat van der Waals interactions were covered by Alex Tkatchenko.

- *The technical foundations* of practical DFT implementations were introduced in lectures by Volker Blum and Björn Lange. The development of low-scaling hybrid functionals and of correlated methods is linked to efficient methods for the localized resolution of identity (RI) and such were introduced by Arvid Ihrig. The underlying concepts for periodic calculations were taught by Sergey Levchenko. The concepts of (augmented) plane waves were covered by Chris Pickard and Christoph Friedrich.

- *Benchmark-level calculations and data sets* for molecules and clusters were introduced by Pavel Hobza. Igor Ying Zhang introduced efforts to create similar reference data sets in the field of bulk materials.

- *Molecular dynamics-based statistical mechanics* were introduced by Roland Netz, while the peculiarities of *first-principle molecular dynamics* were talked about by Luca Ghiringhelli. The *sampling of large structure spaces* of clusters by means of genetic algorithms was exemplified in the lecture by Saswata Bhattacharya. *Electronic as well as thermal transport* were topics of the lectures by Ferdinand Evers and Christian Carbogno.

- *Vibrational spectroscopy* was covered in Markus Reiher's contribution. *Electronic spectroscopy and (opto-)electronic materials* were covered by Patrick Rinke and Chris Van de Walle.

- *Multi-scale and machine learning* are hot topics in current computational materials science, which is also reflected in the program of this school. Talks by Gus Hart, Matthias Rupp, Fawzi Mohamed, and Luca Ghiringhelli focused on such topics. Finally, the *industry perspective* was given by Boris Kozinsky (Bosch, Cambridge, MA, USA) and Jess Wellendorff (QuantumWise, Copenhagen, Denmark).

The workshop was a big success with positive feedback from all the participants, lecturers and students alike. There are multiple important and long-standing workshops in the field of molecular and materials simulations. Our "Hands-On DFT and beyond" series of workshops has established itself among them as **the** DFT school where the foundations of electronic structure theory as well advanced topics are being taught to PhD students and junior-PostDocs by leading experts in the field. Additionally, the success of the format decidedly reflects the high quality of the practical sessions that are organized with great dedication by the tutors, to whom we would here like to express our gratitude as organizers as well.

2 Financial report

This workshop was supported by ESF-Ψ_k with the amount of 10,000 €. This granted budget was used to cover travel expenses and housing of Lecturers and Tutors of the workshop and to supported students with respect to their travel costs. A detailed listing can be found in the following table.

Participant	Role	Accommodation	Travel Support
Saswata Bhattacharya	Lecturer		800.00 €
Volker Blum	Organizer & Lecturer	855.16 €	1633.74 €
Ferdinand Evers	Lecturer		352.50 €
Christoph Friedrich	Lecturer		200.00 €
Gus Hart	Lecturer	261.50 €	800.00 €
William Huhn	Tutor		600.00 €
Boris Kozinsky	Lecturer		600.00 €
Björn Lange	Lecturer		600.00 €
Chris Pickard	Lecturer		277.54 €
Markus Reiher	Lecturer		311.81 €
Patrick Rinke	Lecturer		400.00 €
Chris Van de Walle	Lecturer		800.00 €
Jess Wellendorf	Lecturer		169.53 €
Beata Taudul	Supported Student		400.00 €
Alvaro Vazquez Mayagoitia	Supported Student		400.00 €
Chenchen Wang	Supported Student		400.00 €
Xiaopeng Wang	Supported Student		400.00 €
Sum in total			**9861.78 €**

3 Program

Tuesday, July 14: Basic Formalism of DFT			
8:45 - 9:00	Goethe Hall	Blum, Baldauf & Scheffler	Introductory Remarks
9:00 - 10:00	Goethe Hall	Matthias Scheffler	Electronic Structure Overview
10:00 - 11:00	Goethe Hall	John Perdew	First Principles and ’The Functional’
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Adrienn Ruzsinszky	New Functionals
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 15:00	Goethe Hall	Ferdinand Evers	Electronic Transport
15:00 - 15:30	Meitner Hall	Coffee Break	
15:30 - 17:30	Goethe Hall		Poster parade
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Meitner Hall		Get-Together and Poster Session

Wednesday, July 15: Implementing DFT			
9:00 - 10:00	Goethe Hall	Volker Blum	The Nuts and Bolts of Electronic Structure Theory: Technical Foundations and Numerical Methods
10:00 - 11:00	Goethe Hall	Björn Lange	Self Consistency Cycle, Forces, and Structure Optimization
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Arvid Ihrig	Hybrid Functionals and the Resolution of Identity
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall	Björn Bieniek	Tutorial 1: The Basics of Electronic Structure Theory
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Goethe Hall		Extra computer time with tutors at hand

Thursday, July 16: Periodic Systems

9:00 - 10:00	Goethe Hall	Sergey Levchenko	Periodic Systems
10:00 - 11:00	Goethe Hall	Chris Pickard	Plane-Wave Pseudopotentials and PAW
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Christoph Friedrich	(Augmented) Plane Waves
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall	Will Huhn	Tutorial 2: Periodic Systems
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Goethe Hall		Extra computer time with tutors at hand

Friday, July 17: Molecular Dynamics, Statistical Mechanics, Sampling

9:00 - 10:00	Goethe Hall	Roland Netz	MD-Based Statistical Mechanics
10:00 - 11:00	Goethe Hall	Luca Ghiringhelli	*Ab initio* MD and Nuclear Quantum Effects
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Saswata Bhattacharya	Searching with an Accuracy Cascade
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall	Mateusz Marianski	Tutorial 3: *Ab initio* Molecular Dynamics
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Goethe Hall		Extra computer time with tutors at hand

Saturday, July 18: Weekend Research Project

10:00 - 12:30	Goethe Hall		Weekend Research Project
12:30 - 14:00	Restaurant	Lunch Break	
14:00	Excursion		

Sunday, July 19: Weekend Research Project

10:00 - 12:30	Goethe Hall		Weekend Research Project
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall		Weekend Research Project
18:00 - 19:00	Restaurant	Dinner Break	

Monday, July 20: Validation, optoelectronics, transport

9:00 - 10:00	Goethe Hall	Pavel Hobza	Wave-function Based Methods and Validation Data Sets
10:00 - 11:00	Goethe Hall	Igor Ying Zhang	Test Sets and Benchmark Techniques for Materials Science
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Markus Reiher	Vibrational Spectroscopy
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 15:00	Goethe Hall	Christian Carbogno	Phonons, Electron-Phonon Coupling and Transport in Solids
15:00 - 18:00	Goethe Hall	Christian Carbogno	Tutorial 4: Charge Transport in Solids at Finite Temperature
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Goethe Hall		Extra Computer Time with Tutors at Hand

Tuesday, July 21: Electronic spectroscopy

9:00 - 10:00	Goethe Hall	Alexandre Tkatchenko	Van der Waals
10:00 - 11:00	Goethe Hall	Patrick Rinke	Prediction of Electronic Spectra from First Principles
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Chris Van de Walle	Optoelectronic Materials
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall	Patrick Rinke	Tutorial 5: Excited States
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Meitner Hall		Get-Together and Poster Session

Wednesday, July 22: Navigating Materials and Compound Space I

9:00 - 10:00	Goethe Hall	Fawzi Mohamed	Database infrastructure for electronic structure calculations
10:00 - 11:00	Goethe Hall	Matthias Rupp	Statistical learning
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Gus Hart	Multiscale
12:30 - 14:00	Restaurant	Lunch Break	
14:00 - 18:00	Goethe Hall	Gus Hart	Tutorial 6: Multiscale
18:00 - 19:00	Restaurant	Dinner Break	
19:00 - 22:00	Goethe Hall		Extra computer time with tutors at hand

Thursday, July 23: Navigating Materials and Compound Space II

9:00 - 10:00	Goethe Hall	Luca Ghiringhelli	Big-Data analytics in Materials Science
10:00 - 11:00	Goethe Hall	Jess Wellendorff	How Electronic Structure Theory is Used in Industry
11:00 - 11:30	Meitner Hall	Coffee Break	
11:30 - 12:30	Goethe Hall	Boris Kozinsky	Industrial Applications of Electronic Structure Theory
12:30	Restaurant	Lunch and end of workshop	

4 Participants list

Participants	
Shideh Ahmadi	shideh.ahmadi@gmail.com
Yierpan Aierken	yierpan.aierken@uantwerpen.be
Isaac Alcon Rovira	ialcon@ub.edu
Uri Argaman	argamanu@post.bgu.ac.il
Adam Arvidsson	adam.arvidsson@chalmers.se
Arkamita Bandyopadhyay	arkamitabannerjee@gmail.com
Dennis Barton	d.barton@uni-muenster.de
Larissa Z. Besse	larissa.zibordi@usp.br
Asif Iqbal Bhatti	bhatti.asif.iqbal@gmail.com
Marta Bon	bon.marta@gmail.com
Tiago Botari	tiagobotari@gmail.com
Raffaella Breglia	r.breglia1@campus.unimib.it
Danny Broberg	ddidjbroberg@gmail.com
Fanglin Che	fanglin.che@email.wsu.edu
Lihua Chen	lhc0807@gmail.com
Pan Chen	pan.chen@avt.rwth-aache.de
Sergio Cruz-Leon	scleon@icp.uni-stuttgart.de
Ruben Demuynck	ruben.demuynck@ugent.be
Marco Fronzi	marco.fronzi@tyndall.ie
Joshua Gabriel	joshgabriel92@ufl.edu
Piero Gasparotto	piero.gasparotto@epfl.ch
Janine George	janine.george@ac.rwth-aachen.de
Alvaro González	alvarogonzalez@uninorte.edu.co
Anna Gould	a.gould@ucl.ac.uk
Lütfiye Hallioglu	lutfiye.hallioglu@bilkent.edu.tr
Shashank Shekhar Harivyasi	harivyasi@tugraz.at
Norah Heinz	N.Heinz@uni-koeln.de
Shreyas Honrao	shreyas.honrao@gmail.com
Marie Humbert-Droz	marie.humbert-droz@unige.ch
Erik Jedvik	jedvike@chalmers.se
Kyoung Chul Ko	kcko1982@gmail.com
Krzysztof Kośmider	kosmider@fzu.cz
Malgorzata Krasowska	malgorzata.krasowska@uni-tuebingen.de
Ondřej Krejčí	krejcio@fzu.cz
Krystina Lamb	krystina.lamb@research.usc.edu.au
Chong Liu	c.liu1@tue.nl
Christian Loach	s1355587@sms.ed.ac.uk
Joakim Löfgren	joalof@chalmers.se

Sanjaya Lohani	slohani@tulane.edu
Philipp Metzner	metznerph@gmail.com
Olga Miroshnichenko	olga.miroshnichenko@oulu.fi
Victor Naden Robinson	victornadenrobinson@gmail.com
Sofia Nilsson	sofia.nilsson@helsinki.fi
Irina Piyanzina	i.piyanzina@gmail.com
Thomas Plehn	plehn@physik.hu-berlin.de
Paolo Poli	paolopoli1980@gmail.com
Sergei Posysaev	Sergei.Posysaev@oulu.fi
Nazanin Rahimi	nazanin.rahimi@griffithuni.edu.au
Sven Reichardt	sven.reichardt@uni.lu
Mauricio Antonio Rodríguez Mayorga	marm3.14@gmail.com
Sven Rogge	Sven.Rogge@UGent.be
Wudmir Rojas	eep401@bangor.ac.uk
Trisha Salagaram	trisha.salagaram@up.ac.za
Gökcen Savasci	Goekcen.Savasci@cup.uni-muenchen.de
Hannah Schlott	hannah.schlott@fau.de
Srdjan Stavric	srdjan.stavric@rgf.bg.ac.rs
Yaqiong Su	Y-Q.Su@tue.nl
Beata Taudul	beata.taudul@ipcms.unistra.fr
Alvaro Vazquez Mayagoitia	alvaro@anl.gov
Valeria Verdinelli	vverdinelli@uns.edu.ar
Nicholas Wagner	nicholaswagner2018@u.northwestern.edu
Suzanne Wallace	s.k.wallace@bath.ac.uk
Chenchen Wang	dvdcwangcc@gmail.com
Xiaopeng Wang	xwang24@tulane.edu
Jelle Wieme	Jelle.Wieme@UGent.be
Xi Xu	xuxi@pku.edu.cn
Jiawei Yan	yanjw@shanghaitech.edu.cn
Ruoxi Yang	r.yang@bath.ac.uk
Dirk Ziemann	ziemann@physik.hu-berlin.de
Egbert Zojer	egbert.zojer@tugraz.at

Tutors

Amrita Bhattacharya	amrita@fhi-berlin.mpg.de
Björn Bieniek	bieniek@fhi-berlin.mpg.de
Jan Hermann	jhermann@fhi-berlin.mpg.de
Johannes Hoja	hoja@fhi-berlin.mpg.de
Will Huhn	william.huhn@duke.edu
Arvid Ihrig	ihrig@fhi-berlin.mpg.de
Franz Knuth	knuth@fhi-berlin.mpg.de
Sebastian Kokott	kokott@fhi-berlin.mpg.de
Björn Lange	bjoern.lange@duke.edu
Xiang-Yue Liu	xyliu@fhi-berlin.mpg.de
Mateusz Marianski	marianski@fhi-berlin.mpg.de
Lydia Nemec	lnemec@fhi-berlin.mpg.de

Markus Schneider	markus.schneider@fhi-berlin.mpg.de
Honghui Shang	shang@fhi-berlin.mpg.de
Maria Stournara	stournara@fhi-berlin.mpg.de
Adriana Supady	supady@fhi-berlin.mpg.de
Milica Todorovic	milica.todorovic@aalto.fi
Weiqi Wang	wang@fhi-berlin.mpg.de
Xunhua Zhao	xunhuazhao@fhi-berlin.mpg.de

Speakers

Carsten Baldauf	baldauf@fhi-berlin.mpg.de
Saswata Bhattacharya	saswata@physics.iitd.ac.in
Christian Carbogno	christian.carbogno@fhi-berlin.mpg.de
Christoph Friedrich	c.friedrich@fz-juelich.de
Ferdinand Evers	ferdinand.evers@physik.uni-regensburg.de
Luca Ghiringhelli	ghiringhelli@fhi-berlin.mpg.de
Arvid Ihrig	ihrig@fhi-berlin.mpg.de
Sergey Levchenko	levchenko@fhi-berlin.mpg.de
Roland Netz	rnetz@physik.fu-berlin.de
Matthias Scheffler	scheffler@fhi-berlin.mpg.de
Alexandre Tkatchenko	tkatchenko@fhi-berlin.mpg.de
Igor Ying Zhang	zhang@fhi-berlin.mpg.de
Pavel Hobza	pavel.hobza@uochb.cas.cz
Chris J. Pickard	c.pickard@ucl.ac.uk
Markus Reiher	markus.reiher@phys.chem.ethz.ch
Patrick Rinke	patrick.rinke@aalto.fi
Matthias Rupp	rupp@fhi-berlin.mpg.de
Volker Blum	volker.blum@duke.edu
Gus Hart	gus.hart@gmail.com
Boris Kozinsky	Boris.Kozinsky@us.bosch.com
Björn Lange	bjoern.lange@duke.edu
Fawzi Mohamed	mohamed@fhi-berlin.mpg.de
John Perdew	perdew@temple.edu
Adrienn Ruzsinszky	aruzsinszky@temple.edu
Chris van de Walle	vandewalle@mrl.ucsb.edu
Jess Wellendorff	jess.wellendorff@quantumwise.com

5 Poster abstracts

Local densification, quantum entrapment, and valence charge polarization at the surfaces of metallic nanoclusters

P1

Shideh Ahmadi[1], Xi Zhang[2], Yinyan Gong[3] and Chang Q. Sun[1]
[1] *NOVITAS, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798 Singapore*
[2] *Institute of Nanosurface Science and Engineering, Shenzhen University, Shenzhen 518060, China*
[3] *Center for Coordination Bond and Electronic Engineering, College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China*

Ag, Cu, Pt, and Rh nanostructures have attracted enormous research interests because of their unique properties as compared to the bulk components, including transition from conductor to insulator, from nonmagnetic to magnetic, and extraordinary high catalytic capability. The effect of atomic under-coordination at the surface of metallic nanoclusters have been investigated by density functional theory (DFT) calculations in account of both Cuboctahedral and Marks decahedral structures. Our results are, in trend, consistent with aforementioned experimental observations such as X-ray-absorption fine structure, scanning tunneling microscope/spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectra. This consistency confirmed the predications based on bond order-length-strength correlation (BOLS) theory [1] and nonbonding electron polarization (NEP) [2], proposing that the shorter and stronger bonds between atomic under-coordination at the surface of metallic nanostructures induce local densification, quantum entrapment of the core electrons, and valence charge polarization, which provide perturbation to the Hamiltonian and give rise to the unique properties in metallic nanoclusters.

[1] C. Q. Sun, Relaxation of the Chemical Bond, Springer Series in Chemical Physics, (2014)
[2] C. Q. Sun, Nanoscale 10, 1930 (2010)

P2 Defect-induced faceted phosphorene nanotubes

Yierpan Aierken[1], Ortwin Leenaerts[1] and Francois Peeters[1]
[1] *Department of Physics, University of Antwerp, 2610 Antwerpen, Belgium*

Phosphorene was recently proposed as a new member of the ever increasing family of two-dimensional materials. In contrast to graphene which has pure sp^2 hybridization, phosphorene is sp^3 hybridized due to the extra valence electron of phosphorous. This leads to an essentially tetragonal coordination of the P atoms which results in a buckled character of phosphorene sheets. The buckled nature of the phosphorene sheets gives rise to various possible structural phases, such as black and blue phosphorene. Similar to graphene, it is also possible to create nanotubes from the phosphorene sheets. Due to the buckled nature of the phosphorene family, the traditional rolled-up nanotubes can be modified in various ways. As shown by Guan et al. [1], it is possible to join different structural phases of phosphorene to create so-called faceted nanotubes which can be more stable than simple rolled-up tubes. In our work, we took a different approach to construct more stable phosphorene nanotubes. We started from (single-phase) blue phosphorene sheets and introduced various defect lines to induce kinks with well-defined angles in the system. Combining the defect lines in appropriate ways leads to faceted blue phosphorene nanotubes with low formation energies. We investigated the stability and electronic properties of these faceted tubes and compared them to the traditional rolled tubes and the faceted multiphase tubes.

