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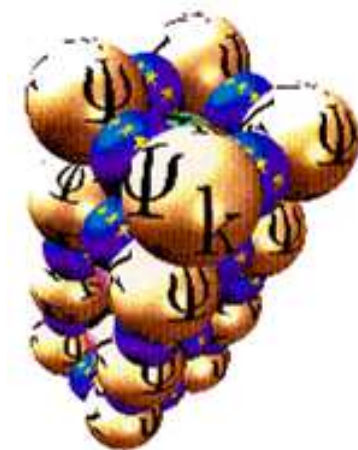
## AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

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Number 116

April 2013

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## Contents

<b>1 Editorial</b>	<b>3</b>
<b>2 General Workshop/Conference Announcements</b>	<b>4</b>
2.1 International ELSTRUC2013 Symposium . . . . .	4
<b>3 General Job Announcements</b>	<b>8</b>
<b>4 Abstracts</b>	<b>11</b>
<b>5 SCIENTIFIC HIGHLIGHT OF THE MONTH</b>	<b>19</b>
<b>1 “Frontiers of Electronic Structure” Sessions and Symposium</b>	<b>19</b>
<b>2 Volker Heine Young Investigator Award</b>	<b>26</b>
<b>3 The European Theoretical Spectroscopy Facility at the DPG</b>	<b>29</b>
<b>4 A bit of everything else...</b>	<b>30</b>

# 1 Editorial

In this second Psi-k Newsletter of 2013 we have an announcement of an International Symposium on “Recent Electronic-Structure Theories and Related Experiments” which will take place in Stuttgart in the middle of June. It is followed by two job announcements and a few abstracts of the newly submitted or recently published papers.

The scientific highlight of this issue is an extensive scientific report by Professor Nicola Marzari (EPF Lausanne, Switzerland) on the DPG 2013 Spring Meeting and the Volker Heine symposium, which took place in March in Regensburg, Germany.

Please check the table of content for details.

The *Uniform Resource Locator* (URL) for the Psi-k webpage is:

<http://www.psi-k.org.uk/>

**Please submit all material for the next newsletters to the email address below.**

The email address for contacting us and for submitting contributions to the Psi-k newsletters is

**function**

**psik-coord@stfc.ac.uk** messages to the coordinators, editor & newsletter

Z (Dzidka) Szotek, Martin Lüders, Leon Petit and Walter Temmerman

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## 2 General Workshop/Conference Announcements

### 2.1 International ELSTRUC2013 Symposium

#### on “Recent Electronic-Structure Theories and Related Experiments”

Wednesday June 12 - Friday 15, 2013

Max Planck Institute for Solid State Research, Stuttgart, Germany

Organization: Ole Krogh Andersen

Email: [ELSTRUC@fkf.mpg.de](mailto:ELSTRUC@fkf.mpg.de)

Webpage: <http://www.fkf.mpg.de/ELSTRUC2013>

The symposium will last three full days (from 8:30 and into the evenings) and take place in the auditorium and the foyer of the Max Planck Institute for Solid State Research. The morning and afternoon sessions will have invited talks. The evening sessions on Wednesday and Friday will have posters with light food and beverages. The posters will be accessible during the entire symposium. Thursday evening will be devoted to a dinner in the canteen. Finally, on the Saturday, there will be a hike in the hills around Stuttgart.

The symposium is open for submission of posters and registration to scientists and students interested in electronic structure, but the number of participants is limited.

#### Deadlines

April 15: Submission of abstracts

May 15: Registration

#### Invited Speakers/Participants (as of March 11, 2013)

Mebarek Alouani (Universite L. Pasteur, Strasbourg, France)

Massimo Altarelli (European XFEL, Hamburg, Germany), “Challenges to theory from X-ray Free-Electron Lasers”

Denis Antonov (MPI-FKF, Stuttgart, Germany), “Investigations on optical properties of the nitrogen-vacancy centre”

Victor Antonov (Institute of Metal Physics, Kiev, Ukraine), “X-ray magnetic dichroism in the (Zn,Co)O diluted magnetic semiconductors from first principle calculations”

Ferdi Aryasetiawan (Univ of Lund, Sweden)

Giovanni B. Bachelet (University of Rome Sapienza, Italy)

Silke Biermann (Ecole Polytechnique, Palaiseau, France)

Peter Blöchl (TU Clausthal, Germany)

Lilia Boeri (TU Graz, Austria)

Shyamal Bose (Brock University, St. Catharines, Ontario, Canada), “Ferromagnetism and half-metallicity of some 3- and 4-d transition metal alloys”

Armin Burkhardt (MPI-FKF, Stuttgart, Germany)

Manuel Cardona (MPI-FKF, Stuttgart, Germany)

Liviu Chioncel (University of Augsburg, Germany)

Niels Egede Christensen (Univ of Aarhus, Denmark), “Quasi-Particle Band Structures and Thermoelectrics of PbX(X=Te,Se,S)”

Gour P. Das (Indian Association for the Cultivation of Science, Kolkata, India)

Indra Dasgupta (Indian Association for the Cultivation of Science, Kolkata, India)

Molly De (SN Bose Center, Kolkata, India)

Volker Deringer (RWTH Aachen, Germany)

Klaus Dransfeld (University of Konstanz, Germany)

Vaclav Drchal (Academy of Sciences, Praha, Czech Republic), “Effective magnetic Hamiltonians”

Richard Dronskowski (RWTH Aachen, Germany)

Ilya Elfimov (University of British Columbia, Canada)

Volker Eyert (University of Augsburg, Germany)

Claudia Felser (MPI-CPfS, Dresden, Germany)

Takeo Fujiwara (Univ of Tokyo, Japan), ”Electronic structure and Li ion dynamics in Thio-LISICON(Li<sub>4</sub>GeS<sub>4</sub> and Li<sub>3</sub>PS<sub>4</sub>)”

Peter Fulde (MPI-PKS, Dresden, and POSTECH, Korea), “Many-electron wavefunctions for solids: a status report”

Antoine Georges (Ecole Polytechnique, Palaiseau, France)

Yuri Grin (MPI-CPfS, Dresden, Germany)

Olle Gunnarsson (MPI-FKF, Stuttgart, Germany), “Origin of the pseudogap in cuprate superconductors”

Liu Guo-Qiang

Philipp Hansmann (Ecole Polytechnique, Palaiseau, France)

Walter Harrison (Stanford Univ, USA), “The Benefits of Giving Up Accuracy”

Maurits W. Haverkort (UBC-MPG, Canada), “Testing the reality of Wannier orbitals and their tight-binding hamiltonian”

Volker Heine (Cavendish Lab, Cambridge, UK), “So near, and yet so far”

Karsten Held (TU Vienna, Austria)

Abdesalem Houari (University of Bejaia, Algeria), “Semiconducting (Half-Metallic) Ferromagnetism in Mn(Fe) Substituted Pt and Pd Nitrides”

Dilip Kanhere (Central University of Rajasthan India)

Debjani Karmakar (Bhabha Atomic Research Centre, Mumbai, India)

Bernhard Keimer (MPI-FKF, Stuttgart, Germany), “Spin and charge correlations in cuprate superconductors”

Giniyat Khaliullin (MPI-FKF, Stuttgart, Germany), “Spin-state crossover model for the magnetism of iron pnictides”

Erik Koch (FZ Jülich, Germany)