[1] J. Guan, Z. Zhu, and D. Tománek, Phys. Rev. Lett. 113, 226801 (2014)

P3 Designing full-organic materials with controllable magnetic and electrical properties

Isaac Alcon[1] and Stefan T. Bromley[1,2]
[1] *Institute of Theoretical and Computational Chemistry of the University of Barcelona (IQTC-UB). Department of Physical Chemistry. 08028 Barcelona, Spain.*
[2] *Catalan Institution of Research and Advanced Studies (ICREA), 08010 Barcelona, Spain.*

Over 100 years ago Mossen Gomberg prepared the first persistent organic radical; the tryphenylmethyl. This discovery launched the field of radical chemistry at the beginning of the 20th century and hundreds of triarylmethyl (TAM) derivatives have since been synthesized and used in multiple different applications. Recent studies have also demonstrated their great potential in the emerging fields of molecular electronics and spintronics. Understanding the essential factors that control the state of the unpaired electron in this class of radicals is of key importance for use in future spintronic

applications. We have found, by DFT calculations, that within TAM radicals the key parameter that fully determines the localization (and thus, energy) of the unpaired electron is the mean dihedral angle (mDA) between the three aryl rings and the central sp2-carbon atom [1]. No matter the chemical functionalization of the TAM derivative, given mDA, the localization (and energy) of the unpaired electron can be derived. Benchmarking our results with experimental ESR data, we have demonstrated how this rule stands for a wide range of TAM derivatives with completely different structures. Moreover, by using ab initio Molecular Dynamics we have found that mDA is constant at room temperature.
Currently, we are designing realistic 2D covalent networks based on TAM radicals. These hypothetical materials (which can be seen as porous graphene materials) could represent the first full-organic multi-radical 2D-networks with unique electronic and magnetic properties. Our aim is finding what polymeric structures maintain the multi unpaired electron system stable; i.e. avoiding electron recombination. Additionally, using force field methods, various stretching/compressing forces are applied to the different networks to see whether the unpaired electron localization can be somehow influenced (thus modifying the magnetic and electrical properties of the material). The accomplishment of the different objectives of this work could represent an important breakthrough within the field of molecular spintronics towards the preparation of full-organic electrical devices for diverse applications.

[1] I. Alcon and S.T. Bromley. Controlling spin localisation in organic radicals. (Submitted)

Thermodynamic properties of titanium from ab initio calculations

P4

Uri Argaman[1], Eitan Eidelstein[2], Ohad Levi[2] and Guy Makov[1]
[1] *Materials Engineering Department, Ben-Gurion University of the Negev, Beer Sheva 8410501, Israel*
[2] *Department of Physics, NRCN, PO Box 9001, IL Beer-Sheva, 84190, Israel*

The lattice parameters, lattice stability and phonon dispersion curves of five proposed phases of Ti: α, β, γ, δ and ω are investigated within density functional theory (DFT). It is found that the sequence of high pressure phases at zero temperature is $\alpha \to \omega \to \gamma \to \delta \to \beta$ with the δ and β phases becoming degenerate at high pressure. However, the γ phase may be unstable as is reflected by the existence of imaginary values in the phonon spectra. The results of the DFT calculations are employed to estimate the entropy and free energies of the α and ω phases. It is found that converged phonon calculations lead to an entropy difference which is much smaller than previous estimates, and a much steeper $\alpha \to \omega$ phase transition line. [1]

[1] U. Argaman, E. Eidelstein, O. Levy and G. Makov, Materials Research Express 2, 016505 (2015)

Direct Conversion of Methane to Methanol over Cu-ZSM-5

P5

Adam Arvidsson[1]
[1] *Chalmers University of Technology, Fysikgränd 3, 411 33, Göteborg, Sweden*

Recent results have shown that zeolites can oxidise methane to methanol under ambient conditions with a very high selectivity (>90%) [1]. It has been seen in both iron and cobalt exchanged zeolites (Fe- and Co-ZSM-5) [2, 3], but especially promising is the copper exchanged Cu-ZSM-5 zeolite, which can oxidise methane to methanol with molecular oxygen [4]. Here, Density Functional Theory (DFT) and the DMol software is used to investigate the reaction in copper exchanged ZSM-5 using three different model systems, copper ion, copper dimer and a cluster model of Cu-ZSM-5. Assuming a simple reaction mechanism, energy landscapes and geometries are obtained for the three models. For further analysis, Mulliken atomic charges for the reaction steps are investigated.

[1] A. E. Shilov, A. A. Shteinman, Russ. Chem. Rev. 81 (2012) 291.
[2] E. V. Starokon et al., J. Phys. Chem. C 115 (2011) 2155-2161.
[3] N. V. Beznis, B. M. Weckhuysen and J. H. Bitter, Catal. Lett. 136 (2010) 52-56.
[4] J. S. Woertink et al., PNAS 106 (2009) 18908-18913.

P6

Photophysical properties of charge transfer pairs encapsulated inside macrocycle cage: A density functional theory study

Arkamita Bandyopadhyay[1] and Swapan K. Pati[1]
[1] *New Chemistry Unit and Theoretical Sciences Unit*
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore-64, India

Density functional theory calculations have been performed on three charge transfer donor-acceptor (D-A) molecular pairs, i.e. naphthalene-diamine (Naph) and tetrathiafulvalene (TTF) molecules as electron donors and benzene-diimide (Diimide) and tetracyanoquinodimethane (TCNQ) as electron acceptors. Structural, charge transfer and optical properties of the systems have been studied. The D-A pairs then has been considered inside a macrocycle (cucurbit[8]uril) cavity and Naph-Diimide and TTF-Diimide pairs have been shown to exhibit changes in their structures and orientations, TTF-TCNQ pair does not show any significant structural change. Our work suggests that these changes in structures or orientations are result of electronic repulsion between the keto group oxygen atoms and it can lead to tuning of charge transfer and optical properties of the systems, but, as the structure or orientation of TTF-TCNQ does not change, they do not show that much change in optical absorption spectra. We have verified our results using different exchange-correlation functionals for the robustness of our results.

[1] Arkamita Bandyopadhyay and Swapan K. Pati, Chem. Phys. Lett., 624, 64-68 (2015)
[2] Arkamita Bandyopadhyay, SRKC Sharma Yamijala and Swapan K. Pati, Phys. Chem. Chem. Phys., 15, 13881-13887 (2013)

P7

Towards a flexible QM/QM Implementation for Adsorption Phenomena and Surface Reactions

Dennis Barton[1] and Johannes Neugebauer[1]
[1] *Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut*
and Center for Multiscale Theory and Computation,
Corrensstraße 40, 48149 Münster

The description of surface reactions like the Glaser-Coupling[1] or polymerizations of linear alkanes[2] by means of quantum chemistry is still only feasible when using cost-effective DFT methods. Due to the limited accuracy of DFT calculations regarding weak interactions or bond breaking, benchmark methods are highly desirable to verify results obtained by periodic DFT calculations.

An alternative to periodic calculations are embedded cluster calculations. Embedding methods can be formulated with an embedding potential based on the slab electron density, calculated with periodic DFT methods[3,4]. The active region in this case can be described with molecular DFT or wavefunction codes.

Here, we are going to outline the structure of a flexible QM/QM implementation that can construct an embedding potential from an electron density obtained in a periodic DFT calculation. The implementation shall be capable of using ingredients obtained from different DFT codes like ADF-BAND[5], VASP[6] or other programs. The specific requirements to deal with different kinds of basis functions (Slater functions, plane waves, etc.) will be analyzed. On the WF side, the focus will be on modern multiconfigurational wavefunction methods as provided, e.g., by MOLCAS[7]. But the design of the implementation shall make it possible to easily interface other WF codes. Additionally, typical approximations made, e.g. for the densities in the construction of the embedding potential, will be reviewed here.

[1] H. Y. Gao et al., Angw. Chem. Int. Ed. 52, 4024 (2013).
[2] D. Zhong et al., Science 334, 213 (2011).
[3] N. Govind, Y. A. Wang, A. J. R. da Silva, and E. A. Carter, Chem. Phys. Lett. 295, 129 (1998).
[4] N. Govind, Y. A. Wang, and E. A. Carter, J. Chem. Phys. 110, 7677 (1999).
[5] Amsterdam density functional program; Theoretical Chemistry, Vrije Universiteit, Amsterdam.
[6] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[7] F. Aquilante et al., J. Comput. Chem. 31, 224 (2010).

P8

The Role of the van der Waals Interactions in the Adsorption of Ethanol on 13-Atoms Transition-Metal Clusters

Larissa Z. Besse[1], Polina Tereshchuk[1], Anderson S. Chaves[1] and Juarez L. F. Da Silva[1]
[1] *São Carlos Institute of Chemistry, University of São Paulo, PO Box 780, 13560-970, São Carlos, SP, Brazil*

The choice of the catalyst in the steam reforming reaction of ethanol (C_2H_6O) has a central role, once it determines the efficiency of hydrogen production for fuel cell applications. Those catalysts are commonly based on transition-metal (TM) particles composed from few atoms (clusters) to layers supported on oxides [1]. Our atomistic understanding of the adsorption of ethanol on TM surfaces are relatively well established based on previous calculations [2], however, our understanding is still incomplete for the interaction of ethanol with finite size TM systems. In this work, we will report an *ab-initio* investigation of the interaction of ethanol with 13-atoms TM clusters (TM = Ni, Cu, Pd, Ag, Pt, and Au), which have a wide range of adsorption sites. Our calculations are based on density functional theory within the PBE functional and van der Waals (vdW) corrections proposed by Tkatchenko-Sheffler [3]. The Kohn-Sham molecular orbitals are described by numeric atomic orbitals as implemented in the FHI-aims package. We found that the $3d$ and $4d$ TM_{13}

clusters have compact hexagonal-bilayer structures, in contrast, the Pt_{13} and Au_{13} systems adopt open structures. In particular, Au_{13} has a planar structure at a DFT-PBE level, and the addition of spin-orbit coupling for the valence states favours a 3D structure [4]. We found that the adsorption energy, E_{ad}, of ethanol ranges from -270 meV for ethanol/Ag_{13} to -627 meV for ethanol/Ni_{13}, and the ethanol-TM_{13} interaction does not affect the cluster structure due to the weak nature of the interactions. As expected, the vdW correction enhances the adsorption energy due to its attractive nature, e.g., from 15.5% for ethanol/Au_{13} to 62.5% for ethanol/Ag_{13}. In contrast with the adsorption energy, the atomic adsorbed configuration is not affected by the vdW correction, since the ethanol-cluster distance changes in a maximum of 0.5% for ethanol/Ni_{13}. From our Mulliken charge analaysis, we found a negligible charge transfer among the systems, which indicates once again the physisorption nature of the interaction, where polarization effects (electron density redistribution) plays an important role in the interaction.

[1] S. Vajda et al., Nat. Mater. 8, 213 (2009).
[2] P. Tereshchuk and J. L. F. Da Silva, J. Phys. Chem. C 116, 24695 (2012).
[3] Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
[4] M. J. Piotrowski, P. Piquini, and J. L. F. Da Silva, Phys. Rev. B 81, 155446 (2010).

P9

Metal on graphene: Competition between interaction strength and lattice mismatch

Asif Iqbal Bhatti[1], Karim Ferhat[2], Johann Coraux[1], Frédéric Lançon[2] and Laurence Magaud [1]
[1] *Univ. Grenoble Alpes, CNRS, Institut Néel, F-38042 Grenoble, Cedex, France*
[2] *Univ. Grenoble Alpes, CNRS, CEA-Leti Minatec, LTM, F-38054 Grenoble Cedex, France*

The aim of this project is to study the interaction parameters between the carbon layer and the underlying substrate. The variation in the position of carbon atoms and lattice mismatch leads to the formation of a pattern called moiré. We have investigated these parameters with the help of ab-initio calculation and implemented Stillinger Weber potential to describe the moiré and the formation of wrinkles.

[1] T. Pedersen et al., Phys. rev. Lett., 100, 136804 (2008).
[2] C. Tonnoir et al., Phys. rev. Lett., 111, 246805 (2013).
[3] F. Varchon et al., Phys. rev. B, 77, 235412 (2008).
[4] G. Trambly de Laissardière et al., Phys. rev. B, 86, 125413(2012).
[5] H. Hattab et al., Nano Lett., 12, 678 (2012).
[6] Y. Murata et al., ACS Nano, 4, 11 (2010).

P10

Determining the thermodynamics of V^{3+}/V^{2+} and VO^{2+}/VO_2^+ reactions: redox potentials and reorganization energies.

M. Bon[1], T. Laino[1], I. Tavernelli[1], A. Curioni[1] and M. Parrinello[2]
[1] *IBM Zurich Research Laboratory, Zurich, Switzerland*
[2] *DCHAB, ETH Zurich, Switzerland.*
Institute of Computational Sciences, USI, Lugano, Switzerland

In the last decades we observed a growing interest in energy storage systems based on the redox flow battery (RFB)[1]. In such electrochemical cell an electrolyte, containing one or more dissolved electro-active species, flows through the device converting the chemical energy directly into electricity. Among all the RFBs presently under study, the vanadium redox flow battery (VRFB) shows good properties such as good electrochemical activity, reversibility, and low maintenance costs [2]. In VRFBs, similarly to most electrochemical processes, the core step to produce electricity is the electron-transfer (ET) event. This process involves the reduction and oxidation of various redox species near to an electrode.

In our study, in order to provide a thermodynamical description of the ET process in a VRFB, we apply the method developed by Blumberger and coworkers [3], performing biased Born-Oppenheimer Molecular Dynamics simulations of half-redox reactions. Using this simulation scheme, the potential energy surfaces of reactant and product states are linearly coupled and the system is relaxed from the reduced state to the oxidized one (and viceversa) by varying the coupling parameter. Then, the redox potential is obtained by Thermodynamic Integration of the energy gaps corresponding to different values of the coupling parameter. Moreover the diabatic Free Energy Curves (FECs) of reduced and oxidized states are obtained by reweighting [4] and combining the set of biased distributions of the ionization energy.

In such a way we estimate the redox potentials and the FECs of the two different half-reactions that occur in the VRFB: i) $V^{3+} + e^- \longrightarrow V^{2+}$ and ii) $VO^{2+} \longrightarrow VO_2^+ + e^-$. We find that both processes can be described by parabolic FEC over a wide range of the reaction coordinate, the energy gap. This is an agreement with the linear response assumption that underlies Marcus theory [5]. The two half-reactions undergo different electrochemical mechanism: while the V^{3+}/V^{2+} reaction completely falls into the Marcus regime, that implies same reorganization energies for both species and also same FEC curvature, the VO^{2+}/VO_2^+ process shows some deviations. The investigation of the first and the second solvation shell can provide an explanation to this behavior: we observe that the reaction ii) can be described as an inner-sphere process, which implies that the ET does not depend entirely on the solvent reorganization.

To compare our theoretical results with the experimental data we also performed some simulations of the Fe^{2+}/Fe^{3+} half-redox reactions, as reference system.

[1] R. F. Gahn et al. 20th Intersociety Energy Conversion Engineering Conference, 2, 2, 1985.
[2] M Skyllas-Kazacos et al., Journal of the Electrochemical Society, 133:1057, 1986.
[3] J. Blumberger et al., The Journal of chemical physics, 124(6):064507, 2006.
[4] K. Shankar, et al., Journal of computational chemistry, 13.8: 1011-1021, 1992.
[5] R. A. Marcus, Electrochimica Acta, 13.5: 995-1004, 1968.

Theoretical Investigation of Carbon Nitride Based Materials

P11

Tiago Botari[1], William Paul Huhn[1], Volker Blum[1], Vincent Wing-hei Lau[2,3] and Bettina V. Lotsch[2,3,4]

[1] *Department of Mechanical Engineering and Material Science, Duke University, Durham, North Carolina 27708, USA*

[2] *Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany*

[3] *Department of Chemistry, University of Munich, Butenandtstraße 5-13, 81377 Munich, Germany*

[4] *Nanosystems Initiative Munich (NIM) and Center for Nanoscience, Schellingstraße 4, 80799 Munich, Germany*

Carbon nitride based compounds are an “old” class of materials, but their suitability as photocatalysts for hydrogen evolution was demonstrated only rather recently [1]. While much attention has focused on a hypothetical two-dimensional layered compound “graphitic carbon nitride” (g-C_3N_4), the structure and morphologies of actual carbon nitride materials depend strongly on the synthesis conditions. Indeed, the crystallographically established phase is a one-dimensional, hydrogen-bonded layered polymer ”melon”. Crystallinity is however inversely correlated with photocatalytic performance, and under-reacted oligomeric melon species appear to correlate with enhanced catalytic activity [2]. Furthermore, the experimental evidence for the existence of hydrogen-free g-C_3N_4 is sparse at best, though this hypothetical structure is commonly depicted in the literature.

We present a theoretical study of the thermodynamic equilibrium conditions for the existence of g-C_3N_4, showing that this material would be very difficult to make under commonly employed synthesis conditions. This conclusion emerges from calculations based on the van der Waals corrected PBE functional (pairwise and many-body dispersion corrections). Our study also addresses modified side chain functionalities that could potentially increase the catalytic activity. A comparison to benchmark experiments show that simple intrinsic molecular properties such as the highest occupied and lowest unoccupied molecular orbitals and their energy levels are not, on their own, reliable descriptors to predict the activity of a given species. We suggest that important aspects of the photocatalytic process are likely determined by factors related to the local environments of carbon-nitride structure units, including local electrostatics, bonding environments, interfaces, and defects.

[1] Wang, X., et al. (2009) Nature Materials, 8(1), 76-80.
[2] Lau, V. W., *et al.* (2015) Journal of the American Chemical Society, 137(3), 1064-1072.

P12

DFT investigation of the Ni-A inactive state of the [NiFe]-hydrogenases: inactivation mechanism under aerobic and anaerobic conditions

Raffaella Breglia[1], Claudio Greco[1], Luca De Gioia[1] and Maurizio Bruschi[2]
[1] *Department of Biotechnology and Biosciences, University of Milano-Bicocca*
[2] *Department of Earth and Environmental Sciences, University of Milano-Bicocca*

Because dihydrogen is considered as a future non polluting source of energy, Hydrogenase enzymes are of fundamental interest for their capability to catalyse the reversible interconversion of protons and reducing equivalents into molecular hydrogen. While the [FeFe]-hydrogenases are irreversibly inactivated by O_2, the oxidized [NiFe]-hydrogenases can be reactivated by one-electron reduction and protonation. This property, in addition to the high catalytic efficiency and the absence of expensive metals in their active site, makes the [NiFe]-hydrogenases a very promising target for reverse engineering studies aimed at the development of bioinspired catalysts. In the active site of [NiFe]-hydrogenases, the iron and nickel atoms are bridged by two cysteine residues. Two further cysteine residues are terminally bounded to the Ni atom while two CN and one CO ligands coordinate the Fe atom. The inactive oxidized Ni-A state of this enzyme have been recently characterized by X-ray diffraction[1], as containing a bridging hydroxide ligand between the two metallic ions and a bridging cysteine oxidized to its sulfanated form. To investigate the mechanism of oxidation of active forms to this state, quantum mechanics calculations have been carried out in the framework of the Density Functional Theory (DFT) on a very large model of the active site. Since it was demonstrated that the Ni-A state can be generated even in the absence of O_2[2], either using chemical agents or imposing positive potential to the enzyme, the formation mechanism was investigated under both aerobic and anaerobic conditions. While under aerobic conditions oxidation is promoted by O_2, under anaerobic conditions two water molecules have been proposed to provide the oxygen atoms included in the Ni-A form.