Jens Kortus (TU Bergakademie, Freiberg, Germany)

Eugene Kotomin (MPI-FKF, Stuttgart, Germany), “A comparative analysis of oxygen vacancy diffusion in LSCF and BSCF perovskite solid solutions: ab initio modeling”

Reinhard Kremer (MPI-FKF, Stuttgart, Germany)

Josef Kudrnovsky (Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic), “Spin-disorder resistivity of ferromagnetic metals: the disordered local moment approach”

Denis Kukusta (Institute of Metal Physics, Kiev, Ukraine and MPI-FKF, Stuttgart, Germany)

Alexander Lichtenstein (Univ of Hamburg, Germany)

Stefan Maintz (RWTH Aachen, Germany)

Richard M. Martin (Univ of Illinois, USA)

Igor Mazin (NRL, Washington, USA)

Michael Methfessel (Innovations for High Performance, Frankfurt a.d. Oder, Germany)

Walter Metzner (MPI-FKF, Stuttgart, Germany), “Superconductivity and competing order in the 2D Hubbard model”

Yoshiro Nohara (MPI-FKF, Stuttgart, Germany)

Tamio Oguchi (Osaka University, Japan)

Luciano Ortenzi (MPI-FKF, Stuttgart, Germany)

Michele Parrinello (ETH, Lugano, Switzerland)

Eva Pavarini (FZ Juelich, Germany)

Tony Paxton Belfast/London)

Rossitza Pentcheva (LMU Munich, Germany)

Helena Petrilli (University of Sao Paolo, Brasil)

Warren E. Pickett (Univ of California, Davis, USA)

Luciano Pietronero (University of Rome Sapienza, Italy), “Economic complexity 1”

Andrei Postnikov (University of Metz, France)

Ponniah Ravindran (University of Oslo, Norway)

Vidya Ravindran (University of Oslo, Norway)

Tanusri Saha Dasgupta (SN Bose Center, Kolkata, India)

Giorgio Sangiovanni (University of Würzburg, Germany)

Dipankar Das Sarma (IISc, Bangalore, India)

Sashi Satpathy (Univ of Missouri, USA), “Magnetism without magnetic atoms: Physics of the vacancy in graphene”

Andreas Savin (Universit er et Marie Curie, Paris, France)

Sergey Savrasov (Univ of Calif, Davis, USA), “Electron-Phonon Interaction and Topological Superconductivity in Cu doped Bi<sub>2</sub>Se<sub>3</sub>”

Dmitry Savrasov (Sberbank Asset Management)

George Sawatzky (Univ of BC, Canada)

Matthias Scheffler (Fritz-Haber Institut, Berlin, Germany)

Tobias Schickling (University of Marburg, Germany)

Mirek Šob (Brno, Czech Republic), “Magnetically dead layers at the impuritysegregated grain boundaries and surfaces in nickel”

Alaska Subedi (Ecole Polytechnique, Palaiseau, France)

Michael Springborg (Univ of Saarland, Germany), “Converse Piezoelectricity”

Axel Svane (Univ of Aarhus, Denmark), “Electronic structure of Rare earth mononictides and monochalcogenides: towards an electronic phase diagram of strongly correlated materials”

Karl Syassen (MPI-FKF, Stuttgart, Germany)

Erio Tosatti (SISSA, Trieste, Italy), “Shot noise, conductance, magnetism, and Kondo effects in atomic and molecular nanocontacts”

Ilja Turek (Inst of Physics of Materials, Brno, Czech Republic), “Relativistic LMTO theory of electron transport in random alloys”

Mark Van Schilfgaarde (King.s College, London, UK)

Wenhui Xie, “Electronic and magnetic properties of La<sub>2</sub>NiMnO<sub>6</sub> and La<sub>2</sub>CoMnO<sub>6</sub> with cationic ordering”

Xiaoping Yang (Nanyang Technological University, Singapore)

Alexander Yaresko (MPI-FKF, Stuttgart, Germany)

Jan Zaanen (Univ of Leiden, Netherlands), “From strange metals to black holes”

Wen-Scheng Zeng

Eva Zurek (SUNY, Buffalo, USA), “Building a Chemical Intuition Under Pressure: Predictions of Novel Hydrides”

Maciej Zwierzycki (Polish Academy of Sciences, Poznan, Poland)

### 3 General Job Announcements

#### POST-DOCTORAL POSITION IN THERMOELECTRICS COMPUTATIONAL MATERIALS THEORY

##### W. M. Keck Computational Materials Theory Center

A postdoctoral position is available in the W. M. Keck Computational Materials Theory Center at California State University Northridge (<http://www.csun.edu/~nkioussi/>) in the area of electronic structure calculations and thermal transport of thermoelectrics. Experience with first-principles electronic-structure calculations of the figure of merit, ZT, Boltzmann transport theory, Seebeck coefficient, electrical conductivity, and power factor, and computer programming is preferred.

The position is available immediately. Initial appointment is for one year and/or second year (based upon satisfactory performance). Interested applicants should submit a curriculum vita, list of publications, and arrange to have two letters of reference sent to: Prof. Nicholas Kioussis, Department of Physics, California State University Northridge, 18111 Nordhoff Street, Northridge, CA 91330-8268 or via e-mail to: [nick.kioussis@csun.edu](mailto:nick.kioussis@csun.edu). CSUN is an Affirmative Action, Equal Opportunity Employer.



**Member of Technical Staff - Computational Chemist**  
**Corporate Strategic Research Laboratory (CSRL), Clinton, NJ**

ExxonMobil Research and Engineering Company has an immediate opening for a Member of the Technical Staff in its Corporate Strategic Research Laboratory located in Clinton, NJ, USA.

Candidates are sought to fill a key position in the area of Computational Hydrocarbon Chemistry. This individual will help advance our internal capabilities in the areas of detailed kinetics, fundamental structure-reactivity and structure-property relationships and thermodynamics/physical property models. The initial focus will be on the development and implementation of multi-scale models (nanometers to micron) for thermal and catalytic reactions of complex hydrocarbon mixtures by extending reaction kinetics calculated from first principles to large length scales in a parallel computing environment. Initial assignments could be in one of several areas that extend hydrocarbon science fundamentals and applications, including hydrocarbon catalysis, biofuels, frontier resources and lubricants.

A Ph.D in theoretical or catalytic chemistry, chemical engineering, material science, surface science, physics or a similar field is required, as are demonstrated research contributions in a results-oriented multi-disciplinary team environment. Preference will be given to candidates with molecular modeling expertise in heterogeneous catalysis, kinetics, and reaction engineering, as well as the demonstrated ability to express ideas mathematically and develop computer code in programming languages such as C++/Fortran in a Linux cluster environment. While not essential, preference will be given to individuals with experience with VASP, CASTEP, DACAPO, ADF, DMol Solids or related density functional theory calculations of solids and surfaces. Additionally, familiarity with classical molecular dynamics simulations using reactive force fields or DFTB is preferred, as is experience with accelerated MD approaches to extend the length and time scales of simulations. Exposure to classical molecular dynamics simulation of ions in liquids, electrochemical surfaces and quantum chemistry methods for characterizing electron transfer processes in solvated species is also advantageous.

The successful candidate will be expected to demonstrate strong scientific leadership within both the corporation and the external scientific community. Strong communication skills are essential, as collaboration with other science areas is critical for success. Candidates with all levels of experience will be considered.

ExxonMobil's Corporate Strategic Research (CSR) laboratory is a dynamic and exciting place to work. CSR is located in scenic western New Jersey, about an hour west of New York city and 45 minutes northwest of Princeton. Within CSR, active research programs exist in all areas of the company's business and which cut across the traditional fields of chemical engineering, materials science, chemistry, physics, geoscience, and mechanical engineering. Interdisciplinary

research is the norm, and close ties are maintained with the academic and national laboratory communities through publication and presentation of results. Collaborations with the external scientific community are encouraged.

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<http://www.exxonmobil.com/ex>

and apply to Computational Hydrocarbon Chemistry.

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## 4 Abstracts

### Electrostatic considerations affecting the calculated HOMOLUMO gap in protein molecules

Greg Lever<sup>1</sup>, Daniel J Cole<sup>1,2</sup>, Nicholas D M Hine<sup>3</sup>, Peter D Haynes<sup>3</sup>  
and Mike C Payne<sup>1</sup>

<sup>1</sup>*Theory of Condensed Matter group, Cavendish Laboratory,  
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<sup>2</sup>*Department of Chemistry, Yale University, New Haven, CT 06520-8107, USA*

<sup>3</sup>*Departments of Materials and Physics, Imperial College London,  
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#### Abstract

A detailed study of energy differences between the highest occupied and lowest unoccupied molecular orbitals (HOMOLUMO gaps) in protein systems and water clusters is presented. Recent work questioning the applicability of KohnSham density-functional theory to proteins and large water clusters (Rudberg 2012 J. Phys.: Condens. Matter 24 072202) has demonstrated vanishing HOMOLUMO gaps for these systems, which is generally attributed to the treatment of exchange in the functional used. The present work shows that the vanishing gap is, in fact, an electrostatic artefact of the method used to prepare the system. Practical solutions for ensuring the gap is maintained when the system size is increased are demonstrated. This work has important implications for the use of large-scale density-functional theory in biomolecular systems, particularly in the simulation of photoemission, optical absorption and electronic transport, all of which depend critically on differences between energies of molecular orbitals.

(J. Phys.: Condens. Matter 25 152101 (2013 ))

<http://iopscience.iop.org/0953-8984/25/15/152101/>

Contact person: gl319@cam.ac.uk

# Ready, set and no action: A static perspective on potential energy surfaces commonly used in gas-surface dynamics

V. J. Bukas<sup>1</sup>, J. Meyer<sup>1</sup>, M. Alducin<sup>2</sup> and K. Reuter<sup>1</sup>

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<sup>2</sup>*Centro de Física de Materiales CFM, Paseo Manuel de Lardizábal 5,  
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## Abstract

In honoring the seminal contribution of Henry Eyring and Michael Polanyi who first introduced the concept of potential energy surfaces (PESs) to describe chemical reactions in gas-phase [Z. Phys. Chem. 12, 279-311, (1931)], this work comes to review and assess state-of-the-art approaches towards first-principle based modeling in the field of gas-surface dynamics. Within the Born-Oppenheimer and frozen surface approximations, the O<sub>2</sub>-Ag(100) interaction energetics are used as a showcase system to accentuate the complex landscape exhibited by the PESs employed to describe the impingement of diatomics on metal substrates and draw attention to the far-from-trivial task of continuously representing them within all six molecular degrees of freedom. To this end, the same set of ab initio reference data obtained within Density Functional Theory (DFT) are continuously represented by two different state-of-the-art high-dimensional approaches, namely the Corrugation-Reducing Procedure and Neural Networks. Exploiting the numerically undemanding nature of the resulting representations, a detailed static evaluation is performed on both PESs based on an extensive global minima search. The latter proved particularly illuminating in revealing representation deficiencies which affect the dynamical picture yet go otherwise unnoticed within the so-called “divide-and-conquer” approach.

(Submitted to Zeitschrift für Physikalische Chemie (March 2013) [preprint: arXiv:1303.2165])

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# Exploring Morphology-Activity Relationships: Ab Initio Wulff Construction for RuO<sub>2</sub> Nanoparticles under Oxidizing Conditions

Tongyu Wang<sup>1</sup>, Jelena Jelic<sup>1</sup>, Dirk Rosenthal<sup>2</sup> and Karsten Reuter\*<sup>1</sup>

<sup>1</sup> *Chair for Theoretical Chemistry and Catalysis Research Center,  
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<sup>2</sup> *Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6,  
D-14195, Berlin, Germany*

## Abstract

We present a density-functional theory based Wulff construction of the equilibrium shape of RuO<sub>2</sub> particles in an oxygen environment. The obtained intricate variations of the crystal habit with the oxygen chemical potential allow for a detailed discussion of the dependence on the oxidizing pretreatment observed in recent powder catalyst studies. The analysis specifically indicates an incomplete particle shape equilibration in previously employed low temperature calcination. Equilibrated particles could be active CO oxidation catalysts with long-term stability in oxidizing feed and then represent an interesting alternative to the previously suggested core-shell concept.

(Submitted to Chem. Cat. Chem.)

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# $MSi_{20}H_{20}$ Aggregates: From Simple Building Blocks to Highly Magnetic Functionalized Materials

Dennis Palagin and Karsten Reuter

*Department Chemie, Technische Universität München,  
Lichtenbergstr. 4, D-85747 Garching, Germany*

## Abstract

Density-functional theory based global geometry optimization is used to scrutinize the possibility of using endohedrally-doped hydrogenated Si clusters as building blocks for constructing highly magnetic materials. In contrast to the known clathrate-type facet-sharing, the clusters exhibit a predisposition to aggregation through double Si-Si bridge bonds. For the prototypical  $CrSi_{20}H_{20}$  cluster we show that reducing the degree of hydrogenation may be used to control the number of reactive sites to which other cages can be attached, while still preserving the structural integrity of the building block itself. This leads to a toolbox of  $CrSi_{20}H_{20-2n}$  monomers with different number of double “docking sites”, that allows building network architectures of any morphology. For  $(CrSi_{20}H_{18})_2$  dimer and  $[CrSi_{20}H_{16}](CrSi_{20}H_{18})_2$  trimer structures we illustrate that such aggregates conserve the high spin moments of the dopant atoms and are therefore most attractive candidates for cluster-assembled materials with unique magnetic properties. The study suggests that the structural completion of the individual endohedral cages within the doubly-bridge bonded structures and the high thermodynamic stability of the obtained aggregates are crucial for potential synthetic polymerization routes *via* controlled dehydrogenation.

(ACS Nano **7**, 1763 (2013) )

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# CO oxidation on Pd(100) vs. PdO: First-Principles Kinetic Phase Diagrams and Bistability Conditions

Max J. Hoffmann, Karsten Reuter

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Lichtenbergstr. 4, D-85747 Garching, Germany*

## Abstract

We present first-principles kinetic Monte Carlo (1p-kMC) simulations addressing the CO oxidation reaction at Pd(100) for gas-phase conditions ranging from ultra-high vacuum (UHV) to ambient pressures and elevated temperatures. For the latter technologically relevant regime there is a long-standing debate regarding the nature of the active surface. The pristine metallic surface, an ultra-thin ( $\sqrt{5} \times \sqrt{5}$ )  $R27^\circ$  PdO(101) surface oxide, and thicker oxide layers have each been suggested as *the* active state. We investigate these hypotheses with 1p-kMC simulations focusing on either the Pd(100) surface or the PdO(101) surface oxide and intriguingly obtain a range of  $(T, p)$ -conditions where both terminations appear metastable. The predicted bistability regime nicely ties in with oscillatory behavior reported experimentally by Hendriksen and coworkers [Catal. Today **105**, 234 (2005)]. Within this regime we find that both surface terminations exhibit very similar intrinsic reactivity, which puts doubts on attempts to assign the catalytic function to just one *active* state.