[1] Volbeda, A.; Martin, L.; Barbier, E.; Gutiérrez-Sanz, O.; De Lacey, A.L.; Liebgott, P.P.; Dementin, S.; Rousset, M.; Fontecilla-Camps, J.C. J. Biol. Inorg. Chem. 2015, 20(1):11-22.
[2] Abou Hamdan, A.; Burlat, B.; Gutiérrez-Sanz, O.; Liebgott, P.-P.; Baffert, C.; De Lacey, A. L.; Rousset, M.; Guigliarelli, B.; Léger, C.; Dementin, S. Nat. Chem. Biol. 2013, 9, 15.

Catalytic Methane Steam Reforming: Using an External Electric Field to Enhance Nickel Catalytic Performance

P13

Fanglin Che[1] and Jean-Sabin McEwen[1]
[1] *Washington State University, Pullman, WA, 99164*

Hydrogen fuel, the fuel of the future, can be applied in vehicles and fuel cells with zero emissions and high efficiency. To generate hydrogen fuel, steam reforming over Ni-based catalysts is widely employed in industries to utilize hydrocarbon fuels[1]. However, this is a highly endothermic reaction when methane is used, which requires temperatures of 900 K or higher. To realize low temperature systems, one possibility is to study the effect of an external electric field on this reaction. A large electric field, on the order of -1 V/Å to 1 V/Å, can rearrange the potential of molecular orbitals, alter the adsorbate-surface interactions, and directly change the overall electrocatalytic activity and selectivity of Ni-based catalysts[2-4]. Our results show that the interaction between H_2O and Ni surfaces is strongly affected by the presence of an electric field. A negative electric field significantly accelerates the water dehydrogenation[5]. In addition, based on energy barriers of all possible MSR mechanisms, we determine the following most favorable reaction pathway:

$$\mathrm{C}H_4 + \mathrm{H_2O} \rightarrow \mathrm{C}H + \mathrm{O}H + 4\mathrm{H} \rightarrow \mathrm{C}HOH + 4\mathrm{H} \rightarrow \mathrm{C}HO + 5\mathrm{H} \rightarrow \mathrm{C}O + 6\mathrm{H}$$

The rate-limiting step of this pathway is the $\mathrm{C}H+\mathrm{O}H\rightarrow\mathrm{C}HOH$ step, which itself is further favored in the presence of a negative electric field. Overall, this work greatly contributes to establishing insights into how an external electric field can alter the underlying reaction pathways. This information can be used in designing new electrochemical systems and to enhance catalytic performance of Ni-based steam reforming operations.

[1] K. Oshima, T. Shinagawa, M. Haraguchi and Y. Sekine, Int. J. Hydrogen Energy, 38(2013), 3003.
[2] Stüve, E. M., Chem. Phys. Lett. 1 (2012), 519.
[3] F. Che, R. Zhang, A. J. Hensley, S. Ha and J.-S. McEwen, Phys. Chem. Chem. Phys. 16(2014), 2399.
[4] F. Che, A. J. Hensley, S. Ha and J.-S. McEwen, Catal. Sci. Technol. 4(2014), 4020.

[5] F. Che, S. Ha and J.-S. McEwen, Catalytic Water Dehydrogenation and Formation on Nickel: Dual Path Mechanism in High Electric Fields, J. Catal. under review.

P14 Unraveling the luminescence signatures of chemical defects in polyethylene

Lihua Chen[1], Huan Doan Tran[1], Chenchen Wang[1] and Rampi Ramprasad[1]
[1] *Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269, USA*

Chemical defects in polyethylene (PE) can deleteriously downgrade its electrical properties and performance. Although these defects usually leave spectroscopic signatures in terms of characteristic luminescence peaks, it is nontrivial to make unambiguous assignments of the peaks to specific defect types. In this work, we go beyond traditional density functional theory calculations to determine defect-derived emission and absorption energies in PE. In particular, we characterize PE defect levels in terms of thermodynamic and adiabatic charge transition levels that involve total energy calculations of neutral and charged defects. Calculations are performed at several levels of theory including those involving (semi)local and hybrid electron exchange-correlation functionals, and many-body perturbation theory. With these critical elements, the calculated defect transition levels are in excellent correspondence to observed luminescence spectra of PE, thus clarifying and confirming the origins of the observed peaks. Based on this work, a prescription with a reasonable computational expense is proposed to accurately predict and assign spectroscopic signatures of defects in other organic polymers as well.

P15 Hydrogen disorder: the nature of crystalline cellulose?

Pan Chen[1]
[1] *Aachener Verfahrenstechnik: Molecular Simulations and Transformations, RWTH Aachen University, Schinkelstraße 2, 52062 Aachen, Germany*

Combination of X-ray and neutron diffraction techniques has demonstrated the hydrogen disorder in highly crystalline native cellulose, yielded two possible hydrogen bonding networks, named pattern A and pattern B, respectively. Nevertheless, based on the same experimental techniques, no similar hydrogen disorder was found in crystalline cellulose II and IIII. MD simulations, employing four carbohydrate force fields (GROMOS, CHARMM, GLYCAM, OPLS), and DFT calculations both suggest an alternative, energetically more stable hydrogen bonding network, for both cellulose II and IIII, named HB pattern B, in contrast to the experimentally founded HB network which can be named pattern A. The difference between these two HB patterns can be clarified by two torsions (HO2-O2-C2-H2, HO6-O6-C6-H6), which is cis in pattern B but trans in pattern A. Energy decomposition analysis shows that the preference of pattern B comes from the local stabilization of hydroxyl groups with respect to the beta carbon. Comparison between calculated diffraction pattern and experimental diffraction pattern shows that the pattern A of cellulose II is slightly better in agreement with experiment, whereas the pattern B of cellulose III is slightly better in agreement with experiment. In summary, MD simulation and DFT calculation proves the existence of another HB pattern in cellulose II and IIII. Together with the founded two HB patterns of native cellulose, hydrogen disorder may be the nature of all crystalline cellulose allomorphs.

Effects of Collectivity in Homology Recognition: a density functional theory based approach

P16

Sergio Cruz[1], Claudia Danilowicz[2], Chantal Prevost[3], Mara Prentiss[1] and Maria Fyta[1]
[1] *Institute for Computational Physics, University of Stuttgart, Germany*
[2] *Physics Department, Harvard University, Cambride, MA, USA*
[3] *LBT - CNRS and Univ Paris Diderot, Sorbonne Paris Cite, Paris, France*
[4] *Physics Department, Harvard University, Cambride, MA, USA*
[5] *Institute for Computational Physics, University of Stuttgart, Germany*

RecA is a family of proteins for performing homology recognition while trying to repair DNA. The atomistic mechanism by which this process occurs is not still fully understood. Crystallographic evidence shows that RecA separates a strand in sequences of three bases (triplet), and then searches for the homologous partner. However, ”recognition in duplets” is suggested as a possible mechanism by recent experiments. In our current investigation, the importance of collectivity in recognition is explored by means of quantum mechanical calculations at the level of dispersion corrected density functional theory. We compare the average binding energy for singlets, duplets, and triplets for canonical Watson-Crick and mismatched base pairs. There is a clear distinction between recognition in singlets, and recognition in duplets or triplets. We calculate the energy for duplets and triplets containing mismatches and compare this with the energetics of the respective singlets. Analysis on the energy difference will shed light to a better understanding of this homology recognition process.

Benchmarking free energy methods for breathing in Metal-Organic Frameworks

P17

R. Demuynck[1], L. Vanduyfhuys[1], A. Ghysels[1], S.M.J. Rogge[1] and V. Van Speybroeck[1]
[1] *Center for Molecular Modeling, Ghent University, Ghent, Belgium*

Metal-organic frameworks (MOFs) are a promising class of materials. Combining metal-oxides with organic linkers yields large 3D frameworks with nanosized pores. Due to these pores the MOFs can be used in many applications such as the detection, storage and separation of gases. MOFs are of particular interest for computational physics hence synthesizing all combinations of metal oxides and organic linker would be an impossible endeavor. With the aid of molecular simulations researchers try to predict the thermodynamic behavior of MOFs. A very interesting feature of some of these MOFs is the inherent flexibility of their framework, for example MIL-53(Al). Other than regular materials will these MOFs their unit cell undergo large deformation under the influence of external stimuli such as pressure [1], temperature, gas adsorption, ... this phenomena is called breathing.

We test cased several simulations techniques to predict the breathing behavior of MOFs. The issues that have to be overcome are twofold. The first step is the construction of a force field (FF). Predicting the breathing behavior requires simulations on long time and large length scale which is not feasible from ab initio methods. With the aid of QuickFF, a new software package we developed [2], we can construct the FF from ab initio input data, This input data is generated using DFT calculations on smaller clusters which are representable for the organic and inorganic MOF parts. Subsequently, molecular dynamic simulations have to be performed to obtain the free energy as function of the MOFs framework. To enhance the sampling in transition regions between stable states we considered several sampling techniques, either by fixing the framework (thermodynamic integration, free energy perturbation) or either by the addition of an external potential (umbrella sampling, metadynamics). Once the free energy is obtained one can determine whether a MOF has an intrinsic bistable behavior. In this work we benchmark the various advanced sampling techniques on their ability to obtain the free energy profile for MIL-53(Al). First we construct a force field for MIL-53(Al) and subsequently apply the different techniques to obtain its free energy profile.

[1] P. Yot et al., Chem. Commun., 2014, 50, 9462.
[2] L. Vanduyfhuys et al., J. Comput. Chem., 2015, in press.

P18 Surface modification of TiO_2 with metal oxide nanocluster

Marco Fronzi[1] and Michael Nolan[1]
[1] *Tyndall National Institute, University College Cork, Cork, Ireland*

TiO_2 photocatalysts have two key challenges: (1) to shift the TiO_2 band gap to the visible region, allowing solar energy to be used and (2) enhancing charge separation after photoexcitation. We discuss our simulation driven work on a new mechanism for band gap modification in TiO_2: surface modification of TiO_2 with metal oxide nanoclusters and the interactions of molecules with these new photocatalysts for water oxidation and CO_2 reduction.. Modifying TiO_2 with transition metal oxide nanoclusters induces visible light activity, which is achieved by introducing nanocluster derived electronic states above the original TiO_2 valence band edge, to shift the VB edge to higher energy. A model of the photoexcited state confirms the band gap reduction which is controlled by the coverage of transition metal oxide nanoclusters. For tin oxide, experiment and simulation show that the change in the band gap is controlled by two factors: the tin oxidation state and the TiO_2 crystal polymorph, with rutile and anatase showing different properties when modified with SnO_2 . The stereochemical lone pair in SnO and PbO induces a band gap reduction. Simple rules for modifying TiO_2 induce visible light absorption are presented. Models of the photoexcited state of modified TiO_2 that the photoexcited hole localises on low coordinated oxygen in the nanocluster and the electron in the TiO_2 surface; the presence of low coordinated atoms is crucial in understanding electron and hole localisation. Finally, we present studies of the interaction of hydrogen, water and CO_2 at these structures to understand how these molecules interact with the supported nanoclusters and can be activated towards, e.g. water oxidation or CO_2 reduction.

P19 High Throughput DFT Framework: A Study of Interfaces and Material Properties

J. Gabriel[1], K. Mathew[2] and R.G. Hennig[1]
[1] *Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611-6400 USA*
[2] *Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853 USA*

Density Functional Theory and versatile computational materials science codes have improved our fundamental understanding of complex processes like solvation in modern technological applications like nanocrystal growth and catalysis. The Vienna Ab initio Simulations Package (VASP) provides a convenient framework for the investigation of the fundamental energetics behind such processes.

The continuum solvation model implemented into VASP called VASPsol by Kiran et al.[1] has made possible the investigation of solvation energies of interfaces and ligands. We are conducting a high throughput search of stable interfaces in the chalcogenide Quantum Dot solids. This has shed light on the importance of the effects of solvents in nanocrystal synthesis. Previous work in the group has supported experimental findings of the evolution of nanocrystal shape and morphology[2]. The high throughput framework was developed based on object oriented python tools of the Materials Project[3] and the Atomic Simulation Environment (ASE)[4]. The high throughput framework has also been applied to study the convergence of materials properties like the bulk moduli of metals with respect to the numerical integration methods implemented in VASP.

[1] K Mathew, R Sundararaman, K Letchworth-Weaver, TA Arias, RG Hennig, The Journal of Chemical Physics 140 (8), 084106.
[2] CR Bealing, WJ Baumgardner, JJ Choi, T Hanrath, and RG Hennig, Predicting Nanocrystal Shape through Consideration of Surface-Ligand Interactions ACS Nano 2012 6 (3), 2118-2127.
[3] A Jain*, S.P. Ong*, G Hautier, W Chen, WD Richards, S Dacek, S Cholia, D Gunter, D Skinner, G Ceder, K.A. Persson (*=equal contributions),The Materials Project: A materials genome approach to accelerating materials innovation Applied Physics Letters Materials, 2013, 1(1), 011002.
[4] SR Bahn and KW Jacobsen, An object-oriented scripting interface to a legacy electronic structure code. Comput. Sci. Eng., Vol. 4, 56-66, 2002.

A machine learning approach to clarify the structural properties of organic-inorganic interface systems

P20

Piero Gasparotto[1] and Michele Ceriotti[1]
[1] *Laboratory of Computational Science and Modeling, IMX, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

Recently, Gasparotto *et al.* have proposed a machine learning technique to recognize structural patterns in an atomistic simulation (PAMM: Probabilistic Analysis of Molecular Motifs [1]). Starting from a (possibly) high-dimensional description of groups of atoms, PAMM can provide an out-of-sample probabilistic definition of the structural motifs, which can be used to identify the same patterns in new configurations of the system being studied. PAMM introduces a univocal, unbiased, and adaptive way to classify the stable structures shown by a specific system.

Another extremely powerful application of machine learning is that of dimensionality reduction. In order to present an intuitive picture of the physics of the problem, one would like to obtain a low-dimensional, coarse-grained description of the possible configurations explored by the system during a simulation. This can be done by applying a non-linear dimensionality reduction scheme, such as Sketch-map [2]. PAMM and Sketch-map complement one each other and provide a fully automated framework to assist standard structural analysis. They can capture appropriate low-dimensional structural order parameters which can be used to accelerate the exploration of the complex conformational landscape in an a simulation. Here we demonstrate their application to the identification of hydrogen-bonding and secondary structure motifs, and discuss their potential to rationalise the behavior of biological molecules in uncoventional environments, such as those encountered at inorganic interfaces. [3,4]

[1] Piero Gasparotto and Michele Ceriotti. Recognizing molecular patterns by machine learning: An agnostic structural definition of the hydrogen bond. J. Chem. Phys. 141, 174110 (2014).

[2] Michele Ceriotti, Gareth a Tribello, and Michele Parrinello. Simplifying the representation of complex free-energy landscapes using sketch-map. Proc. Natl. Acad. Sci. U. S. A. 108, 13023 (2011).

[3] Rinke Gordon, Rauschenbach Stephan, Harnau Ludger, Albarghash Alyazan, Pauly Matthias and Kern Klaus. Active Conformation Control of Unfolded Proteins by Hyperthermal Collision with a Metal Surface. Nano Lett. 14, 5609 (2014).

[4] Deng Zhitao, Thontasen Nicha, Malinowski Nikola, Rinke Gordon, Harnau Ludger, Rauschenbach Stephan and Kern Klaus. A close look at proteins: submolecular resolution of two-and three-dimensionally folded cytochrome c at surfaces. Nano Lett. 12, 2452 (2012).

P21

Anisotropic displacement parameters from dispersion-corrected DFT-methods

J. George[1], A. Wang[1], V. L. Deringer[1], R. M. Wang[1], R. Dronskowski[1] and U. Englert[1]
[1] *RWTH Aachen, Landoltweg 1, 52074 Aachen*

Anisotropic displacement parameters (adps) are omnipresent in crystallography: they can be used to rationalize thermal motions or to identify problems in the structure determination. In experimentally difficult cases, it would be desirable to predict such adps reliably from theory.

We compare calculated adps for urea to experimental ones derived from neutron diffraction at 12 K [1]. This is done on the basis of first principle quasi-harmonic phonon calculations, as described in ref. 2. In doing so, we use different *a posteriori* dispersion-corrections to the PBE-functional and the dispersion-corrected functional vdW-DF2 for the calculations. All dispersion-corrected methods result in nearly perfect adps.

Moreover, we contrast the calculated adps of pentachloropyridine (Cl_5py) at different temperatures derived from one dispersion-corrected method, PBE+TS [3], to experimental ones newly obtained by X-ray diffraction [4]. The influence of anharmonicity on the adps in Cl_5py should be smaller than in a compound including hydrogen atoms. There is a good agreement of the adps from PBE+TS with the experimental ones up to 200 K.

[1] S. Swaminathan, B. M. Craven, R. K. McMullan, Acta Cryst., 1984, B40, 300–306.

[2] V. L. Deringer, R. P. Stoffel, A. Togo, B. Eck, M. Meven and R. Dronskowski, CrystEngComm, 2014, 16, 10907–10915.

[3] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865; A. Tkatchenko and M. Scheffler, Phys. Rev. Lett., 2009, 102, 073005.

[4] J. George, A. Wang, V.L. Deringer, R. M. Wang, R. Dronskowski and U. Englert, manuscript in preparation.

P22

Magnetic properties of Co-Cu codoped ZnO : Density functional calculations

Alvaro González-García[1], Víctor Mendoza- Estrada[1] and William López-Pérez[1]
[1] *Universidad del Norte*

We are currently carrying out ab-initio spin-polarized calculations in order to study the structural, electronic and magnetic properties of the Co-Cu codoped ZnO wurtzite semiconductor using the vienna ab-initio simulation package (VASP)[1]. Calculations are based on density functional theory (DFT) within GGA and GGA+U formalisms for exchange and correlation potential.

The effects of both distance between Co impurities and Co concentrations on magnetic properties in Co-Cu codoped ZnO will be studied. Therefore, electronic structure calculations for ferromagnetic (FM) and antiferromagnetic (AFM) states of $Co_xCu_{0.056}Zn_{0.944-x}O$ (x=0.0294 and 0.0588) and $Co_xCu_{0.125}Zn_{0.875-x}O$ (x=0.071 and 0.143) for the closest and farthest Co settings will be performed. In order to gain insight about magnetic properties of Co-Cu codoped ZnO, the electronic and magnetic properties of Co doped-ZnO and Cu doped-ZnO will be previously studied. The effects of oxygen vacancies on both magnetism and system stability will also be taken into account.