(Submitted to Topics Catal. )

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# Projection potentials and angular momentum convergence of total energies in the full-potential Korringa-Kohn-Rostoker method

Rudolf Zeller

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*Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

## Abstract

Although the full-potential Korringa-Kohn-Rostoker Green function method yields accurate results for many physical properties, the convergence of calculated total energies with respect to the angular momentum cutoff is usually considered to be less satisfactory. This is surprising because accurate single-particle energies are expected if they are calculated by Lloyd's formula and because accurate densities and hence accurate double-counting energies should result from the total energy variational principle. It is shown how the concept of projection potentials can be used as a tool to analyse the convergence behaviour. The key factor blocking fast convergence is identified and it is illustrated how total energies can be improved with only a modest increase of computing time.

(Published: J. Phys.: Condens. Matter, **25**, 105505 (2013))

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# Structure and energetics of benzene adsorbed on transition-metal surfaces: Density-functional theory with van der Waals interactions including collective substrate response

Wei Liu, Victor G. Ruiz, Guo-Xu Zhang, Biswajit Santra,  
Xinguo Ren, Matthias Scheffler, and Alexandre Tkatchenko  
*Fritz-Haber-Institut der Max-Planck-Gesellschaft,  
Faradayweg 4-6, 14195 Berlin, Germany*

## Abstract

The adsorption of benzene on metal surfaces is an important benchmark system for hybrid inorganic/organic interfaces. The reliable determination of the interface geometry and binding energy presents a significant challenge for both theory and experiment. Using the PBE, PBE+vdW, and the recently developed PBE+vdW<sup>surf</sup> methods (density-functional theory including the collective many-electron response of the metal substrate), we calculated the structures and energetics for benzene on transition-metal surfaces: Cu, Ag, Au, Pd, Pt, Rh, and Ir. Our calculations demonstrate that vdW interactions significantly increase the binding energy by more than 0.70 eV for physisorbed systems (Cu, Ag, and Au) and also for strongly bound systems (Pd, Pt, Rh, and Ir). The collective response of the metal electrons, which implies beyond pairwise vdW interactions, plays a significant role in most metals, shortening the equilibrium distance by 0.25 Å for Cu, and decreasing the binding energy by 0.27 eV for Rh. The reliability of our results is assessed by comparison with calculations using the random-phase approximation including renormalized single excitations, and the experimental data from temperature-programmed desorption, microcalorimetry measurements, and low-energy electron diffraction.

(Submitted to New J. Phys. (February 2013))

Contact person: Alexandre Tkatchenko (tkatchenko@fhi-berlin.mpg.de)

# Stabilization of Semiconductor Surfaces through Bulk Dopants

Nikolaj Moll, Yong Xu, Oliver T. Hofmann, and Patrick Rinke

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, 14195 Berlin, Germany*

## Abstract

We show that by employing density-functional theory (DFT) (including a hybrid functional) polar ZnO surfaces can be stabilized by bulk dopants. As an example, we study the bulk-terminated ZnO (000 $\bar{1}$ ) surface covered with half a monolayer of hydrogen (2 $\times$ 1-H). We demonstrate that deviations from this half-monolayer coverage can be stabilized by electrons or holes from bulk dopants. The electron chemical potential therefore becomes a crucial parameter that cannot be neglected in semiconductor surface studies. As a result, we find that to form the defect-free 2 $\times$ 1-H surface, ambient hydrogen background pressures are more conducive than high vacuum pressures.

(Submitted to Phys. Rev. Lett. (January 2013))

Contact person: Patrick Rinke (rinke@fhi-berlin.mpg.de)

## 5 SCIENTIFIC HIGHLIGHT OF THE MONTH

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### A report on the DPG 2013 Spring meeting and the Volker Heine symposium

Nicola Marzari

*Theory and Simulation of Materials (THEOS), École Polytechnique Fédérale de Lausanne*

#### Abstract

We report on selected activities that took place at the 2013 Spring Meeting of the German Physical Society (DPG) in Regensburg, including the focused sessions and symposium on “Frontiers of Electronic Structure Theory”, the Volker Heine Young Investigator award to Michele Ceriotti, the activities of ETSF (the European Theoretical Spectroscopic Facility), the plenary talk of Olle Eriksson, and anything else that caught the fancy of the group members.

### 1 “Frontiers of Electronic Structure” Sessions and Symposium

Together with Matthias Scheffler (FHI Berlin) and Ralf Drautz (ICAMS Bochum), we organized seven focused sessions on “Frontiers of Electronic Structure Theory” (supported by the Surface Science division, and in addition by the Semiconductor and Low Temperature divisions) together with a final Friday morning Symposium on “Frontiers of Electronic Structure Theory: Discovery of Novel Functional Materials” (supported, in addition, by the divisions of Thin Films, Magnetism, and Metals and Materials). This activity encompassed 10 invited talks, 64 contributed talks, and 5 invited talks from the speakers that had been selected by Psi-k for the Volker Heine Young Investigator Award. A chronological summary of the 10 invited talks and of the Volker Heine session is presented here first.

**Jörg Neugebauer (Max-Planck-Institut für Eisenforschung, Düsseldorf):** *Fully ab-initio determination of free energies: Basis for high-throughput approaches in materials design.*

Jörg reported their results on calculating partition functions and heat capacities fully from first-principles, using a combination of LDA or GGA calculations to determine phonon frequencies and quasi-harmonic contributions to the vibrational free energies, plus electronic, magnetic and anharmonic contributions, and applying it to metals, with of course a focus on iron and iron alloys (see Psi-k Highlight 105 for an introduction on the topic).

Magnetic excitations were included calculating a spin Hamiltonian based on the Heisenberg model, with 30-or-more neighbors, and shown to reproduce correctly experimental magnon dispersions. Three techniques were used to solve the problem - Classical Monte Carlo (that was

shown to fail below  $T_c$ ), analytical approaches (RPA) and quantum Monte Carlo in combination with a renormalized magnetic Hamiltonian (valid everywhere). Applications to e.g. cementite ( $\text{Fe}_3\text{C}$ ) were shown to be dominated by vibrational entropy, but with magnetic excitations essential in describing the singularities around  $T_c$ . Jörg commented that one of the remaining challenges is the accurate description of the relative energies of the paramagnetic fcc and bcc phases of iron, given the very tiny competing contributions that make iron become bcc again just before reaching the melting temperature.

After a presentations of the successes and challenges of first-principles simulations in addressing these fundamental questions, the question of steel design was raised. In fact, optimizing total elongation before fracture, and tensile strength, is a key metric for new structural steels, and a great challenge for simulations. Microtwinning allows to go in these desired directions, and stacking fault energies become key quantities that determines the type of steel obtained. It was highlighted how an accurate description of the paramagnetic phase is essential to predicting correctly these energies. The talk concluded applying a constitutive model developed by Raabe, based on stacking fault formation energies and elastic constants, and showing how this model, augmented with first-principles parameters, was able to reproduce successfully stress-strain curves in TWIP (Twinning Induced Plasticity) steels.