The present calculation reveals that when the Zn atom is substituted by the Co atom in the ZnO semiconductor, a Co-Co distance-dependent FM-AFM ground state is observed for $Co_xZn_{1-x}O$ (x= 0.125). The system prefers FM (AFM) state for the nearest (farthest) configuration. An energy difference (E_{AFM-FM})and magnetic moment per Co atom of about 11 meV (-1.4 meV) and 3.00 μ_B are predicted respectively for $Co_xZn_{1-x}O$ (x= 0.125) in the FM (AFM) state. In contrast, $Cu_xZn_{1-x}O$ (x= 0.125) presents a FM behavior for both Co configurations. It was also found that energy difference and magnetic moment per Cu atom for $Cu_xZn_{1-x}O$ (x= 0.125) are about 48.5 meV (16 meV) and 1.00 μ_B for the nearest (farthest) configuration.

On the other hand, it was found, for the farthest Co configuration, that when $Cu_xZn_{1-x}O$ (x= 0.125) is doped with Co ($Co_xCu_{0.125}Zn_{0.875-x}O$, x=0.071) both the magnetic moment (2 μ_B) and energy difference (551 meV) per Co increase.

To finish, our research is not concluded yet. There are still missing calculations to study of the electronic and magnetic properties for both the closest and farthest Co configurations of $Co_xZn_{1-x}O$ (x= 0.056), $Cu_xZn_{1-x}O$ (x= 0.056), $Co_xCu_{0.056}Zn_{0.944-x}O$ (x=0.0294 and 0.0588) and $Co_xCu_{0.125}Zn_{0.875-x}O$ (x=0.143); as well as the effects of oxygen vacancies on both magnetism and system stability.

[1] G. Kresse, J. Furthmüller. Phys. Rev. B 54 (1996) 11169.

Properties of AuAg Bimetallic Nanoparticles

P23

Anna L. Gould[1], A. J. Logsdail[1] and C. R. A. Catlow[1]
[1] *UCL Chemistry, Kennington United Kingdom*

AuAg bimetallic nanoclusters (nanoalloys) have been proven to enhance catalytic activity for CO and H2 oxidation, acting as co-catalysts for a semiconducting support while simultaneously lowering production costs [1,2,3]. However, the introduction of a secondary species introduces significant complications; a greater variety of chemical arrangements are possible within the nanocluster and they are not easily determinable via experimental means. Thermodynamic reasoning supports the formation of alloys, facilitated by their similarity in atomic radius and an appreciable degree of charge transfer due to their differing electronegativities [4]. Nonetheless, chemical synthesis of core@shell structures is still viable through optimisation of the operating environment. We investigate the changes in electronic properties for bimetallic AuAg nanoalloys as a result of differing composition ratios and differing structural motifs, providing additional insight to experimental data. We have thus far obtained favourable arrangements for particular composition ratios from a combined use of interatomic potentials and Density Functional Theory (DFT) methods [5]. These low energy/high stability arrangements have also been assessed in terms of their differing electronic properties, as well as using ensemble Molecular Dynamics (MD) to assess thermal stability under a simulated heat treatment [6]. Finally, we also look to molecular adsorption to determine the influence of environmental gases on nanoalloy reactivity, which will be coupled with experimental combined x-ray absorption fine structure (XAFS) and diffuse infrared fourier transform spectroscopy (DRIFTS) characterisation.

[1] A. Primo, A. Corma and H. García, Phys. Chem. Chem. Phys., 2011, 13, 886-910.
[2] R. Ferrando, J. Jellinek and R. L. Johnston, Chem. Rev., 2008, 108, 845–910
[3] T. Déronzier, F. Morfin, M. Lomello and J.-L. Rousset, J. Catal., 2014, 311, 221–229
[4] G. Rossi, R. Ferrando, A. Rapallo, A. Fortunelli, B. C. Curley, L. D. Lloyd and R. L. Johnston, J. Chem. Phys., 2005, 122, 194309
[5] A. L. Gould, C. J. Heard, A. J. Logsdail, C. R. A. Catlow, Phys. Chem. Chem. Phys., 2014, 16, 21049-21061
[6] A. L. Gould, A. J. Logsdail, C. R. A. Catlow. To be submitted.

P24 Phosphorization of Monolayer Boron Nitride: Stable Single Layer Boron Phosphide

Lutfiye Hallioglu[1], Huseyin Sener Sen[1], ngin Durgun[1], Hasan Sahin[2] and Francois Peeters[2]
[1] *UNAM-National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey*
[2] *Department of Physics, University of Antwerp, 2610 Antwerp, Belgium*

The synthesis of graphene and its unique properties have increased the focus on novel two dimensional (2D) materials. Hexagonal boron nitride (h-BN) is the runner-up material in the field of 2D systems. h-BN has a stable and mechanically strong honeycomb structure which consists of B and N atoms and also called as “white-graphene” due to its white colour in the visible range. However h-BN is an insulator with a large band gap and it is a good thermal conductor. It has an even higher chemical stability than graphene which makes it suitable for various applications. In this study, by using *ab-initio* methods based on density functional theory, we examined the phosphorization of h-BN with varying concentrations, which leads to stable 2D boron phosphide at the ultimate limit. The lattice constant of the h-$BN_{1-x}P_x$ alloy increases with increasing x. The planar geometry of h-BN is deformed and alloy turns into buckled structure until $x > 0.75$ (corresponding to (75% P) concentration). Beyond this point, planarity is recovered and planar monolayer h-BP achieved when all N atoms are replaced. Although 2D BP has not been synthesized yet, phonon spectrum analysis and high temperature molecular dynamics calculations indicate the stability of the system. Interestingly while h-BN is an insulator, h-BP is semiconductor with 1.3 eV direct band gap. The band gap decreases with increasing x, which also allows band gap engineering. Our results indicate h-$BN_{1-x}P_x$ alloy is suitable material for different applications including nano-electronic applications.

[1] L.Hallioglu and et al., to be published.

Investigating organic monolayer/layered inorganic semiconductor hybrid systems

P25

Shashank S. Harivyasi[1], Oliver T. Hofmann[1] and Egbert Zojer[1]
[1] *Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, Austria*

In recent years, led by graphene, there has been an increased interest in 2D materials because of their unique properties. Certain transition metal oxides and chalcogenides (TMO&C) represent a class of these 2D materials forming layers that are held together by 'weak' interactions. Monolayers of these materials have been reported to have unique electronic properties (such as edge states [1]) in comparison to the traditional 3D lattice based semiconductors. Many of these TMO&Cs also exhibit thickness-dependent electronic properties which themselves are a focus of contemporary research [2]. In this work, we present our attempts at simulating the structural and electronic properties of a few TMO&Cs using density functional theory. We highlight the importance of accounting van der Waals interactions [3] to attain good agreement with experimental findings of structural parameters. We also outline our plan to study organic monolayer/layered inorganic semiconductor hybrid systems to explore and exploit the effects of (patterned) monolayer adsorption on the unique electronic properties these layered semiconductors.

[1] Pan, Hui and Yong-Wei Zhang. J. Mater. Chem. 22, 7280 (2012).
[2] Splendiani, Andrea, et al. Nano Lett. 10, 1271 (2010).
[3] Tkatchenko, Alexandre and Matthias Scheffler. Phys. Rev. Lett. 102, 073005 (2009).

Lanthanoid(III) and Actinoid(III) Hydration

P26

Norah Heinz[1], Jun Zhang[1] and Michael Dolg[1]
[1] *Institute for Theoretical Chemistry, Universität zu Köln,*
Greinstr. 4, 50939 Cologne, Germany
e-mail: N.Heinz@uni-koeln.de, phone: (+49)221 - 470 - 6885

The investigation of the hydration of lanthanoids and actinoids is and has been an challenging and important task. Understanding the behaviour of lanthanoid and actinoid ions in aqueous solutions is crucial in, e.g., the context of nuclear waste separation, since the burnup of nuclear fuel contains a mixture of different radio active substances including lanthanoid and actinoid ions. Developing efficient separation procedures is vital to allow efficient storage of nuclear waste on the basis of half life periods as well as the extraction of elements of economical interest. Lanthanoid ions are involved in many practical applications and efficient extraction processes are economically relevant. First principle Gibbs energies of hydration of the whole trivalent actinoid (An^{3+}) and lanthanoid series (Ln^{3+}) were determined based on DFT-optimized structures of 8- and 9-fold coordinated cations at the Coupled Cluster level of theory (CCSD(T)) applying basis sets of triple zeta quality[1,2]. Relativistic effects regarding the lanthanoid and actinoid ions are taken into account by employing scalcar relativistic *f-in-core*-pseudopotentials. The results are compared to first principle Gibbs energies completely calculated at the DFT level of theory.

Additionally, a new correction term was evaluated to describe successive hydrogen bonding to the surrounding aqueous phase. Coordination numbers as well as the bonding structure of the aquo-complexes are also discussed. Special attention is given to differing properties of the chemically very similar lanthanoid(III) and actinoid(III) series.

The obtained results are used in current projects focussing on the determination of efficient separation processes at the level of density functional theory as well as first principle studies on the hydration properties of Texaphyrin complexes containing trivalent actinoid and lanthanoid ions, including the calculation of absorption spectra in gas and aqueous phase using TDDFT.

[1] J. Zhang, N. Heinz, M. Dolg, Inorg. Chem. 2014, 53, 7700.
[2] N. Heinz, J. Zhang, M. Dolg, J. Chem. Theory Comput. 2014, 10, 5593.

P27

Thermodynamics and Kinetics of Oxygen Defects in FCC Transition Metals

Shreyas Honrao[1] and Richard G. Hennig[2]
[1] *Department of Materials Science and Engineering, Cornell University,*
[2] *Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA.*

Transition metals and their oxides are particularly interesting materials because they exhibit a wide range of properties. They may be dielectrics, semiconductors or metals; they exhibit unique magnetic and optical properties; they possess a variety of surface structures, which affect the surface energies of these compounds and influence their chemical properties, making them catalytically active. Even though we know a lot about the structure, synthesis, and properties of these materials, very little is known about the equilibrium defects present in these materials and how they move about.

In this project, we use DFT to study the thermodynamics, kinetics and diffusion processes involved in the transformations that take place as Co, Ni and Cu are converted to their respective oxides. We look at various point defects, both simple and complex, present in these systems, calculate their formation energies, and factor in entropic contributions to predict their stability. Once we know the most likely defect structures, we use them to study the possible diffusion pathways in these systems. We observe that, in addition to simple vacancy and interstitial diffusion, there are also a few other interesting mechanisms that can contribute to material transport. Studying the migration barriers helps us determine the most probable ones. We use three different FCC metals in our study in order to compare, and look for trends and relationships in these systems. We try to explain these trends with the help of our calculations and observations.

P28

Study of the excited state geometries of organic chromophores

Marie Humbert-Droz[1] and Tomasz A. Wesolowski[1]
[1] *Department of physical chemistry, Université de Genève, 30, quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland*

The deformation a chromophore encounters upon electronic excitation can be crucial to understand its absorption (and emission) spectrum. Accounting for the environment effect on the excitation energies is sometimes necessary, but this can be a very expensive task. FDET [1] is a multilevel method of choice when it comes to simulate local excitations of various chromophores. It has been shown that the environment density (ρ_B) in such calculations can be generated with a lower level of theory [2] without loosing accuracy on the excitation energies and environment induced shifts. Having this in mind, the excited state properties of several experimentally relevant organic chromophores are evaluated and analysed[3,4].

[1] T. A. Wesolowski and A. Warshel. Frozen density-functional approach for ab-initio calculations of solvated molecules. J. Phys. Chem., 97(30):8050-8053, JUL 1993. T. A. Wesolowski. One-electron equations for embedded electron density: challenge for theory and practical payoffs in multi-level modelling of soft condensed matter. In J. Leszczynski, editor, Computational Chemistry: Reviews of Current Trends, volume X, pages 1-82. World Scientific, Singapore, 2006. T. A. Wesolowski. Embedding a multideterminantal wave function in an orbital-free environment. Phys. rev. A, 77(1), JAN 2008.
[2] M. Humbert-Droz, X. Zhou, S. V. Shedge, T. A. Wesolowski, Theor Chem Acc (2013), 132:1405.
[3] K. Fujisawa, C. Beuchat, M. Humbert-Droz, A. Wilson, T. A. Wesolowski, J. Mareda, N. Sakai, S. Matile, Angew. Chem. Int. Ed. (2014), 53, 11266
[4] M. Humbert-Droz *et al*, to be published

Size and shape of oxygen vacancies and protons in acceptor-doped barium zirconate

P29

Erik Jedvik[1], A. Lindman[1], M. Benedictsson[1] and G. Wahnström[1]
[1] *Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

The defect induced chemical expansion in acceptor-doped barium zirconate is investigated using density-functional theory (DFT) calculations. The two defect species involved in the hydration reaction, the +2 charged oxygen vacancy and the proton interstitial forming an hydroxide ion, are considered both as free defects and in association with the dopants Y, In, Sc and Ga. The defect induced strain tensor λ is introduced, which provides a natural generalisation of the ordinary chemical expansion to three dimensions and to anisotropic distortions. Both the addition of a vacancy and a proton causes anisotropic distortions and a net contraction of the lattice, indicating that both the vacancy and the hydroxide ion are smaller than the oxygen ion. The contraction is considerably larger for the vacancy and the net effect in hydration, when a vacancy is filled and two protons are added, is an expansion, consistent with the experimental findings. The effect of the dopants on the chemical expansion in hydration is found to be quite small, even if it is assumed that both the vacancy and the proton are fully associated with a dopant atom in the lattice.

[1] E. Jedvik, A. Lindman, M. Benedictsson and G. Wahnström, Solid State Ionics

---

Modified hybrid functional with optimal Hartree-Fock exact exchange for TiO2 materials

P30

Kyoung Chul Ko[1], Oriol Lamiel-García[1] and Francesc Illas[1]
[1] *Departament de Química Física and Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1,08028 Barcelona, Spain*

It is nowadays well known that broadly used local-density approximation (LDA) and generalized gradient approximation (GGA) based functionals severely underestimate the band gap of oxides to the point that antiferromagnetic insulators such NiO are described as metals. Bulk TiO2 is not an exception and the LDA and GGA calculated values for the stable polymorphs are too small. Hybrid functionals such as PBE0 or B3LYP properly describe these materials as insulators but, on the contrary, the calculated band gap appears to be too large. Here, the overestimation comes from the too large fraction of Fock exchange included in these hybrid functionals. In order to provide a simple yet efficient way to treat these systems, we explored the influence of HF exchange percentage in PBE0 hybrid functional in the calculated properties. A quantitative correlation between HF exchange and band gaps for anatase/rutile TiO2 at the experimental crystal structure is found suggesting that reducing the amount of HF exchange in PBE0 to 12.5 percentage can correctly predict the band gap of TiO2 systems, in agreement with earlier work for rutile [1]. Further refinement of crystal structure of anatase and rutile with this functional leads to values close to experiment indicating that this modified hybrid functional provides a pragmatic approach to describe the electronic structures for various TiO2 systems. The study of reduced TiO2-x systems with this modified hybrid functional is now being carried out in our laboratory by using FHI-aims code.

[1] Y. Zhang, W. Lin, Y. Li, K. Ding, J. Li, J. Phys. Chem. B., 109, 19270 (2005)

P31

Electronic structure of ferrocene and selected ferrocene-based molecules

Krzysztof Kośmider[1], Vladimír Zobač[1] and Pavel Jelínek[1]
[1] *Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-16200 Prague, Czech Republic*

Metallocenes M(C_5H_5)$_2$ —the molecules composed of a metal (M) atom in between two planar cyclopentadienyl anions (C_5H_5)— has received an interest over past three decades mainly as catalysts and organometallic polymers. Now a days, with increasing capabilities of a solid surface control and development of molecular electronics, they are considered as building blocks of a number of nano-devices. For example ferrocene Fe(C_5H_5)$_2$ molecule —due to its proven stability under an increase of oxidation state— is expected [1] to exhibit suitable properties for building a quantum cellular automata [2-4] made of molecules. In such a device a couple of ferrocene molecules (or its derivatives) would act as a quantum wells for a charge which moves between them. Density functional theory (DFT) became a standard tool supporting investigation of structural and electronic properties at the atomic scale. However, proper description of ferrocene enforces non-standard treatment going beyond classical DFT, including non-local exchange-correlation functionals and Van der Walls (VdW) interactions.

Here we present our DFT study on a geometric and electronic structure of the ferrocene, selected ferrocene-related molecules, and their two-dimensional structures. Properties of free-standing molecules as well as their adsorption at chosen metallic substrates is shown. We use different basis sets (plane waves, atomic orbitals), exchange-correlation functionals (LDA, PBE, B3LYB), and description of the VdW interactions. We test those methods against geometric structure, energy alignment, and charge localization. This benchmark is then used to tune a proper description of the system, and to address practical questions appearing during our experimental as well as theoretical research.

[1] Y. Lu, and C.S. Lent, Nanotechnology 19, 155703 (2008)
[2] Lent C.S *et al.*, Nanotechnology 4, 49 (1993)
[3] Orlov A.O *et al.*, Science 277, 928 (1997)
[4] Amlani I. *et al.*, Science 284, 289 (1999)

P32

Reactions of boriranes and borirenes with unsaturated hydrocarbons: a computational study.

Małgorzata Krasowska[1] and Holger F. Bettinger[2]
[1] *Institut für Organische Chemie, Universität Tübingen Auf der Morgenstelle 18, 72076 Tübingen, Germany*

Boriranes and borirenes are the three-membered ring compounds containing one boron atom. They can be obtained for instance by the photorearrangement of boranes [1], by the acetone or diphenylacetylene cycloaddition reaction with methyleneborane [2], by the addition of HCl or $HN(SiMe_3)_2$ to boranediylboriranes [3], or by the borylene transfer to unsaturated hydrocarbons [4]. Either boriranes as well as borirenes are highly strained molecules which makes them reactive. Borirenes, the boron analogues of cyclopropene, were widely studied experimentally and theoretically both as free molecules and as base-stabilized adducts [5]. Boriranes, boron counterparts of cyclopropane, were mainly synthesized as base- or NHC-stabilized molecules [6].

To study their reactivity towards unsubstituted and substituted unsaturated hydrocarbons (ethyne or ethene), boriranes and borirenes with various electron donating and electron withdrawing substituents on boron atom (R = H, Me, Ph, NH_2, Cl, F) where chosen. All the individual species on the potential energy surface were optimized using the M062X functional in combination with the 6-311+G** basis set. The energies were further refined using the CCSD(T) method in conjunction with the def2-TZVP basis set.