**Chris Wolverton (Northwestern University):** *Materials for alternative energies: Computational materials discovery and crystal structure predictions.*

Chris highlighted how the number of inorganic materials known ( 150,000) is comparable to those that are only partially recorded (also 150,000) and for which full structural information is missing. So he contrasted structure-prediction methods (now a very active field of research) with structure-solving approaches, that start from partial experimental data and use those to maximum effect by combining them with total energy calculations - an approach that combines the strength of experimental diffraction studies (that are “blind” to total-energies in the refinement process) and traditional structure-prediction methods. Their approach, named First-principles assisted structure solution (FPAS), has been recently published in Nature Materials (12, 123127 (2013)), and shown to be of broad utility in determining materials’ structures - examples were drawn from hydrogen-storage materials, Li-air batteries, and high-pressure phases.

Chris then discussed how first-principles calculations produce lots of data, with hidden correlations embedded in the databases collecting these results - so the question arises on how to identify those correlation through appropriate materials descriptors. The eponymous materials maps first introduced by David Pettifor were one of the first examples of this search for descriptors (or, more recently, Darken-Gurry solubility maps) - so if one could organize materials around relevant variables, materials would organize themselves in ways that would allow to predict or invent new materials’ combinations.

How to automatize the search for these descriptors? Chris presented their approach, called CRR (for “Clustering, Ranking and Regression”). The clustering task sorts  $n$  data points into different sets such that each point is closer to the centroid of its set than to any other set (allowing for a Voronoi tessellation of space). This technique, applied to doped zirconia, automatically sorted dopants into a  $p$  block, a group of heavy elements, early TMs, divalent TMs... Then, he

used the Maximal Information Coefficients method (MIC, see Reshef et al. Science 334 1518 (2011)) to bin data, so that two variables have high mutual information if their joint probability distribution is much lower in entropy. Descriptors can then be ranked in order of MIC score. Last, regression methods were used to identify the optimal candidates.

**Boris Kozinsky (Robert Bosch Research Technology Center, Cambridge MA):** *Challenges in data-intensive computational materials design: methodology and infrastructure.*

Boris discussed some of the materials' design projects that involve industrial applications. Among them, he mentioned recent research efforts at Bosch for new catalysts that are poison-tolerant for HBr flow batteries, searches for new lead-free piezoelectrics, and screening of solvents for Li-air batteries. The piezoelectric projects (done in collaboration with Rickard Armiento and Gerd Ceder at MIT, Marco Fornari at CMU, and Nicola Marzari at EPFL) exemplified the need to identify key descriptors of materials properties that are amenable to rapid, high-throughput screening - in this case band gap, relative energies and free energies of different phases, and the facility to switch phases across the morphotropic phase boundary. Interestingly, a high-throughput search yielded back all known tetragonal perovskites, and a number of promising new compositions. A new project on solid-state Li electrolytes, running on Titan (currently the largest supercomputer in the world) was also mentioned. Last, the challenges in software engineering were described: with computer time ever less expensive, and manpower a precious commodity, it becomes natural and compelling to run, organize, and store computer experiments using the tools of computer science. Key objectives identified to manage large amounts of calculations were flexibility, automation, easy lookup, sharing, and total recall of workflows. So, any computational platform would need to support these needs: Reproducibility, provenance, automation and storage, dataqueries, workflows. Boris described an effort that started a couple of years ago, in collaboration with EPFL, for an Automated Infrastructure and Database for Atomistic Design (AIDA), that is used and developed to serve these goals - data repositories, scripting interfaces, plugins for computational codes, queue integration... The platform will be released in the next few months under a BSD open source licence.

**Georg Madsen (ICAMS, Ruhr-Universität Bochum):** *Screening high-throughput density functional theory calculations using simplified models.*

Georg introduced a hierarchy of high-throughput environments and illustrated them through studies of antimonides and silicides in the searching for new thermoelectric materials. A simplified model of the electronic structure was introduced to rationalize trends in structural stability, and screening of known antimonide compounds using their calculated thermoelectric properties was demonstrated. The LiZnSb compound was identified and experimentally measured transport properties were found to be in good agreement with the predicted one. The doping asymmetry observed in antimonides, which have all been found to be *p*-type, was explained by the low formation energies of negatively charged zinc vacancies, pinning the chemical potential to the lower part of the band gap. Using known host lattices and a systematic replacement technique, convex hulls of the binary transition metal silicides were calculated. It was shown how the experimentally known binary transition metal silicides were mainly found within 50 meV/atom of the calculated convex hulls. All the known and a few unknown binary transition metal semi-

conductors were furthermore found within this range. Stability of silicides was rationalized in terms of their band filling using a generic tight binding model. Starting from the TII and  $\text{ZrSi}_2$  structure types as examples, it was shown how the stability of structures with different compositions could be related to the same structural building blocks. Finally, using half Heusler, sodium chloride and zinc-blende structures as an example, it was shown how the stability of ternary structures could be related to the stability of simpler binary structures. (*thanks to Georg for helping out with the summary*)

**Karsten Jacobsen (DTU Lyngby):** *Atomic-scale design of energy materials.*

While Karsten could not attend the meeting (we missed you Karsten!), his talk would have focused on recent work on high-throughput screening materials for photocatalytic water splitting (see e.g. I. Castelli et al., *Energy Environ. Sci.*, 5, 5814 (2012), *ibid.*, 5, 9034 (2012)), and on machine learning for new energy functionals (see e.g. *Phys. Rev. B*, 85, 235149 (2012)). I report here below the abstract of the talk.

“The design of new materials for more efficient production and use of sustainable and clean energy is of utmost importance for the standard of living all over the World the coming years. In the talk I shall describe some computational efforts to design new materials related to solar energy in particular to the conversion of light into hydrogen fuel through water splitting. We have employed computational screening to search for stable semiconductor materials with an appropriate bandgap, band edge alignment, and with sufficient stability to be relevant for light-induced water splitting. In particular we have focused on materials in the cubic perovskite structure but also more generally materials in the ICSD database. The screening of bandgaps is performed using the so-called GLLB-functional which is shown to give reasonable estimates of light absorption for a number of different systems. The stability of the materials towards dissolution in water is investigated through the construction of Pourbaix diagrams combining DFT calculations and experimental information about solution energies.

The talk will also cover some recent efforts in using machine-learning techniques to develop new electronic density functionals. The functional construction uses Tikhonov regularization to obtain smooth functionals and employs bootstrapping to avoid overfitting. The new functionals are named Bayesian Error Estimation Functionals (BEEF) because they automatically offer error estimation on calculated results.”

**Michele Parrinello (ETHZ and USI Lugano):** *Molecular dynamics simulations of nucleation and growth of crystals from solution.*

Michele’s talk was dedicated to understanding growth mechanisms of crystals and the role of growth inhibitors at the molecular scale - with a special focus on drugs and pharmaceuticals. A first example was that of urea, that exhibits crystals of needle-like shape if grown from a supersaturated solution. The reasons for this behaviour are the very different growth rates of certain fast facets (e.g. 001) vs slow facets (110) that exhibit a completely different mechanism of growth. Adding a very small amount of a different molecule (4-to-8% biuret) makes the shape of the crystal change completely and become much more cubic. A realistic model was studied using classical force fields simulations, coupled to thermostats and barostats (both developed more recently or in the past by Parrinello). Defining a (local) order parameter allows to identify

which molecules are in the crystal, and what is the growth rate of the facets - highlighting how the fast-growing 001 facets have a continuous growth profile, that can be contrasted with the step-growth process of the slow facets, that have an activated “birth-and-spread” mechanism. The addition of biuret doesn’t really affect the mechanisms of growth, but it competes with urea for surface sites. Using well-tempered metadynamics it was possible to determine the free energies of adsorption and the selectivity ratio, and show that biuret is 32 times more likely to adsorb on the 001 surfaces (as a counterexample, acetone would bring that ratio to 0.26, and lead to needle shaped crystals). To go further, and predict the shape of crystals, it became necessary to calculate the free energies of all surfaces, and classify shapes according to growth rates. All these crystals were peculiar in the sense that kinetics, rather than thermodynamics (and hence the Wulff construction) determined shape. So, a simple growth model was developed based on the free energies for adsorption barriers, and those were calculated in a variety of solvents, including water, methanol, ethanol, and acetonitrile. Most interestingly, it was shown that the theoretical predictions of crystal shapes matched closely the shapes of the nanoparticles grown, both as a function of solvent chosen, and the addition of biuret, even preceding, and thus guiding, experiments. A second case study was presented on the growth of a NaCl crystal from solution. There, the challenge was to identify a new order parameter to be used as a collective variable that would be unbiased towards different crystal shapes. This was chosen as the square gradient of the concentration. In the simulations it was discovered that NaCl crystallizes first as wurtzite, since that allows for very favorable ice-like pattern of hydrogen bonds. Classical nucleation theory and the volume vs surface free energy differences identified then the critical radii at which sodium chloride becomes stable again (roughly above 1 nm).

**Claudia Draxl (Humboldt-Universität zu Berlin)** *Describing, understanding, and discovering hybrid materials from first principles.*

Claudia started with the question of what is a good photovoltaic material: nearly free charge carriers, high absorption cross sections, and high carrier mobilities. Inorganic/organic photovoltaic materials could be these materials - excitons are created in the organic material, and diffusion brings them to the interface with the inorganic material, where the exciton is broken apart, and the electron/holes are transported at the respective electrodes, creating a current. Computational methods can deal with the different challenges of determining structure (DFT+van-der-Waals), electronic structure (many-body perturbation theory + GW), optical properties (Bethe-Salpeter on top of GW), and transport (Kubo) - ideally, getting all of these right would allow to describe not only properties, but also performance. It was noted that a key missing point in the current computational technologies are also the calculation of anharmonic interactions [see the talk of Cheol Hwan Park, described later, highlighting also some of these issues]. Claudia commented that given the challenges of this field, the theoretical work needs really to take place in tight collaborations with experiments, and expressed the need/desire for meaningful collaborations on the shared ground of studying e.g. crystalline interfaces with well characterized interfaces. An example was shown for light-emitting nanopeapods, with benzene rings tightly packed inside a carbon nanotubes. It was also noted that while much progress has been made in predicting the structure of even complex materials, accurate electronic-structure calculations, and in particular level alignment, remains a big challenge. The case of PTCDA on

a metal (Ag(111)) was presented - the challenge being that if the band gap of DFT is poorly (under) estimated, spurious charge transfer into the LUMO takes place. So, if the charge density is incorrect to begin with, GW calculations won't be able to correct such a poor starting point. In addition to the HOMO-LUMO underestimation, image charge effects (missing in standard local/semi-local) also count, as the lack of electron-vibration interactions (as an example, from Cardona 2005, the band gap of diamond can be off by up to 0.37eV when el-ph coupling is not accounted for). Finally, Claudia reminded us that DFT is flawed by self-interaction errors, with "different" errors on each side of the interface. An example of the image charge effect was shown for PPP, with a band gap decreasing from 3.95eV to 2.70eV when PPP was supported on graphene (an effect first pointed out by Neaton PRL 2006). The talk finished with a discussion of optical excitations on encapsulated molecules inside a CNT, with very delocalized excitons, contrasted by holes localized mostly on the molecule.

**Krishna Rajan (Iowa State University):** *Mapping the Electronic Structure Landscape for Materials Discovery.*

Krishna focused his talk on how statistical learning methods can be used to guide the materials' discovery process. The talk covered mathematical concepts, data-dimensionality reductions, and high-dimensional model representations. In materials discovery, Krishna mentioned that we face a data landscape of high-dimensionality - so the goal is to find the map(s) that capture maximum information to make predictions and/or discover classifications of data that were not considered or known before. Data-dimensionality reduction, and thus the choice of data topologies, is critical in this respect. Two applications were given, covering the design of piezoelectric materials, and of alloys. In mapping data, two broad classes of techniques are usually encountered - discrete methods, where dimensionality reduction is obtained by projection onto linear or non-linear subspaces (e.g. principal component analysis, PCA), and high-dimensional model representations (HDMR), where dimensionality reduction is obtained by non-linear expansion within hierarchical subspaces. This latter captures higher-order correlations (discrete methods typical stop at the  $2^{nd}$  order covariance) and basis functions can be e.g. determined by fitting with splines or Monte Carlo sampling of data. Last, data analytics methods were also presented - from feature selection (e.g. genetic algorithms, PCA, information entropy) to feature extraction (PCA, cluster analysis, factor analysis), to prediction, to discovering of association patterns (e.g. using association rule mining). In a real-world example, Krishna discussed how high-temperature piezoelectrics in the perovskite structure could be identified through the discovery and use of an "inorganic gene". While the tolerance factor (ratio of the sum of the A cation and O radii, vs.  $\sqrt{2}$  times the sum of the B cation and O radii) gives often useful regression relations with the experimental critical temperature at the morphotropic phase boundary - the approach taken here was slightly different, with a descriptor data base of 20-30 different descriptors for compounds, supplemented with additional 40 elemental descriptors, that were used to develop a quantitative structureactivity relationship (QSAR) for Tc - so the process started with 22 perovskites and 30 descriptors, where PCA was used to reduce those, and then least squares was used for regressions, and QSAR development. Recursive partitioning was used for classification modeling, finally leading to the identification of novel high-temperature perovskites (Rajan et al Proceedings of the Royal Society A 2011). The talk ended with a quick example on band gap



engineering in semiconductor alloys.

**Karin Rabe (Rutgers University):** *New ferroelectrics and antiferroelectrics by design*

Karin introduced her talk by reminding everyone why we search for new materials - to look for performance, compatibility with other materials in novel devices, and design of new functionalities. The goal of this talk was on finding new materials, while moving from perovskite oxides to intermetallic semiconductors. To search for new ferroelectric materials a design principle is needed, and Karin highlighted two elements that were identified: 1) a ferroelectric materials has a polar crystal structure that is a distortion of a high-symmetry reference structure, and 2) it is switchable by an applied electric field to one or more symmetry-related variants.

So, they needed to search polar crystals with an additional descriptor being the energy barrier to uniform switching through a high-symmetry reference structure (a low barrier correlated with low coercive fields (0.015 eV/f.u. and 0.2 eV/f.u. in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> respectively)).