The reaction of electron deficient boron atom and the π-system of the hydrocarbon can proceed according to two competitive mechanisms depending on the substitution of hydrocarbon. The reaction of borirane or borirene with unsubstituted hydrocarbon is the stepwise ring expansion. On the other hand, the reaction of boron heterocycle toward hydrocarbon with strongly electron withdrawing substituents can lead to the borylene transfer to the hydrocarbon.

[1] S. E. Denmark, K. Nishide, A. M. Faucher,J. Am. Chem. Soc. 1991, 113, 6675.
[2] H. Klusik, A. Berndt, Angew. Chem., Int. Ed. 1983, 22, 877.
[3] P. Willerhausen, G. Schmidt-Lukasch, C. Kybart, J. Allwohn, W. Massa, M. L. McKee, P. v. R. Schleyer, A. Berndt, Angew. Chem., Int. Ed. 1992, 31, 1384.
[4] a) H. Braunschweig, T. Herbst, D. Rais, F. Seeler, Angew. Chem., Int. Ed. 2005, 44, 7461; b) M. Krasowska, H. F. Bettinger, J. Am. Chem. Soc. 2012, 134, 17094.
[5] a) P. H. M. Budzelaar, S. M. Van der Kerk, K. Krogh-Jespersen, P. v. R. Schleyer, J. Am. Chem. Soc. 1986, 108, 3960; b) M. A. Kropp, G. B. Schuster, J. Am. Chem. Soc. 1989, 111, 2316; c) A. Höfner, B. Ziegler, W. Massa, A. Berndt, Angew. Chem., Int. Ed. 1989, 28, 186.
[6] H. Braunschweig, C. Claes, A. Damme, Dei, R. D. Dewhurst, C. Horl, T. Kramer, Chem. Comm. 2015, 51, 1627.

P33

Role of orbital structure in High-resolution STM of molecules

O. Krejčí[1], P. Hapala[1], M. Ondráček[1] and P. Jelínek[1]
[1] *Institute of Physics, Academy of Science of the Czech Republic, Cukrovarnicka 10, 162 53, Prague, Czech Republic*

Recently, we demonstrated that most features visible in high-resolution AFM images of molecules can be explained by simple mechanical model considering relaxation of an atomistic particle attached to the tip. On top of this, we introduced a simple model for calculating STM current considering only inter-atomic hoppings between relaxed atomistic particle and molecule [1]. The simple model is able to reproduce the main characteristics of high-resolution STM maps in close distance regime where the relaxation effects prevail. But since it completely neglects an electronic structure of the scanned sample, it fails at far distances where the electronic structure is dominating in the STM current. In this work, we implemented an efficient method for simulation of the high resolution STM images considering the molecular electronic structure and the atomistic particle relaxation as well. The method is able to reproduce observed contrast in both the close distance and the far distance regimes, including the gradual transition between them. It gives solid theoretical background for better understanding of high-resolution STM experiments.

[1] Hapala, P. et al., Phys. Rev. B 90,085421 (2014).

P34

Electrostatic design of monolayer properties

Bernhard Kretz[1], David A. Egger[2] and Egbert Zojer[1]
[1] *Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria*
[2] *Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria and Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel*

For raising the full potential of molecular electronics, it is necessary to control the nature of the electronic states within organic layers. In this contribution we present the concept of a modular toolbox that allows realizing a high level of control as far as the energetics and spatial localization of the states is concerned. By quantum-mechanical modelling we show that - based on this toolbox - it is, for example, possible to realize monolayer-based quantum-cascades and electron or hole quantum-well structures. This becomes possible by exploiting collective electrostatic effects naturally emerging in ensembles of polar molecules. As another element of the toolbox we discuss neutral radicals that can be applied for generating locally spin-polarized layers. (cf.: B. Kretz, D. A. Egger, and E. Zojer, ?A toolbox for controlling quantum states in organic monolayers?, Advanced Science, 1400016 (2015). DOI: 10.1002/advs.201400016)

Investigating HPA functionalized mesoporous silica materials for use as high temperature proton exchange membranes

P35

Krystina Lamb[1], Roland De Marco[1], John Bartlett[1], Vanessa K. Peterson[1] and San Ping Jiang[1]
[1] *University of the Sunshine Coast, Locked Bag Maroochydore DC, QLD 4558 Australia,*
Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia
Fuel and Energy Technology Institute, 1 Turner Ave, Technology Park, Bentley, Perth WA 6102, Australia

Medium temperature proton exchange membrane fuel cells (MT-PEMFCs) are solid-state energy conversion devices that electrochemically convert chemical energy (e.g., from alcohols) into electricity. MT-PEMFCs have advantages over low temperature fuel cells, such as elimination of carbon monoxide poisoning of the electrocatalyst [1], enhanced oxidation kinetics of alcohol fuels such as methanol [2], and the use of liquid fuels [3]. Heteropoly acids (HPA) such as phosphotungstic acid (HPW) can be used to impregnate ordered mesoporous silica (MSN) to make nanocomposite proton exchange membranes (PEMs) [4].

While these HPW MSN mixes have been studied extensively as catalysts [5], HPW MSNs have only recently be studied for use in MT-PEMFCs using methanol as a fuel [6]. Previous studies have investigated the correlations between physical stability, temperature, and fuel cell performance [6]. However, the structure of the HPW MSNs and how this affects the proton conduction efficiency and mechanism of proton conduction in these materials has not been investigated.

In this project, MT-PEMFCs with HPW MSN have been studied using synchrotron, desktop and neutron scattering and spectroscopic techniques. The results show that the physical properties vary with increased HPW content, however further analysis is required to demonstrate the exact functional changes and how this impacts the proton conduction mechanism.

[1] L. Carrette, K. Friedrich, M. Huber and U. Stimming, Phys. Chem. Chem. Phys3, 320 (2001)
[2] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D. Wilkinson, Z.-S. Liu and S. Holdcroft, J. Pow. Src., 160, 872 (2006)
[3] C. Winter, Int. J. Hydrogen Energy 30, 681 (2005)
[4] J. Zeng, S. Jiang and L. Li, ECS Trans. 41 1603 (2011)
[5] T. Balsco, A. Corma, A. Martinez and P. Martinez-Escolano, J. Catal., 177, 306 (1998)
[6] J. Zeng, P. Shen, S. Lu, Y. Xiang, R. De Marco and S. Jiang, J. Mem. Sci. 397, 92 (2012)

Speciation of Extraframework Aluminium in Faujasite Zeolite

P36

Chong Liu[1], Guanna Li[1], Emiel J.M. Hensen[1] and Evgeny A. Pidko[1]
[1] *Inorganic Materials Chemistry group, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.*

Zeolite Y with faujasite topology is widely used as acidic catalyst for fluid catalytic cracking (FCC) and hydrocracking in the oil refinery[1]. The as-synthesized zeolites with high lattice Al concentration show only low acidity and stability. Further steaming calcination to form extraframework Al-containing (EFAL) species can significantly improve its catalytic activity and hydrothermal stability. The enhancement of Brønsted acidity of the steamed zeolite is often associated with the synergy between the EFAL species and neighbouring Brønsted acid sites (BAS) in zeolite pores [2]. However, the nature of these EFAL species and their intrinsic interaction mechanism with BAS are still not understood well yet.

In this study, we present a comprehensive periodic DFT study combined with ab initio thermodynamic analysis. The results point to a strong preference of mononuclear EFALs towards self-organization into multinuclear species. The resulting tri- and tetra-nuclear clusters are preferentially located in sodalite cages of the faujasite structure. Ab initio thermodynamic analysis points to the predominant formation of such species under experimentally relevant conditions. It is proposed that multinuclear oxygenated and hydroxylated EFALs located in sodalites cage are dominant species in faujasite zeolite after high-temperature steaming treatment.

[1] A. Primo, H. Garcia, Chem. Soc. Rev. 43 (2014) 7548.
[2] E. A. Pidko and E. J. M. Hensen et al., ChemCatChem 5 (2013) 452; ACS Catal. 3 (2013) 1504.

P37 Stacking Characteristics of Close Packed Materials

Christian H. Loach[1] and Graeme J. Ackland[1]
[1] *University of Edinburgh School of Physics and Astronomy*

Density functional theory calculations are used to study the effect of screening interactions on the energies of stacking configurations in close packed materials. It is found by calculating the energies of all possible unique stacking configurations for up to ten atomic layers, that this interaction manifests itself in some materials as an aversion to double hexagonal close packed stacking. Lindhard theory [1] predicts that effective screening at the Fermi energy results in a decaying oscillatory potential in real space. The addition of this oscillatory term to Lennard Jones style pair potentials enables qualitative reproduction of the observed dependence on different stacking configurations. Further work it is hoped will result in classical potentials which reproduce the *ab initio* data and are usable for real materials.

[1] N.W. Ashcroft, N.D. Mermin Solid State Physics. Saunders College, 1976.

P38 Ab initio atomistic thermodynamics modeling of thiolate adsorption on Au{111} : The importance of van der Waals interactions

Joakim Löfgren[1], Henrik Grönbeck[1], Kasper Moth-Poulsen[2] and Paul Erhart[1]
[1] *Department of Applied Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden*
[2] *Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296. Gothenburg, Sweden*

Adsorption of alkylthiolates on Au(111) and the formation of self-assembled monolayers (SAMs) has been extensively studied for several decades and is important for many applications in e.g., sensing and nanofabrication. Over the years, understanding of the interface and adsorption geometry has been elucidated by the combined efforts of experiment and density functional theory (DFT) calculations. One of the major challenges in the modeling of SAMs from a DFT point of view is the lack of dispersive interactions in conventional exchange-correlation (XC) functionals. When considering alkylthiolates with longer hydrocarbon chains this becomes problematic since experimentally well-documented observations such as the stabilizing effect of having a longer chain and the existence of low coverage lying-down (striped) phases cannot be reproduced by local and semi-local XC functionals. In this study we present DFT calculations with the recently developed vdW-DF-CX [1] functional which properly accounts for dispersive interactions while providing an excellent description of both the late transition metals and covalently-bonded systems. Our aim is to show that many of the previous difficulties in the modeling of long alkylthiolates can now be overcome. In particular, we investigate high coverage standing-up phases and show that adsorption energies and their scaling with chain length are in line with experimental results. Furthermore, we consider several different models for lying-down phases and examine their stability as a function of the chemical environment using the ab initio atomistic thermodynamics approach [2].

[1] K. Berland and P. Hyldgaard, Phys. Rev. B 89, 035412 (2014)

[2] J. Rogal and K. Reuter, Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007), p. 2-1—2-18

FHI-aims Benchmark on CYPRESS and SPHYNX

P39

Sanjaya Lohani[1], Charles D. Maggio[2] and Noa Marom[1]

[1] *Department of Physics and Engineering Physics, Tulane University, New Orleans, LA 70118, USA*

[2] *High Performance Computing Team, Technology Services, Tulane University, New Orleans, LA 70118, USA*

In the present work we demonstrate the scaling of FHI-aims on two Super Computers of Tulane University, Sphynx and Cypress, using the generalized gradient approximation technique of Perdew-Berke-Ernzerhof (PBE). We plotted CPU time for single Self-Consistent Field (SCF) iteration as a function of the number of CPU cores. The benchmarking systems consisted of a broad range of molecular crystals (Glycine, Alanine, Paracetamol) and dye sensitized TiO_2 clusters (Ti_3INA_3, Ti_2cat_2 and $Ti_{17}INA_4$). Benchmark results were obtained for up to 128 CPU cores on Sphynx and 240 CPU cores on Cypress. For large molecules on Sphynx, our experiments showed that computational speed was dependent upon choice of node. On both systems we observed linear scaling of iteration time as function of the number of cores.

G_0W_0 calculations based on long-range corrected hybrid functionals: charge-transfer in a molecular donor-acceptor compound

P40

Philipp Metzner[1], Lukas Gallandi[1] and Thomas Körzdörfer[1]

[1] *Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, Potsdam, Germany*

Many-body perturbation theory in the GW approximation is an increasingly popular tool for calculating electron removal energies and fundamental gaps for molecules, solids, and interfaces. Due to their high numerical costs, however, fully self-consistent GW calculations can be bothersome and often not feasable at all. Hence, one frequently employs a non-self-consistent variant of GW, hereafter referred to as G_0W_0. In this method, one uses a perturbative correction to eigenvalues obtained from density functional theory (DFT) to obtain the quasiparticle energies, that is, ionization potentials (IPs) and electron affinities (EAs). The reliability of the results obtained from these calculations, however, depends decisively on the accuracy of the DFT starting point. This problem of non-self-consistent GW calculations is particularly severe in situations in which standard exchange-correlation functionals lead to a wrong ground-state density. This is the case, for example, for molecular donor-acceptor interfaces such as TTF/TCNQ, for which standard semilocal and global hybrid functionals yield a spurious charge-transfer in the ground-state. [1] As a consequence, G_0W_0 calculations are doomed to fail for this system as long as they are based on standard DFT approaches.

Non-empirically tuned long-range corrected hybrid functionals have been suggested as an alternative approach to calculate ionization potentials (IPs) and band-gaps at reduced computational costs as compared to G_0W_0.[2-4] In these functionals, the range-separation parameter is tuned separately for each system to match the IP-theorem. The IP-tuning procedure can be used to predict very accurate IPs and band-gaps. Hence, it can be expected that this new class of functionals yields an improved starting point for non-selfconsistent GW calculations compared to semilocal and global hybrid functionals.

We have recently implemented a long-range corrected (LRC) hybrid functional with ωPBE exchange, PBE correlation, a flexible range-separation parameter (ω), and a flexible amount of global HF-exchange (α) in FHIaims.[5] The non-empirical tuning of the range-separation parameter is performed by an automated script that acts as a wrapper around FHIaims. Here, we demonstrate that this methodology allows predicting an accurate energy level ordering at the TTF-TCNQ interface. To do this, we calculated several electronic properties of planar stacks with varying size as well as stacks in herringbone structure, including the HOMO-LUMO gap, dipole moments and the charge transfered at the interface.[6] Finally, it is demonstrated that using tuned LRC hybrids as a starting point for G_0W_0 provides for robust and efficient means of calculating highly accurate IPs and EAs for finite systems.

[1] F. Caruso, et al., Phys. Rev. B 90, 085141 (2014).
[2] T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. 131, 2818 (2009).
[3] S. Refaely-Abramson, et al., Phys. Rev. Lett. 109, 226405 (2012).
[4] T. Körzdörfer et al., Phys. Rev. B 86, 205110 (2012).
[5] L. Gallandi and T. Körzdörfer, in preparation.
[6] P. Metzner and T. Körzdörfer, in preparation.

P41

The effect of adsorbates on the structure, electronic, and optical properties of TiO_2 nanoparticles.

Olga Miroshnichenko[1,2], Sami Auvinen[3] and Matti Alatalo[1]
[1] *University of Oulu, Center for Molecular Materials, Theoretical Physics, P.O. Box 3000, FI–90014 Oulu, Finland*
[2] *St. Petersburg State Polytechnical University, Department of Theoretical Mechanics, Polytechnicheskaya 29, 195251 St. Petersburg, Russian Federation*

[3] *Department of Mathematics and Physics, Lappeenranta University of Technology, P.O. Box 20, FI–53851 Lappeenranta, Finland*

Titanium dioxide nanoparticles are used in countless applications ranging from photocatalysis and solar cells to UV protection. The optical and electronic properties of titanium dioxide nanoparticles have shown to be strongly dependent on the structure and size of the particle [1-2], and this has to be taken into account in light scattering measurements of the nanomaterials. Besides these size and shape dependent changes, in the case of small particles, the effects of adsorbates become increasingly important, because in the applications, the nanoparticles often reside in water or other, more complicated solutions. Moreover, in the manufacturing processes OH and SO_4 groups, may be attached on the surface from the surrounding medium.

In order to understand the behaviour of TiO_2 nanoparticles in real-world applications it is important to study the effect of attached molecules or fragments on their structure, electronic, and optical properties. We have performed density functional theory (DFT) and time-dependent DFT calculations for titanium dioxide nanoparticles covered with varying number of OH [3] and SO_4 groups. We find that OH groups affect the structure of nanoparticles and also change the photoabsorption characteristics: enlarging the dimensions of the particle and enhancing light absorption. SO_4 groups have a significant effect on the properties of TiO_2 nanoparticles and influence the structure during the particle growth, so they allow the particle to form in anatase structure instead of rutile.

[1] S. Auvinen, M. Alatalo, H. Haario, J.-P. Jalava, R.-J. Lamminmäki, J. Phys. Chem. C 115, 8484 (2011).

[2] S. Auvinen, M. Alatalo, H. Haario, E. Vartiainen, J.-P. Jalava, R.-J. Lamminmäki, J. Phys. Chem. C, 117, 3503 (2013).

[3] O. Miroshnichenko, S. Auvinen, M. Alatalo, Phys. Chem. Chem. Phys., 17, 5321 (2015).

The Utilization of Density Functional Theory to Support Experimental Mass Spectrometry Results in Reaction Mechanism Studies

P42

Nilsson, S.[1], Scotti, G.[1], Haapala, M.[1] and Kotiaho, T.[1]
[1] *Division of Pharmaceutical Chemistry and Technology, Faculty of Pharmacy, Viikinkaari 5E (PL 56), Biokeskus 2, 00014 Helsingin yliopisto, FINLAND*

The monitoring of reaction mechanisms has a great scientific significance, since it through the understanding of the reaction pathways of chemical reactions is possible to steer the direction of the reaction and thereby affect the yeild and selectivities of it. By studying reaction mixtures of varying concentrations, infused with shifting flowrates into microchips and detecting the outcome in real time with on-line mass spectrometry (MS) it is possible to obtain an experimental indication of the reaction mechanism of a reaction. However, to solidify these results, density functional theory (DFT) calculations are with increasing popularity practised. By MS detection, a plausible mechanism for the conversion of heptafulvenes to tropones has been found. This mechanism is suggested due to the MS detection of the intermediates of the reaction. The next step in this mechanism investigation should be to confirm (or reject) the tentative mechansim by utilizing DFT and subsequently research the reaction's kinetics. When the mechanism of the transformation of heptafulvenes into tropones is determined, future reaction mechanisms to be assayed in our research will be famous name reactions whose mechanism still remain obscure.

P43

Density Functional Theory characterisation of azobenzene derivatives

Irina Piyanzina[1] and Benoit Minisini[2]
[1] *Laboratory for Computer Design of New Materials, Institute of Physics, Kazan Federal University, Kremlyovskaya Str., 18, Kazan, Russia*
[2] *Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, 44 Avenue Bartholdi, 72000 Le Mans, France*

Since the year 1937, when Harley published his work [1] about *cis* isomerization of azobenzene, this photochemical phenomena became widely studied. The idea behind it is photoisomerization of azobenzene under irradiation when non-polar *trans*-azobenzene can be photoisomerized into the polar *cis*-azobenzene. Due to relatively simple molecular structure and unique characteristics, azobenzene and its derivatives were investigated in different studies as photoswitchable substances, as dyes, as surface with controlable wettability.