A search of crystallographic databases and systematic-replacement high-throughput studies were put to good use for the case of ABC half-Heusler compounds (“stuffed” zincblends), that had been highlighted by Claudia Felser as a very promising novel class of materials with a rich variety of physical properties. So, the ICSD was used to identify the seven most common structures for composition ABC, and intercalating a third atom into a wurtzite structure allowed for low switching barriers, leading to a search in the hexagonal LiGaGe intermetallics. A initial set of 72 combinations of ABC compounds led to 17 insulating compounds (Bennett et al. PRL 109, 167602), and in particular to novel ferroelectrics with large theoretical polarization and band gap small than 2eV (filling a large empty space in the gap/polarization map).

Last, the talk turned to the search for antiferroelectrics. An antiferroelectric is obtained by a nonpolar distortion of a high-symmetry reference structure, which can be transformed to a ferroelectric phase by application of an electric field (i.e. to a polar distortion of the same high-symmetry reference structure). So, here the design principle was to look for nonpolar crystals that can be considered as small distortions of the same high-symmetry reference structure of a polar structure. This led to a high-throughput search for antiferroelectrics in the orthorhombic MgSrSi class, identifying at least 5 prominent candidates (PRL 110, 017603 (2013)).

**Gerbrand Ceder (MIT):** *The Materials Project: The design of materials using high-throughput ab-initio computations.*

Gerd started mentioning the Edisonian approach - Edison searched intensively for more than 3000 materials for a light-bulb filament (even if at the end he didn't find tungsten!). He also mentioned that there are between 50,000 and 200,000 known inorganic compounds, and even for those the full set of elastic constants is know for only 200 compounds; similarly, the critical temperature for superconductivity (probably one of the must studied properties) is know for about 1000 materials [MgB<sub>2</sub> anyone...?], and dielectric constants are known only for 3-400 materials.

Some of the challenges mentioned for materials design efforts were those of structure prediction, quality of databases (junk in/junk out), accuracy of ab-initio methods across large chemical spaces, and the need to deal with data obtained from different sources.

The first example discussed was on mixing data from different functionals - e.g. while GGA

for metals/covalent systems is 90-97% correct in finding the correct ground state (Curtarolo Calphad 2005) transition-metal oxides are much more challenging (e.g. using the case of iron phosphate, it was noted that in the ternary diagram along the the Fe-P axis the system is mostly metallic/covalent (hence requiring GGA), while the other axes require GGA+U, and these data cannot be used together). So the solution suggested was to use different functionals in different regions (GGA for metals, GGA+U for oxides) - these regions need then to be connected through (experimental) reference reactions, so e.g. an elemental metal oxidation becomes the reference reaction used to connect the two regions. Thanks to this calibration the materials project now has phase diagrams for more than 28,300 systems, and reaction energies for more than 35,000 reactions. Another example was from the dissolution of solids in water - where the solid world is described with GGA/GGA+U, and for aqueous solutions experimental free energies are used (K. Persson et al, PRB 85 235438 (2012)). The reference reaction takes the elements of simple compounds and uses experimental solvation energies. This allowed to calculate Pourbaix diagrams (essentially phase stability as a function of pH and applied electrochemical potentials) with great accuracy.

Last, the discussion moved on to learning from the data, with new materials discovered as battery cathodes. This was made possible by data mining on voltages (identifying vanadium as promising, thanks to the possibility of double-electron exchanges) and on safety (in a Li-ion battery, the cathode is an oxidant, and the electrolyte is the fuel), with extensive data mining on ion substitutions (Hautier et al, Inorg, Chem. 50, 658 (2011)). Not only stable phases could be identified, but also metastable phases - e.g. DFT confirmed that no Li-containing carbonophosphates exist. So, alternatives were identified where other ions are used instead of Li, such as sodium in Na-containing carbonophosphate could be made; these could then be transformed into metastable Li-containing materials via ion exchange.

This led to the last topic, and the introduction of the Materials Project with the goal to make materials data widely available to the entire community. In particular, a couple of projects mentioned, of relevance to the Psi-k computational community, are that of a Materials API, that is an open platform to access materials data through a REST interface, and the creation of a well documented pymatgen library to perform materials analysis.

## 2 Volker Heine Young Investigator Award

This was the second edition for the Volker Heine Young Investigator Symposium and Award (the inaugural one having taken place at the Berlin Psi-k 2010 meeting, with the award to Christoph Freysoldt). This time it was hosted at the DPG meeting, and Risto Nieminen, our Psi-k Chair, was in charge of the session and of the selection committee. The five finalists highlighted below presented their work on Tuesday afternoon, and that same evening a Psi-k get together was held, with more than 300 Psik-ers in attendance. Michele Ceriotti was announced as the awardee; the committee commented on the outstanding quality of all contributions, and gave their congratulations to all.

**Xavier Andrade (Harvard University):** *A computational perspective for the development of electronic excited-state calculations.*

Xavier presented three topics from his recent research, going from fundamentals to algorithms to computational applications. In the first case he described a simple but effective approach (Phys. Rev. Lett. 107, 183002 (2011)) to approximate the exchange and correlation (XC) term of density-functional theory. The XC potential is considered as an electrostatic potential, and generated thus by a fictitious XC density (following an earlier suggestion of Görling), that is both well defined and for which the asymptotic-behavior conditions are clear (normalization and localization). A simple approximation to localization was suggested, setting it to zero when the local value of electronic density is below a certain threshold, and adding a rescaling factor. Since the correction procedure gives the value of the XC derivative discontinuity, it can directly predict the fundamental gap as a ground-state property, and it was shown to give a very good description of finite-size systems. The second part of the talk discussed the use of compressed sensing in electronic-structure calculations. Currently compressed sensing is the state-of-the-art for image reconstruction, and it is based on sparsity (i.e. the signal is, in a basis set, described with coefficients that are mostly zero) (PNAS 109 13928 (2012)). Last, implementation of GPU support in electronic-structure calculations, and in particular in Octopus, was presented, showing a GPU speed up of 5-6 times on large fullerene molecules and biomolecules, with ongoing investigations on full light-harvesting complexes (see also Psi-k Highlight 110).

**Michele Ceriotti (University of Oxford):** *Nuclear quantum effects in first-principles molecular dynamics with colored-noise thermostats.*

Michele stressed the importance of nuclear quantum effects (NQEs) in molecular dynamics simulations - given that room temperature is comparable to  $200 \text{ cm}^{-1}$ , any system that has vibrations much higher than that will behave differently if the nuclei are treated classically or quantum-mechanically (e.g. the specific heat of “classical” water would be 50% larger than it is in reality, and its pH would be 8.5). While NQEs can be addressed with path-integral techniques, these simulations are extremely expensive. An intriguing alternative developed from an analysis of Langevin dynamics (obtained adding to Newtonian dynamics both a viscous friction and white-noise forces). Langevin dynamics is typically used for constant-temperature molecular dynamics, but the suggestion was to extend it with a “colored” noise term, with a memory kernel. This allows for the introduction of a frequency-dependent thermalization - exactly what is needed for a quantum oscillator, since a quantum oscillator at temperature  $T$  behaves like a classical oscillator at a renormalized temperature that is frequency dependent (Phys. Rev. Lett. 102, 020601 (2009), 103, 030603 (2009), 109, 100604 (2012)). Proton momentum distribution in lithium imide, competing quantum effects in water (that actually make the difference in the freezing points of normal and heavy water much more similar than they should) and H-bond fluctuations for hydrogen bonding in water were used as examples. The talk concluded with an overview of other techniques recently introduced to deal with configurational complexity, namely sketch maps (PNAS 108, 13023 (2011), 109 5196 (2012)).