The physical and chemical properties of azobenzene derivative depend on molecular groups used as ring substituents and stability of the configurations. In the present study, we have analyzed the effect of structural diversity on electronic and molecular properties. We have selected 10 derivatives with azobenzene as a parent compound. The first group is electron donating substituents: CH_3, C_6H_5, NH_2, SO_2-NH_2, N-$(CH_3)_2$. The second one is an electron acceptor substituents: OH, NO_2, CH_2-CH_2-OH. The last group contains derivatives with an electron-acceptor at the para-position and an electron-donor at the other para-position of another phenyl ring.

We performed density functional calculations in the GAUSSIAN03 [2] program with B3LYP functional and 6-31++G(d,p) basis set. For each molecule we have examined *trans* and *cis* forms and all possible configurations concerning spatial position of functional group. More details could be found in our previous works [3-5].

The planar *trans* structure has been obtained for all considered molecules. This configuration were found to be more stable than *cis*. The relative difference in the dipole moment between the *trans* and *cis* configurations was found to be lower than for azobenzene for all considered molecules except for molecule with N-$(CH_3)_2$ and NH_2 groups, for which the difference was obtained equal to 4.7 Debye. For this molecule, the largest polarizabilities have been obtained as well. The highest reactivities were found for this molecule and for molecule with NH_2 and NO_2 groups.

[1] G. Hartley, Nature, 1937, 140:281.
[2] A. Frisch et al., Gaussian Incorporated, 2003.
[3] B. Minisini et al. J.Mol.Model., 2007, 13:1227-1235.
[4] I. Piyanzina et al., J.Mol.Model., 2015, 21:34.
[5] B. Minisini et al., J.Str.Chem., 2014, 5:843-851.

Energy Transfer in a realistic Hybrid Inorganic/Organic System: Frenkel to Wannier-Mott Exciton Transition

P44

Thomas Plehn[1] and Volkhard May[1]

[1] *Institut für Physik, Humboldt Universität zu Berlin, Newtonstraße 15, D-12489 Berlin (Germany)*

Transfer processes across hybrid inorganic/organic interfaces have become one of the key research topics. While very much data has been gathered by measurements, so far their detailed understanding still lacks in theoretical models. The poster on show presents a theoretical study which gives insight into the nature of excitation energy transfer processes in a very realistic hybrid semiconductor/molecular system. Inspired by experiments, it consists of a spherical CdSe nanocrystal (4.5 nm diameter) placed nearby a gigantic tubular cyanin dye aggregate (63 nm length and 15 nm diameter). Transitions are described across the interface from Frenkel excitons in the tube to Wannier-Mott excitions in the nanocrystal. Despite the huge size of the system the whole study is implemented in a full atomistic picture [1].

The nuclear structure of the tube is obtained by molecular dynamics simulations and the Frenkel excitons follow from the single molecular excited states [1,2]. First of all, both are based on diverse ab-initio DFT studies. The Wannier-Mott excitons, on the other hand, are described in terms of Coulomb correlated electron-hole pair states. The latter approach uses effective single particle states of electrons and holes which themselves result from a tight-binding model of the nanocrystal.

Finally, excitonic couplings among both bodies and FRET-type rates are presented for various spatial set-ups. Even placed in direct contact, the transfer stays incoherent as indicated by rates somewhat larger than $10^9/s$. In rather coincidence with preliminary experiments [3], it demonstrates the power of the approach and calls for further practice.

[1] T. Plehn, D. Ziemann, J. Megow and V. May, J. Phys. Chem. B, Article ASAP, DOI: 10.1021/jp5111696

[2] J. Megow, M. Röhr, M. Schmidt am Busch, Th. Renger, R. Mitric, S. Kirstein, J. Rabe, and V. May, Phys. Chem. Chem. Phys. 17, 6741 (2015)

[3] Y. Qiao, F. Polzer, H. Kirmse, E. Steeg, S. Kühn, S. Friede, S. Kirstein and J. Rabe, ACS Nano 9, 1552 (2015)

The interaction of a carbon monoxide molecule with an adsorbed porphyrin molecule on a metal surface.

P45

Paolo Poli[1]

[1] *Surface Science Research Centre, Dep. of Chemistry, University of Liverpool, UK*

Tetraphenylporphyrin molecules (TPP) with a metal centre belong to a class of molecules that play important roles in biological systems, for example, oxygen transport and light-harvesting [1]. These class of molecules could also have possible applications in the development of molecular devices such as colorimetric gas sensors, photonic wires, field-effect transistors, and light emitting diodes. Recent sum frequency generation (SFG) experiments of the internal CO stretch mode have shown that the anharmonicity parameter is anomalous for CO adsorbed on a dense overlayer of Ru-TPP on Cu(110), indicating an unusual interaction [2].

In order to elucidate the interactions that can give rise to such an anomalous anharmonicity parameter, we are carrying out density functional theory calculations of this parameter for CO in various chemical bonding situations including Ru-TPP/Cu(110). In the case of an isolated CO molecule and CO adsorbed on Cu(110), the calculated values are normal and in good agreement with experiments. In the case of Ru-TPP/Cu(110), we are currently investigating different adsorption geometries of CO molecule as done for similar systems [3]. . The structure of the Ru-TPP overlayer is very similar to the Co-TPP overlayer on Cu(110) with an unusual conformation [4].

[1] Willi Auwärter, David Ecija, Florian Klappenberger and Johannes V. Barth. Nature Chemistry 7, 105 (2015)
[2] Private communication, Heike Arnolds
[3] Knud Seufert, Marie-Laure Bocquet, Willi Auwärter, Alexander Weber-Bargioni, Joachim Reichert, Nicolás Lorente and Johannes V. Barth, Nature Chemistry 3, 114 (2011)
[4] Philip Donovan, Abel Robin, Matthew S. Dyer, Mats Persson and Rasmita Raval, Chem. Eur. J. 16, 11641 (2010)

P46

Dependence of VO_2 structure on substrate configuration from first principles

Sergei Posysaev[1,2] and Matti Alatalo[1]
[1] *University of Oulu, Center for Molecular Materials, Theoretical Physics, P.O. Box 3000, FI–90014 Oulu, Finland*
[2] *St. Petersburg State Polytechnical University, Department of Theoretical Mechanics, Polytechnicheskaya 29, 195251 St. Petersburg, Russian Federation*
[3] *University of Oulu, Center for Molecular Materials, Theoretical Physics, P.O. Box 3000, FI–90014 Oulu, Finland*

Development of microelectronics technology nowadays requires implementation of new materials with novel functionalities, such as metal insulator transition (MIT) effect for the devices beyond Moore's law[1]. Metal-Insulator Transition (MIT) in vanadium dioxide (VO_2) typically happens at elevated temperatures and/or by virtue of deviatoric stresses[2]. MIT material undergoes a transition in which its crystal structure also changes from one type of symmetry to another. These transformations cause changes in the material properties, e.g., degree of conductivity and conductivity mechanisms, magnetic ordering, optical transmittance, and refractive index, leading to new electronic occupation densities and energy band structure. All these phenomena accompanying MIT effect are available for various applications like reconfigurable electrical circuits, RF components, adaptive optical elements for photonics components.

My work will be as a part of the larger project about Mott transitions based nanoparticles. The objective of this research project is to achieve major breakthroughs in fundamental research on vanadium oxide MIT-effect materials for integrated circuits beyond CMOS technology. My role will be to investigate how the atomistic and electronic structure as well as the optical properties of vanadium oxides depend on different substrate configurations. For small structures quantum mechanical methods are needed. I will use state-of-the-art first principles calculations for calculating the properties of the VO_2-substrate interface. This will be done using density functional theory.

[1] R.K. Cavin, et al., Science and engineering beyond Moore's law. Proc. IEEE 100, 1720-1749 (2012).

[2] M. Imada, et al., Metal-insulator transitions. Reviews of Modern Physics 70, 1039–1263 (1998).

Band-gap engineering of hydrogen-modified TiO_2 P47

Nazanin Rahimi[1] and Evan Gray[1]
[1] *Queensland Micro- and Nanotechnology Centre, Nathan Campus, Griffith University, Brisbane, Queensland 4111, Australia*

This project aims to elucidate the role of hydrogen in producing oxygen-deficient titania with significantly improved electrochemical transport properties [1]. The phases of interest are $TiO_{2-\delta}$ and the Magnéli phases [2], Ti_nO_{2n-1}, with $3 < n < 10 : n \to \infty \equiv TiO_2$. The key point is that the electrical properties in particular of O-deficient TiO_2 phases are strongly dependent on O vacancy concentration and structural modification, providing the ability to ”tune” the oxide to enhance its functional performance as a battery electrode, photocatalyst, etc. The part played by hydrogen is not understood, but it is suspected that H absorption into lattice or interstitial sites may generate mid-gap states that effectively lower the band gap.

If oxygen is removed from the lattice, the two electrons previously associated with the anion have to be retained in the lattice to preserve neutrality. There is some debate as to whether these electrons locate at the vacancy site, forming helium-like donors, or whether the two adjoining Ti^{4+} ions are transformed into Ti^{3+}. The inability of standard density functional theory (DFT) to describe impurity states in hydrogen-modified TiO_2 has so far prevented a clear assignment of Ti^{3+}, hydrogen or oxygen vacancy band-gap states to the spectroscopic features observed in experiments. In this study, DFT with different exchange-correlation functionals will be employed to explore the electronic structure and density of states of hydrogen-modified rutile, TiO_2 [3, 4]. A companion experimental study of deuterium-modified TiO_2 by in-situ neutron diffraction will provide the structural information on which to build the DFT model.

[1] J. Qiu, S. Li, E.MacA. Gray, et al., J. Phys. Chem. C. 118 (2014) 8824–8830.
[2] A. Magnéli, Acta Chem. Scand. 2 (1948) 501.
[3] M. Landmann, E. Rauls and W. G. Schmidt, J. Phys. 24 (2012) 195503.
[4] C. D. Valentin, G. Pacchioni, A. Selloni, J. Phys.: Condens. Matter. 113 (2009) 20543-20552.

Raman Spectroscopy as Probe of Nanometer-Scale Strain Variations in Graphene P48

Christoph Neumann[1,2], **Sven Reichardt**[3,1], Pedro Venezuela[4], Marc Drögeler[1], Luca Banzerus[1], Michael Schmitz[1], Kenji Watanabe[5], Takashi Taniguchi[5], Francesco Mauri[6], Bernd Beschoten[1], Slava V. Rotkin[7] and Christoph Stampfer[1,2]
[1] *JARA-FIT and 2nd Institute of Physics, RWTH Aachen University, 52074 Aachen, Germany*
[2] *Peter Grünberg Institute (PGI-9), Forschungszentrum Jülich, 52425 Jülich, Germany*
[3] *RU Physique et Matériaux, Université du Luxembourg, 1511 Luxembourg, Luxembourg*
[4] *Instituto de Física, Universidade Federal Fluminense, 24210-346 Niterói, RJ, Brazil*
[5] *National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan*

[6] *IMPMC, UMR CNRS 7590, Sorbonne Universités – UPMC Univ. Paris 06, MNHN, IRD, 4 Place Jussieu, 75005 Paris, France*
[7] *Department of Physics and Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, Pensylvania 18015, USA*

Confocal Raman spectroscopy is a versatile, non-invasive investigation tool and a major workhorse for graphene characterization. In general, the Raman spectrum is influenced by both the electronic and phononic properties of the investigated graphene sheet. However, by applying a perpendicular magnetic field, the electronic influence on the width of the Raman G line can be suppressed [1]. By comparing the widths of the G and 2D lines, we show that the origin of the residual broadening is the same for both peaks. Furthermore, we find strong evidence that the residual broadening is due to caused by nanometer-scale strain variations [2]. As the 2D line width is B field independent, it is thus a good quantity to monitor the nm-scale flatness of a graphene sheet, even without a magnetic field. In the near future, the experimental results will be complemented by theoretical studies in which the effects of charge doping, strain, and subtrate influences on the Raman spectrum will be simulated using a combination of many-body perturbation theory, density functional theory and semi-empirical approaches.

[1] C. Neumann, S. Reichardt, M. Drögeler, B. Terrés, K. Watanabe, T. Taniguchi, B. Beschoten, S. V. Rotkin, and C. Stampfer Low B Field Magneto-Phonon Resonances in Single-Layer and Bilayer Graphene Nano Letters 15, 1547-1552 (2015)
[2] C. Neumann, S. Reichardt, P. Venezuela, M. Drögeler, L. Banszerus, M. Schmitz, K. Watanabe, T. Taniguchi, F. Mauri, B. Beschoten, S. V. Rotkin, and C. Stampfer Raman Spectroscopy as Probe of Nanometer-Scale Strain Variations in Graphene *In preparation*

P49

Selective hybridization, a path for DFT evolution.

M. Rodríguez-Mayorga[1,2], N. Abulí[2], S. Sitkiewicz[2], M. Garcia-Borràs[2], J. M. Luis[2] and E. Matito[1,2]
[1] *Donostia International Physics Center(DIPC)*
[2] *Institut de Química Computacional i Catàlisi (IQCC)*

Due to its very favorable efficiency-cost ratio, density functional theory (DFT) is one of the most utilized methodologies in modern quantum and computational chemistry. Nevertheless, the exact density functional for exchange and correlation (E_{xc}) is still unknown and the failures arising from current approximations to it are known and well documented[1]. Hopefully, as it happens in nature (where majestic creatures, like ligers and tigons, are born from hybridization of lions and tigers), hybridization is a step forward in DFT E_{xc} functionals. This poster presents new E_{xc} hybrid functionals (built from B3LYP[2] functional) to face two different problems:

1. Get an accurate description of the two- and three-electron Harmonium Atom (HA) systems using DFT. The HA model systems are systems where the Coulomb electron-nucleus potential is replaced by a parabolic confinement ($-Z/r_i \to 1/2\omega^2 r_i^2$, where ω is known as the confinement strength; which plays a crucial role in correlation) and where the actual Coulomb electron-electron potential is kept unchanged ($1/r_{ij}$). It has been used previously for benchmarking and calibrating DFT functionals but some ω regions represent a real challenge for standard DFT functionals making these model systems excellent for testing and building new DFT functionals[3].

2. Overcome the well-known problem of DFT to describe non-linear optical properties (NLOP) (also known as “the catastrophe of DFT for NLOP”[4]). New hybrid functionals are constructed to face this problem and give accurate results for properties like polarizabilities and hyperpolarizabilities.

[1] M. Swart. Int. J. Quant. Chem., 113:2, 2013.
[2] C. Lee; W. Yang and R. G. Parr Phys. Rev. B, 37:785, 1988.
[3] M. Rodríguez-Mayorga. Master Thesis: Improved hybrid functionals for an accurate description of doublet-quartet splitting in three-electron harmonium atom. 2013 Universitat de Girona (UdG)
[4] B. Champagne; E. A. Perpète; D. Jacquemin; S. J. A. van Gisbergen; E. J. Baerends; C. Soubra-Ghaoui; K. A. Robins and B. Kirtman. J. Chem. Phys. 104:4755, 2000.

Water Ammonia Mixtures at Extreme Conditions

P50

Victor Naden Robinson[1] and Andreas Hermann[1]

[1] *Centre for Science at Extreme Conditions, School of Physics and Astronomy and SUPA, The University of Edinburgh, Edinburgh, United Kingdom*

Understanding the structural, dynamic, and electronic evolution of molecular materials at extreme compressions is crucial for our understanding of the formation and properties of giant gas planets. The typical ices expected to make up large parts of, for example, Uranus and Neptune - water, ammonia, and methane - have been studied by themselves extensively in recent years, both computationally and experimentally [1]. For a more complete understanding, however, a thorough investigation of true molecular mixtures is needed [2]. High-pressure experiments are often very complex and only deliver indirect information on the compounds formed under extreme conditions. Guidance from calculations is therefore of utmost importance – both to interpret the data and to inspire new experimental studies.

Molecular materials feature a ladder of interactions, all of which need to be described accurately by the first principles method chosen: covalent bonding, electrostatics, hydrogen bonding, and dispersion interactions all play an important role, and their relative magnitude as a function of external pressure is often the driving force for intriguing phase transitions. The monohydrate of ammonia, for example, shows a transition to an ionic compound [3]. Here, we present results on mixtures of ammonia and water at high pressures, using crystal structure prediction methods and first-principles calculations, and focussing on the semi-, mono-, and dihydrates of ammonia at pressure conditions relevant to planetary interiors.

[1] C. Cavazzoni, et al. Science 283, 44 (1999). C.J. Pickard, R.J. Needs, Nat. Mater. 7, 775 (2008). Y. Wang et al., Nat. Commun. 2, 563 (2011). A. Hermann, N.W. Ashcroft, R. Hoffmann, Proc. Natl. Acad. Sci. 109 745 (2012). S. Ninet et al., Phys. Rev. B 89, 174103 (2014). T. Palasyuk et al., Nat. Commun. 5, 3460 (2014).
[2] J.S. Loveday, R.J. Nelmes, High Press. Res. 24, 45–55 (2004). M-S. Lee, S. Scandolo, Nat. Commun. 2, 185 (2011).
[3] A.D. Fortes et al., J. Chem. Phys. 115, 7006 (2001).

P51

A comparison of barostats for the mechanical characterisation of MOFs

S.M.J. Rogge[1,2], L. Vanduyfhuys[1,2], T. Verstraelen[1,2], G. Maurin[1,2] and V. Van Speybroeck[1,2]
[1] *Center for Molecular Modeling, Ghent University,*
Technologiepark 903, 9052 Zwijnaarde, Belgium
[2] *Institut Charles Gerhardt Montpellier, Université Montpellier 2,*
Place Eugène Bataillon, 34095 Montpellier, France

Metal–organic frameworks (MOFs) are microporous crystalline materials, compromising metallic clusters or chains connected by organic linkers, forming a scaffold–like network with cavities and/or channels. Because of the theoretical abundance of linkers and metal centers, these materials are very versatile, and can be tuned for the given application [1]. Some of these frameworks, such as MIL–53, may undergo reversible, large–amplitude structural deformations. These transitions can, amongst others, be induced by applying a mechanical pressure [2], paving the way for mechanical storage applications.

However, these applications require a clear understanding of the response of the material on the applied pressure, especially of the pressure at which the transition is induced. We determine this transition pressure and geometrical properties with the aid of Molecular Dynamics and an in–house developed force field [3] and simulation code [4]. We will compare three prevalent pressure coupling methods, the Berendsen [5], Langevin [6,7] and Martyna–Tuckerman–Tobias–Klein barostat [8,9], for the characterisation of two types of MOFs, MIL–53(Al) and MOF–5.

In this comparison, we will focus on the calculation of static variables, such as equilibrium geometries and free energy landscapes as function of volume, from which the transition pressure of MIL–53(Al) can be derived. Furthermore, we will determine the transition pressure based on dynamic simulations, and show how the choice of barostat may induced unexpected transitions. However, by determining the steering force of these transitions, we can easily distinguish between two simple models to explain these transitions. This analysis allows to extract a transition pressure which is in agreement with the static calculation based on the free energy profile. A complete overview of this comparison is given in Ref. 10.

[1] S.T. Meek, J. A. Greathouse, *et al.*, Adv. Mater., 23, 249 (2011).
[2] I. Beurroies, M. Boulhout, *et al.*, Angew. Chem., Int. Ed., 49, 7526 (2010).
[3] L. Vanduyfhuys, T. Verstraelen, *et al.*, J. Chem. Theory Comput., 8, 3217 (2012).
[4] T. Verstraelen, L. Vanduyfhuys, *et al.*, *Yaff*, http://molmod.ugent.be/software/.
[5] H.J.C. Berendsen, J.P.M. Postma, *et al.*, J. Chem. Phys., 81, 3684 (1984).
[6] S.E. Feller, Y. Zhang, *et al.*, J. Chem. Phys., 103, 4613 (1995).
[7] D. Quigley, M.I.J. Probert, J. Chem. Phys., 120, 11432 (2004).
[8] G.J. Martyna, D. Tobias, *et al.*, J. Chem. Phys., 101, 4177 (1994).
[9] G.J. Martyna, M.E. Tuckerman, *et al.*, Mol. Phys., 87, 1117 (1996).
[10] S.M.J Rogge, L. Vanduyfhuys, *et al.*, *to be submitted.*

P52

Theoretical search of Half Metallic Antiferromagnetic double perovskites with [001] stacking

Ramiro Cardona[1], **Jairo Roa-Rojas**[1] and Dadiv A. Landinez Tellez[1]
[1] *Universidad Nacional de Colombia. Grupo de Fisica Nuevos Materiales.*

Half metals [1,2] (HM) are a class of materials which are metallic in one spin channel, while insulating in the opposite spin channel due to the assymetric band structure. HM materials in which the total magnetic moment is zero are called HM antiferromagnet (AFM). An HM-AFM does not generate a macroscopic magnetic field and it can transport a 100% spin polarized charge without any net magnetization. HM-AFMs have several applications, e.g., as probes in spin-polarized scanning tunneling microscopes without perturbing the spin character of samples. HM-AFMs are expected to be a species of important materials for spintronics; however, there is still no experimental verification for them up to date.

The double perovskite structure appears to be an ideal system for a search for HM-AFM member. There are two kinds of the ordered double perovskites structure LaABB’O6 (A = Ca, Sr, Ba). One is [111] stacked structure, which its B and B’ layers are stacked along the [111] direction. The other is [001] stacked structure. S. H. Chen *et al.* [3] investigate all the possible candidates of HM-AFM with the structure $\mathrm{LaABB'O_6}$ double perovskites where pairs BB’ are any combinations of two 3d, 4d, 5d transition elements and A are Sr and Ba with the [111] structure.

The purpose of this work is to do a theoretical search of HM-AFM double perovskites LaABB’O_6 where pairs BB’ are any combinations of two 3d, 4d, 5d transition elements and A are Sr and Ba with the [001] structure and compare the results with the [111] structure.

[1] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. 50, 2024 1983.

[2] Y. K. Wang and G. Y. Guo, Phys. Rev. B 73, 064424 2006.

[3] S. H. Chen, Z. R. Xiao, Y. P. Liu, and Y. K. Wang. Journal of Applied Physics 108, 093908 (2010); doi: 10.1063/1.3488642

A simple algorithm for constructing the Brillouin zone

P53

T. Salagaram[1], R. C. Andrew[2] and N. Chetty[2,3]

[1] *Department of Science, Mathematics and Technology Education, University of Pretoria, Pretoria, 0001, South Africa*

[2] *Department of Physics, University of Pretoria, Pretoria, 0001, South Africa*

[3] *National Institute for Theoretical Physics, Gauteng, 2000, South Africa*

The calculation of many properties of crystals which depend on electronic structure involves integrating periodic functions of the wave vector over the entire Brillouin zone (BZ) or specified portions of thereof [1,2]. Therefore the construction of the BZ in electronic structure calculations and solid state physics is of extreme importance. The concept of the BZ is dealt with in undergraduate solid state physics textbooks and courses. However many students still have difficulty grasping the physical significance of the BZ. We have devised a simple algorithm to construct the BZ. The purpose of devising this algorithm is pedagogical. It provides students with an opportunity to quickly construct and visualise the BZ on a computer. Although the algorithm is staighforward, a student will have to understand all aspects of the problem (theoretical, numerical/algorithmic and computational aspects) at a fundamental level in order to construct and visualise the BZ on the computer. Therefore we believe that getting students to study the BZ in this manner will enable them to understand the physical significance of the BZ more deeply compared to traditional methods of teaching the BZ. Such an exercise may also give students an insight into the construction of the BZ in sophisticated scientific codes which are used to perform electronic structure calculations. We present results for the BZ in 2D and 3D for various reciprocal lattices obtained using the algorithm we have devised.

[1] S.L. Cunningham, Phys. Rev. B, 10 12, 4988 (1974).
[2] H.J. Monkhorst and J.D. Pack, Phys. Rev. B, 13 12, 5188 (1976).

P54

Quantum-Chemical Investigations on a Photocatalytically Active Covalent Organic Framework

Gökçen Savaşçı[1], Vijay S. Vyas[1,2], Frederik Haase[1,2], Linus Stegbauer[1,2], Bettina V. Lotsch[1,2] and Christian Ochsenfeld[1]
[1] *Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, 81377 Munich, Germany.*
[2] *Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany.*

Covalent Organic Frameworks (COFs) are a novel class of crystalline organic materials with well-defined and predictable pore structures, assembled from molecular building blocks [1]. Emerged from a successful result of reticular design, thoroughly selected organo-molecular building blocks are reacted in dynamic covalent reactions to form predesigned layered frameworks. These materials do not only have exceptional thermal stabilities, they also show permanent porosity with high specific surface areas. Their extraordinary and versatile properties have offered these materials superior potential in diverse applications, such as in gas storage, adsorption, catalysis and even for the use in biosensors [2]. A recently discovered azine-linked COF shows promising photocatalytic activity [3], another one within a tunable framework for visible light-induced hydrogen generation [4].

In order to rationalize experimentally observed trends in photocatalytic activity, quantum-chemical calculations were performed. Model systems were selected as molecular clusters from building block units, to mimic the extent of the framework in small and systematic steps. Kohn-Sham band gaps as well as difference densities for the brightest excited states were calculated. Molecular orbitals for model systems were extracted and compared with more extended model systems for the investigated framework. Different terminations on selected model systems as well as their stacking were probed for their impact, utilizing calculations with up to 1248 atoms. Currently, reactive intermediates formed during the photocatalytic process are investigated as part of our ongoing research.

[1] X. Feng, X. Ding, and D. Jiang, X. Chem. Soc. Rev. 41, 6010 (2012).
[2] P. Wang, Q. Wu, L. Han, S. Wang, S. Fang, Z. Zhang, and S. Sun, RSC Adv. 5, 27290 (2015).
[3] L. Stegbauer, K. Schwinghammer, and B. V. Lotsch, Chemical Science 5, 2789 (2014).
[4] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, C. Ochsenfeld, and B. V. Lotsch, to be published.

P55

Using CO as a probe molecule for exploring rutile TiO_2 surface structures

Hannah Schlott[1] and Bernd Meyer[1]
[1] *Interdisciplinary Center for Molecular Materials and Computer- Chemistry-Center, Friedrich-Alexander-Universität Erlangen-Nürnberg*

Using density-functional theory (DFT) we investigated the adsorption of CO molecules on various structural models of the reconstructed rutile $TiO_2(011)$ surface. While the adsorption of CO on rutile $TiO_2(110)$, the most thoroughly studied oxide surface in surface science, is well understood [1,2], the situation is less clear for the reconstructed $TiO_2(011)$ surface. Thermal treatment and infrared spectroscopy indicate a similar stability of the CO molecules as on $TiO_2(110)$, albeit with the molecules lying flat on the surface [3]. In the DFT calculations, however, we find for the recently proposed structural models of the reconstructed $TiO_2(011)$ surface only adsorption sites either with horizontal CO orientation and lower binding energy or with similar binding energy as on $TiO_2(110)$ and vertical CO orientation. Implications of this observation will be discussed.

[1] P.M. Kowalski, B. Meyer, D. Marx, Phys. Rev. B 79, 115410 (2009).
[2] M. Kunat, F. Traeger, D. Silber, H. Qiu, Y. Wang, A.C. van Veen, Ch. Wöll, P.M. Kowalski, B. Meyer, C. Hättig, D. Marx, J. Chem. Phys. 130, 144703 (2009).
[3] M. Buchholz, F. Bebensee, Ch. Wöll, in preparation.

First-principles study of metal atoms and their dimers on monolayer MoS_2

P56

Srdján Stavrić[1] and Željko Šljivančanin[2]
[1] *Faculty of Mining and Geology, University of Belgrade,*
DJ ušina 7, 11000 Belgrade, Serbia
[2] *Vinča Institute of Nuclear Sciences (020),*
P.O. Box 522, RS-11001 Belgrade, Serbia

Monolayer MoS_2 attracted considerable interest due to its two-dimensional atomic structure, absence of dangling bonds and an intrinsic direct band gap. Since contacts of this ultrathin material with metals are of key importance for applications in nanoelectronics, understanding of adsorption of metal atoms at MoS_2 would facilitate design of MoS_2-based devices with improved functionalities. We used density functional theory (DFT) calculations to study structural and electronic properties of several metal atoms (Li, Ca, Al, Ti, Pd and Au) and their dimers adsorbed on MoS_2. MoS_2 is composed of three atomic layers, which give rise to much more complex adsorption picture compared to the one accounted on graphene. In addition to favorable binding of metal adatoms to outer S layer, we found that Ti atom as well as Al, Ca and Ti dimers show tendency toward formation of mixed metal-sulfur layers. This tendency is in contrast with existing atomistic models which assume presence of a sharp interface between MoS_2 and metal films, and thus could strongly alter its band structure and influence mobility of charge carriers.

[1] S. Stavrić and Ž. Šljivančanin (manuscript in preparation).

A DFT study of CO oxidation over $Pd_3O_x/CeO_2(111)$

P57

Yaqiong Su[1], Weiyu Song[1] and Emiel J.M. Hensen[1]
[1] *Inorganic Materials Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*

Catalytic conversion of tail gases of automotive car engines and other combustion processes remains a challenge. Although well-developed, the technology depends on the use of scarce noble metals.

Understanding how to decrease the noble metal content in such catalysts is an important research topic. For CO oxidation, Pd is one of the most active metals, especially when in contact with ceria [1]. Ceria is a good oxygen storage material, allowing operation under O_2-lean conditions. It is increasingly recognized that CO oxidation can take place at the interface between noble metal and metal oxide particles and the ceria support; the exact mechanism for Pd remains to be resolved. It will dependon the nature of the Pd phase under reaction conditions. Candidate active sites are from Pd nanoparticles [2], Pd^{2+} incorporated into the ceria lattice [3] and Pd oxides [4]. DFT calculations are well suited to compare such surface models.

In the present study, we use a $Pd_3O_x/CeO_2(111)$ model to study the composition and stability Pd_3O_x clusters and reaction mechanism of CO oxidation. Thermodynamic analyses indicate that Pd_3O is the most stable species during CO oxidation. The catalytic cycle proceeds preferentially involving Pd3O and Pd_3O_2 over $CeO_2(111)$ surface. Another route involves Pd_3O_3 that also involves Pd_3O_4. Microkinetics simulations are carried out to establish the contribution of the several routes to overall CO oxidation. The involved catalytic cycles all involve ceria lattice oxygen atoms. The resulting vacancies are necessary for O_2 activation. The electronic structure of the relevant surface species is also discussed. The catalytic cycle for CO oxidation proceeds at the interface between PdO_x and ceria.

[1] R.V. Gulyaev et al, Appl. Catal. B: Environ, 147, 2014, 132-143
[2] G. Li et al, Appl. Catal. B: Environ, 158-159, 2014, 341-347
[3] M.S. Hegde, Acc. Chem. Res. 42, 2009, 704-712
[4] L. Meng et al, J. Phys. Chem. C, 115, 2011, 19789-19796

P58

Calculated double oxygen vacancies within MgO

B. Taudul[1] and M. Alouani[1]
[1] *Institute de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504*
CNRS–Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France

Tunnel magnetoresistance (TMR) effect is key to developing magnetoresistive random access memories, magnetic sensors and novel logic devices [1]. Current theoretical calculations predict TMR ratio up to a 1000% for magnetic tunnel junctions (MTJs) with crystalline MgO barrier due to coherent spin and symmetry preserving tunnelling of electrons [2]. Experimental results, however, show values of TMR which are one order of magnitude below prediction. One of possible causes for this discrepancy is attributed to the existence of defects in the MgO barrier. Defects create additional energy levels within the insulator energy band gap which effectively reduce the barrier hight and affect the coherent spin-polarized transport [3-6].

In our work, we investigate the properties of double oxygen vacancies in MgO structure and their impact on spin polarized transport through the insulating barrier. The calculations are carried out using density functional theory as implemented in VASP package within the projector augmented wave (PAW) method. To this end, we used several types of exchange–correlation functionals: generalized gradient approximation (GGA), metaGGA (MBJ) and hybrid functionals. By adjusting the parameters of MBJ functional or HSE06 hybrid functional the value of the MgO band gap (7.8 eV) can be obtained. These parameters are then used to determine the position of the defect states. To make contact with future experimental results, we computed the complex dielectric function within the electric dipole approximation. We show that the oxygen vacancy peaks in the dielectric function, which emanate from interband transitions between MgO electronic structure and defect levels, are located within the band gap.

[1] S. Ikeda et al., IEEE Transactions on electron devices, 54, No. 5, 991-999 (2007).
[2] S. Yuasa and D.D.Djayaprawira, J. Phys. D.: Appl. Phys. 40, R337 (2007).
[3] J. M. Teixeira et al., Phys. Rev. Lett. 106, 196601 (2011).
[4] J. P. Velev et al., Appl. Phys. Lett. 90, 072502 (2007).
[5] K. P. McKenna and J. Blumberger, Phys. Rev. B 86, 245110 (2012).
[6] F. Schleicher et al., Nat. Comm., 5, 4547 (2014).

Speeding-up FHI-aims code with OpenMP for Kohn-Sham Density Functional Theory calculations on BG/Q computers

P59

Álvaro Vázquez-Mayagoitia[1]
[1] *Argonne Leadership Computing Facility, Argonne National Laboratory, Lemont, Il, 60439, USA*
**alvaro@anl.gov*

Nowadays, most of the modern computers for scientific simulations have more than one processing unit. This fact challenges developers of science applications. If developers want to exploit efficiently the calculating power of many-core and co-processor architectures, they have to look for alternative strategies to add new layers of parallelism. FHI-AIMS code has a very effective parallel model for distributed memory super computers, and lately this code has shown a good scalability when is executed over thousands of processors. Nonetheless, there are operations in Density Functional Theory (DFT) calculations that rely on single-processor parallelism that has been provided only by external threaded algebra subroutines and by the automatic shared memory parallelization of loops done by the low level optimizers instrumented by Fortran90 compilers.

In this work it is shown the performance and profiling of FHI-AIMS code when is computing single points energies from pure and hybrid functionals within DFT. The simulations were carried out using threaded versions of libraries like ELPA and ESSL (IBM). Also, it is shown the performance of FHI-AIMS with new Fortran90 subroutines explicit coded with OpenMP. Also, it is discussed some perspectives and changes needed towards an efficient threaded version of the code for petaflop computers.

Hydrogen Adsorption on TM-doped SWCNT: A DFT Study

P60

Valeria Verdinelli[1], Estefanía Germán[1], Carla Luna[1] and Alfredo Juan[1]
[1] *Departamento de Física, Universidad Nacional del Sur & IFISUR (UNS-CONICET), Av. Alem 1253, 8000 Bahía Blanca, Argentina*

Hydrogen based energy sources is one of the promising solution to environmental pollution. Nevertheless, one of the major drawbacks is to find new materials capable of storing hydrogen in large per mass at a low cost. Single walled carbon nanotubes (SWCNTs) have many potential advantages for hydrogen adsorption over currently available adsorbents. However, SWCNTs do not adsorb considerable amount of hydrogen at normal conditions [1]. Experimental and theoretical studies have showed that CNT turn more active for hydrogen adsorption at ambient conditions when CNT are doped with transition metal atoms (TM) [2]. In this work, we studied the hydrogen adsorption on (8,0) single walled carbon nanotubes decorated by Ru and Rh atoms. Spin polarized functional theory calculations with van der Waals corrections were performed using VASP code. Several decoration sites on the CNT surface were investigated before atomic or molecular hydrogen adsorption. We also included a systematic study on the electronic and bonding properties of the different systems by means of Density of states (DOS) and overlap population density of states (OPDOS) calculation. TM decoration increases hydrogen atom adsorption energy compare to pristine CNT. When a hydrogen molecule is considered on Ru/SWCNT its adsorption is dissociative with an $Eads(H_2) = -0.70\ eV$ while H_2 adsorption on $Rh/SWCNT$ has an $Eads(H_2) = -0.99\ eV$. Furthermore, TM-decorated SWCNT systems exhibit magnetic properties. According to our results, TM decorated zig-zag nanotubes are great candidates for hydrogen storage applications.

[1] G.E. Ioannatos, X.E. Verykios H2 storage on single- and multi-walled carbon nanotubes Int J Hydrogen Energy 35 (2010) 622-628
[2] Z Zhang, J Li, Q Jiang Density functional theory calculations of metal-doped carbon nanostructures as hydrogen storage systems under electric fields: A review Front Phys. 6(2) (2011) 162-176

P61

Searching for Structural Descriptors for Electronic function in Complex Perovskite Oxides

Nicholas Wagner[1] and James Rondinelli[2]
[1] *Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA*

Predicting materials with useful, novel properties from first principles requires an understanding of the causal connections between the underlying atomic structure of the material and its macroscopic properties. Once the important structural features are known, they can then be used to construct predictive models of a target property for the purposes of guiding synthetic discovery of new materials [1]. However, it is often difficult to know *a priori* which atomic scale features are most important, especially in complex structure types. Moreover the composition space is exceedingly large, making the simulation of every possible chemical combination undesirable. As a consequence, materials researchers are applying machine-learning methods to uncover missing functional compounds from materials datasets [2, 3], and formulate structure-property descriptors [4]. Here we describe the robustness of the Goldschmidt tolerance factor [5] and other structural-descriptors, which for example, include mode-crystallographic representations of crystallographic distortions and bond valences, in predicting the electric polarizations in a dataset consisting of 127 polar and nonpolar ABO_3 oxides. The electric polarizations and energetic switching barriers are computed from density functional theory methods, whereas informatics methods are used to construct predictive models and capture the variation in the data. We conclude by illustrating how this new domain knowledge may be used to predict high polarization values and low electric field switching barriers for yet to be synthesized polar perovskite oxides.

[1] A. Kumar, A.S. Verma, and S.R. Bhardwaj, The Open Applied Physics Journal, 1 11 (2008).
[2] T. Le, C. Epa, F.R. Burden, and D.A. Winkler, Chem. Rev. 112 2889 (2012).
[3] G. Hautier, C.C. Fisher, A. Jain, T. Mueller, and G. Ceder, Chem. Mater., 22 3762 (2010).
[4] L.M. Ghiringhelli, J. Vybiral, S.V. Levchenko, C. Draxl, and M. Scheffler, Phys. Rev. Lett. 114 105503 (2015).

[5] V.M. Goldschmidt, Die Naturwissenschaften 21 477 (1926).

Chemical disorder and inhomogeneity in Cu_2ZnSnS_4 from multi-scale simulations

P62

Suzanne K. Wallace[1], Jarvist M. Frost[1] and Aron Walsh[1]
[1] *University of Bath, Bath, England*

Kesterite-structured Cu_2ZnSnS_4 (CZTS) is a promising earth-abundant and non-toxic material for the active layer of thin-film solar cells due to its high optical absorption coefficient of $> 10^4$ cm^{-1} and sunlight matched band gap of 1.5 eV. Device efficiencies are hampered by low open circuit voltage (V_{OC}) compared to the optical band gap. One possible origin of this is disorder amongst the Cu and Zn ions. Such disorder could lead to sub band-gap recombination centres, either due to varying band gap of the non-stoichiometric regions of material, or recombination across regions of fluctuation in electrostatic potential. We investigate this by writing custom Monte-Carlo codes to simulate the on-lattice disorder. A generalised Ising Hamiltonian is parameterised with hybrid density functional theory (DFT) total-energy calculations on defect pairs. The resulting disorder is simulated as a function of temperature, and the order-disorder behaviour and resulting electrostatic potential variation due to Cu/Zn disorder is quantified. Understanding the origin of these sub-gap states, and the resulting impediment on device performance, is essential to discover design and processing rules for high efficiency kesterite, and other multi-component semiconductor, devices.

Benchmark of GW methods for electron acceptors

P63

Joseph Knight[1], **Xiaopeng Wang**[1], Noa Marom[1], Lukas Gallandi[2], Xinguo Ren[3], Patrick Rink[4] and Thomas Körzdörfer[2]
[1] *Department of Physics and Engineering Physics, Tulane University, New Orleans, LA 70118, USA*
[2] *Computational Chemistry, University of Potsdam, 14476 Potsdam, Germany*
[3] *Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, 230026, China*
[4] *Aalto University School of Science, FI-00076 Aalto, Finland*

Many-body perturbation theory in the GW approximation, where G is the one-particle Green's function and W is the screened Coulomb interaction, is often used to calculated electronic properties associated with charged excitations. Here, the performance of GW methods at different levels of self-consistency is assessed for a set of 24 organic acceptors. Errors are calculated with respect to coupled cluster singles, doubles, perturbative triples [CCSD(T)] reference data for the vertical ionization potentials (IPs) and electron affinities (EAs), extrapolated to the complete basis set limit. Additional comparisons are made to experimental data, where available. We consider fully self-consistent GW (scGW), partial self-consistency in the Green's function ($scGW_0$), non-self-consistent G_0W_0 based on various mean-field starting points, and a "beyond GW" second order screened exchange (SOSEX) correction to G_0W_0. The best performers overall are G_0W_0+SOSEX and G_0W_0 based on an IP-tuned long range corrected hybrid functional. These methods yield the lowest mean absolute errors (MAEs) for the IPs and EAs and provide valence spectra in good agreement with photoemission spectroscopy (PES) experiments.

P64 Advanced molecular simulations to accurately characterize Metal-Organic Frameworks

Jelle Wieme[1], Louis Vanduyfhuys[1], Kurt Lejaeghere[1], Sven M.J. Rogge[1] and Veronique Van Speybroeck[1]
[1] *Center for Molecular Modeling (CMM), Ghent University, Technologiepark 903, 9052 Ghent, Belgium*

Metal-organic frameworks (MOFs) are a unique class of porous crystalline materials which are made up by metal clusters connected by organic linkers. These materials can be synthesized with a large versatility and can easily be tuned both chemically and structurally [1]. They show great promise for different industrial applications such as separation, catalysis and storage.

In this work, the textural, thermal and mechanical properties of MOFs will be studied using force fields derived from first-principles molecular calculations on smaller building units. Textural properties, e.g. accessible surface area, are important for porous materials. Molecular dynamics simulations are used to determine the thermal expansion coefficients, whereas the mechanical properties at 0 K are studied by the determination of the full stiffness tensor. One spectacular property is the structural flexibility or so-called breathing phenomenon observed for some MOFs [2]. Recent studies have shown that a characterization of the anisotropic elastic behavior can predict this flexibility [3]. Molecular simulations are performed with YAFF [4], an in-house developed code based on force fields.

The methodology will be tested on the well-known MOF-5, which was synthesized for the first time by Yaghi [5]. Several theoretical and experimental results are available for this MOF, which allows for a direct validation of the obtained results. A second test case concerns the MIL-53(Al) material, belonging to a family of flexible frameworks that undergo a transition from large pore to narrow pore under mechanical pressure [6]. The simulations on these materials use in-house developed force fields [7,8] parametrized by means of Density Functional Theory (DFT) calculations.

In a second step, the test set is expanded. To this end a series of ab initio parametrized force fields are generated with QuickFF [9]. The required input consists of DFT calculations on non-periodic clusters representing the metal clusters and organic linkers respectively. The proposed characterization will be applied to this extended set of MOFs. If possible, structure-property relations will be identified to allow for a more rationalized design of high-performance MOFs.

[1] G. Férey, Chem. Soc. Rev., 37, 191 (2008).
[2] A. Schneemann, V. Bon, *et al.*, Chem. Soc. Rev., 50, 6062 (2014).
[3] A. U. Ortiz, A. Boutin, *et al.*, Phys. Rev. Lett., 109, 195502 (2012).
[4] T. Verstraelen, L. Vanduyfhuys, *et al.*, http://molmod.ugent.be/software/.
[5] H. Li, M. Eddaoudi, *et al.*, Nature, 402, 276 (1999).
[6] I. Beurroies, M. Boulhout, *et al.*, Angew. Chem. Int. Edit., 49, 7526 (2010).
[7] L. Vanduyfhuys, T. Verstraelen, *et al.*, J.Chem. Theory Comput., 8, 3217 (2012).
[8] L. Vanduyfhuys, S. Vandenbrande, *et al.*, J. Comput. Chem., in press (2015).

P65 First-principles study of electronic band structure of semiconductor alloys

Xi Xu[1] and Hong Jiang[1]
[1] *College of Chemistry and Molecular Engineering, Peking University Beijing, 100871, China*

Mixing different materials to form semiconductor alloys has attracted ever-increasing interest as one of the most important ways to tune the band gap of semiconductors. Alloyed semiconductors can often exhibit novel electronic properties dramatically different from simple mixing of properties of each component. First-principles modeling of semiconductor alloys poses a great challenge because the lack of long-range order leads to the failure of many standard band theoretical treatments. The two widely used approaches, the virtual crystal approximation and the coherent potential approximation, are both based on the simplification of the mean field theory and therefore cannot consider the fluctuation of atomic arrangements. Another approach, the special quasi-random structure (SQS) method[1], use a special structure to represent the real perfectly random alloy according to the proximity of correlation functions in a few local shells, which, however, neglects any possible local ordering or long range-ordering in alloyed compounds. In this work, we use the SQS method to model several semiconductor alloys, including (Cd, Zn)S, Zn(S, O) and Ba(Sn, In)O3-y, and calculate their electronic properties using the HSE06 hybrid functional. The trend of the band gap as a function of composition is found to agree well with experiments. We are also exploring other new theoretical approaches that combine the cluster expansion (CE) method with Monte Carlo simulation to describe electronic properties of structurally disordered systems more accurately.

[1] Wei, S.-H., Ferreira, L. G., Bernard, J. E. & Zunger, A. Electronic properties of random alloys: Special quasirandom structures. Phys. Rev. B 42, 9622–9649 (1990).

First Principles Method for Simulation of Nano-electronic Device with Atomic Disorder

P66

Jiawei Yan[1] and Youqi Ke[1]
[1] *ShanghaiTech University, 100 Haike Rd., Pudong New Area, Shanghai*

In realistic nano-electronic devices, disordered impurities/defects are inevitable and the electron transport properties of the device can be significantly influenced by or even built on these disorders. However, due to the lack of effective theoretical tools, the important effects of disorder in nanoelectronic devices remains largely un-explored or poorly understood. To make a predictive modeling of electron transport in realistic device without using any phenomenological parameter, a first principle quantum transport method is required to correctly include the non-equilibrium nature of electron transport and efficiently treat the disorder average over impurity configurations. To realize the first principles calculation of non-equilibrium transport through disordered device, we are developing a quantum transport method and its associated software within the framework of Non-equilibrium Green's Function(NEGF)[1] based Density Functional Theory(DFT) combined with the Non-equilibrium Vertex Correction(NVC)[2] to treat disorder averaging at nonequilibrium-density-matrix level. In this poster, we present the algorithm of NVC and our new formulation of NEGF-DFT-NVC using exact Muffin-Tin Orbital(MTO) method instead of less accurate TB-LMTO used previously. Fe/Vacuum/Fe magnetic tunneling junction with disordered interface roughness is investigated and it is found that the disorder induced inter-channel scattering quickly reduces the tunneling magnetoresistance ratio of the junction.

[1] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 121104(R) (2001); 63, 245407 (2001)
[2] Y. Ke, K.Xia, H. Guo, Physical Review Letters 100, 166805 (2008)

P67 Electronic Structure Optimisation of Hybrid Antimony Sulfides for Photovoltaics

Ruo Xi Yang[1], Keith T. Butler[1] and Aron Walsh[1]
[1] *Department of Chemistry, University of Bath, UK*

Antimony sulfide has been studied for decades as an attractive material for photovoltaic devices owning to its narrow band-gap (1.7 eV), high optical absorption coefficient, and environmentally-friendly characteristics[1]. Due to the lone pair of Sb(III), and its asymmetric local coordination environment ranging from 3 to 6, it is able to form various complex structures. Multi-component antinomy sulfides, made with additional metals and/or organic ions, can adopt chain, sheet and three-dimensional network structures.

Hybrid organic-inorganic solar cells are currently the subject of intense interest for their attractive properties and high-performance, including the ability to tune both structural and electronic properties. Novel materials, beyond the hybrid perovskite $CH_3NH_3PbI_3$, [2] can be designed and synthesized to achieve favorable properties.

The crystal structure of $(CH_3NH_3)_2Sb_8S_{13}$ is formed of double chains of corner-linked $[SbS_3]^{3-}$ pyramids and methylammonium cations located in the ring apertures created within the double chains. The double chains are interlocked by the Sb–S interactions, which form a sheet perpendicularly [3,4,5], hence providing interesting prospect as a pseudo two-dimensional semiconductor.

A full description of these crystals has been provided using density functional theory (DFT), including structural, elastic and electronic properties. Based on a thorough understanding of these multi-component antimony sulfides, further screening of other hybrid antimony sulfides will be carried out to achieve a full range of optimal properties for application in thin-film solar cells.

[1] Manolache, S. A., Dut, A. The Development of Crystalline Sb_2S_3 Thin Films as a Component of the Three-Dimensional Solar Cells. Thin Solid Films, 2008, 11(2), 109-121.

[2] Frost, J. M. *et al*, Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. Nano Letters, 2014, 14, 2584.

[3] Wang, X., Liebau, F. Synthesis and Structure of $[CH_3NH_3]_2Sb_8S_{13}$: A Nanoporous Thioantimonate(III) with a Two-Dimensional Channel System. Journal of Solid State Chemistry, 1994, 111(2), 385-389.

[4] Tan, K., Ko, Y., Parise, J. B. A novel antimony sulfide templated by ethylenediammonium. Acta Crystallographica, Section C, 1994, 50(9), 1439-1442.

[5] Lees, R. J. E., Powell, A. V., Chippindale, A. M. Methylammonium antimony sulfide. Acta Crystallographica, Section C, 2005, 61(Pt 12), m516-8.

P68 Atomistic Modeling of Excitation Energy Transfer in a Metal Semiconductor Core Shell Nanostructure

Dirk Ziemann[1] and Volkhard May[1]
[1] *Institut für Physik, Newtonstr. 15, Humboldt Universität zu Berlin, D-12489 Berlin, Germany*

The potential of metal semiconductor core-shell systems for applications in photovoltaics and plasmonics has led to an increasing number of experimental studies in this field. Of particular interest is the interaction of metal nanoparticle plasmons with semiconductor excitons in such a system.

This poster focuses on the excitons in the semiconductor shell. These excitons are on the one side modified by the polarisation of the metal and on the other side quenched due to excitation energy transfer from the semiconductor shell to the metal core. The metal nanoparticle is described by an effective Hamiltonian, which also accounts for higher plasmon modes, while the semiconductor shell is modeled on an atomistic level where the exciton states are described by a configuration interaction scheme. The resulting lifetimes of plasmons as well as semiconductor excitons are in line with recent experiments [1].

[1] S. Lambright et al. ACS Nano 2014, 8, 352-361.

P69

First-Principles prediction of Near Edge X-ray Absorption Fine Structure from graphene: effects of synthesis and processing

W. Y. Rojas[1], S. Kim[2], A. D. Williams[2], F. Ouchen[2], J. Grote[2], D. Prendergast[3] and E. M. Campo[1,4]

[1] *School of Electronic Engineering, Bangor University, Bangor LL57 1UT, UK*
[2] *Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFM, Ohio 45433 USA*
[3] *The Molecular Foundry, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[4] *Department of Physics and Astronomy, University of Texas at San Antonio, TX 78249, USA*

Graphene -a layer of single carbon atom thickness- exhibits exceptional mechanical, thermal and electronic properties [1], which makes it very attractive for, amongst other, fabrication of graphene-based organic field-effect transistors (GOFETs) [2]. However, both synthetic growth procedures and subsequent processing (all prone to defect introduction), alter transport capabilities and lead to significant mobility reduction. In this scenario, Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the carbon K-edge provides information of the bonding environment of graphene carbon atoms, by the analysis of peak positions, intensities, and spectral lineshapes and constitute a suitable technique to elucidate native structure and unintended surface impurities and defects [3]. The aim of this work is to interpret the measured experimental NEXAFS spectra by means of computer simulations based on first-principle Density Functional Theory (DFT). In this scheme, structural and electronic properties are calculated following the excited electron and Core-Hole approach (XCH) [4]. In this work, we focus on the identification of specific defects (rippling, surface adsorbates and doping) at graphene/Cu and transferred graphene/SiC interfaces.

[1] Katsnelson, M. I. Graphene: carbon in two dimensions. Materials Today 2007, 10 (1–2), 20-27.

[2] Dharmendar, R.; Leonard, F. R.; Gary, D. C.; Sanjay, K. B. Graphene field-effect transistors. J. Phys. D: Appl. Phys. 2011, 44 (31), 313001. And Singh, B.; Sariciftci, N. S.; Grote, J. G.; Hopkins, F. K. Bio-organic-semiconductor-field-effect-transistor based on deoxyribonucleic acid gate dielectric. J. Appl. Phys. 2006, 100.

[3] Schultz, B. J.; Patridge, C. J.; Lee, V.; Jaye, C.; Lysaght, P. S.; Smith, C.; Barnett, J.; Fischer, D. A.; Prendergast, D.; Banerjee, S. Imaging local electronic corrugations and doped regions in graphene. Nat Commun 2011, 2, 372.

[4] Prendergast, D.; Galli, G. X-Ray Absorption Spectra of Water from First Principles Calculations. Phys. Rev. Lett. 2006, 96 (21), 215502.

P70

Intrinsic point defects in thermoelectric materials: a computational study of SnSe

Danny Broberg[1] and Mark Asta[1]

[1] *Department of Materials Science and Engineering, 210 Hearst Mining Building, University of California Berkeley, CA 94720-1760 USA*

Thermoelectric (TE) device engineering has the potential to propel new energy effi- cient mechanisms into the global energy mix. Currently the practical utility of TE devices is limited by the availability of suitable, cheap materials, with relatively few cheap compounds that exhibit large figures of merit. To enable discovery of new inexpensive, scalable TE materials, initiatives such as the Material Project (materialsproject.org) aim to exploit high-throughput density functional theory calculations to screen for materials based on computed figures of merit and the ability to further optimize performance with selective point defect doping ("dopability") [1]. For the latter property, a central issue is assessing an optimal computational methodology for calculating relevant properties of charged defects in semiconductors within the framework of high-throughput computation. The challenges inherent in the calculation of charged defect calculations have been extensively discussed in the literature, and tend to be associated with errors in the predicted band gap within semi-local density functional theory, as well as to the spurious defect interactions introduced by the use of periodic boundary conditions. While solutions to these problems have been proposed, the computational cost can be prohibitively high for enabling the application of high-throughput screening. The work presented in the poster is part of an effort aimed at establishing the suitability of various computationally efficient schemes for deriving charged-defect properties in candidate thermoelectric materials. The primary focus of this study is on the intrinsic charged defects of SnSe and other mono-chalcogenide materials, which are anisotropic materials that have shown considerable promise for future TE application. We survey the performance of several well known charge correction schemes as applied to intrinsic defects in SnSe and SnS. We also investigate the relative performance for calculated bulk properties using the recently developed Van der Waals functional by Berland et. al. [2], as compared to those calculated within the local density approximation, finding considerable improvements in the lattice constants but poorer predictions for the dielectric response. Finally, we analyze the effect of anisotropy in the dielectric and structural properties of SnSe on the charged defect properties. The lessons learned from this study are expected to help in providing a basis for scaling defect analysis to the coarse screening of dopability for different chemistries in a high-throughput framework.

[1] (In submission) H. Zhu, G. Hautier, U. Aydemir, Z. M. Gibbs, G. Li, S. Bajaj, J. Pohls, D.Broberg, W. Chen, A. Jain, M. Asta, G. J. Snyder, K. Persson, and G. Ceder, Advanced Functional Materials (2015).

[2] K. Berland and P. Hydlgaard, Phys. Rev. B, 89, (2014).