**Nicholas DM Hine (University of Cambridge):** *Semiconductor nanocrystal simulations with linear-scaling PAW DFT.*

In the first part of his talk Nicholas gave an introduction to linear-scaling DFT and the ONETEP code (of which he is one of the main developers) and stressed how system sizes affordable for DFT

simulations, and of nanostructures used in electronics, are going to intersect (from below and above, respectively) in just a few years. Nicholas was instrumental in implementing in Onetep PAW with density matrices, and the calculation of unoccupied states, allowing for accurate simulations of very large scale systems containing “difficult” elements (e.g. d- and f-) and their optical properties - recent applications include pressure-induced phase transformations in nanomaterials, light-harvesting in bacterial complexes, and nanomaterials for photovoltaic applications. The complexity of correlated-electron materials was tackled by implementing both a linear-scaling DFT + Hubbard U approach, and combining linear-scaling DFT with DMFT site-corrections. The second part of the talk focused on a case study of Fermi-level pinning in finite-size semiconducting nanorods, studied using realistic large-scale nanostructures. This allowed to show that even if surface-counting arguments would point to huge changes in surface charges depending on termination, the electronic charge that re-organizes itself largely screens out all these ionic surface charges, pinning the Fermi level. On the other hand, polarization is greatly affected by size, shape, and termination, with long thin nanorods requiring a greater surface charge density to maintain the same potential difference. The talk concluded with a discussion of HOMO-LUMO gaps in water and proteins.

**Cheol Hwan Park (Seoul National University):** *Intrinsic electrical resistivity and carrier dynamics in graphene.*

Cheol Hwan focused his talk on scattering mechanisms in graphene - depending on the energy range considered, these determine the intrinsic electrical resistivity of graphene (at low energies), or its spectroscopic properties (at high energies). Cheol Hwan first discussed electrical resistivity in real, ordinary metals, showing that at high temperature resistivity is linear in temperature, while at low temperature it becomes quintic (or quartic for 2D) in temperature (with a crossover around 20% of the Debye temperature), finally plateauing at low temperatures to a flat behaviour dominated by impurity scattering. This behavior is not displayed by graphene, that shows only a linear behaviour well below the Debye temperature (2800K), with no sign of a quartic behaviour, as seen e.g. in the experiments from 200K downwards by the Fuhrer group at U. of Maryland (Nature Nanotechnology (2008)), or the Kim group at Columbia U. (Phys. Rev. Lett. (2010)). As first pointed out by Das Sarma, this is due to the fact that at the low densities of graphene the Fermi surface is much smaller than the Brillouin zone, and only few acoustic phonons can scatter electrons. Using the Allen formalism (Phys. Rev. B 1978), and density-functional perturbation theory the phonon-limited resistivity was calculated, highlighting not only the role of transverse acoustic phonons (as opposed to longitudinal acoustic phonons) in determining the resistivity, but also of high-energy optical phonons, responsible for 30% of the total resistivity at room temperature. An effective model for the electron-phonon coupling was fit on the first-principles calculations and allowed for the inclusion of GW corrections for electron-phonon couplings and phonon frequencies, leading to excellent agreement with the experimental data by Kim on doped graphene. Last, the scattering rate of high-energy carriers in graphene was discussed, and in particular the momentum distribution curve in ARPES experiments, where it was shown that electron-electron interactions are necessary to describe correctly the experiments (Phys. Rev. Lett. (2007), (2009)).

**Tim Wehling (University of Bremen):** *Theory of nanomagnetic and graphene hybrid sys-*

*tems: adatoms and multiorbitals Kondo physics.*

Tim addressed the question of how large-scale, disordered graphene-based systems as well as strongly correlated nanosystems can be described in a realistic, material specific way. The topics of disordered graphene and magnetic nanosystems were discussed: It has been shown that first row elements can form strong chemical bonds with graphene (Phys. Rev. B 80, 085428 (2009)) and lead to impurity resonances which are specific to two-dimensional Dirac materials. These impurity states can cause very efficient electron scattering if they are sufficiently close to the Dirac point. Using density functional calculations it has been shown that this is indeed the case for various organic groups as well as hydrogen atoms adsorbed to graphene (Phys. Rev. Lett. 105, 056802 (2010)). These impurities can well explain experimentally measured dependencies of the conductivity in graphene samples on charge carrier concentrations assuming impurity concentrations as low as  $10^{-5}$ /atom. At higher impurity concentrations a competition of metallization by midgap states and Anderson localization due to electron scattering emerges which has been shown to control the dielectric properties of covalently functionalized graphene (Phys. Rev. Lett. 109, 156601 (2012)). Afterwards the electronic structure of Mn, Fe, Co, and Ni adatoms on the Ag (100) surface has been discussed. These systems feature strong electronic correlations and experimental photoemission spectra show a highly non-monotonous evolution of spectral weight near the Fermi edge (arXiv:1212.1654). Using multiorbital Anderson impurity models which were derived from DFT calculations this effect has been explained. It has been shown that the amount of charge fluctuations and, thus, the weight of quasiparticle peaks at the Fermi level varies non-monotonously through this 3d series of adatoms due to a distinct occupancy dependence of effective charging energies. The talk concluded that first-principles theory and quantum lattice models can be usefully combined to address the electronic structure of large disordered as well as complex strongly correlated systems in a material specific way. *(thanks to Tim for helping out with the summary)*

### **3 The European Theoretical Spectroscopy Facility at the DPG**

The European Theoretical Spectroscopy Facility (ETSF; [www.etsf.org](http://www.etsf.org)) is a knowledge center for theoretical spectroscopy. Over the years, the ETSF has endorsed and supported several focus sessions on electronic structure theory at the DPG March Meeting. For the ETSF, the March Meeting has now become the second most important conference after the ETSF annual meeting. Almost all ETSF member groups are present at the DPG conference and use to present ETSF research to the wider community and discuss ETSF related activities. Especially for young researchers this is a great opportunity to present their work to an international audience and to meet other young researchers.

This year the ETSF scientist Claudia Draxl presented her work on the electronic structure and the excitation spectrum of hybrid materials in the invited symposium of the Frontiers of Electronic Structure Theory symposium. This symposium also attracted many ETSF scientists to attend the DPG March Meeting. They reported on recent advances in density functional and density matrix functional theory. Both improved algorithms as well as improved functionals were being discussed. Particularly exciting for the ETSF was work on new density functionals

for excited states. We also heard about new many-body inspired density functionals and Green's function based total energy approaches. The random-phase approximation continued its popularity rise that began at previous DPG meetings. New work on the convergence of Green's function based methods was followed by an assessment of the *GW* approach for quasiparticle excitations and the solution of the Bethe-Salpeter equation (BSE) for optical spectra. These methods are now widely applied to a variety of systems ranging from (organic) molecules to complex oxides. First beyond *GW* schemes were presented together with dynamical mean field calculations for strongly correlated systems. Complementing BSE for optical spectra, we saw the application and further development of time dependent density-functional theory. Of special interest to the ETSF were the talks on spin and magnetic excitations, an area that does not yet feature prominently in the network. Last but not least, several talks discussed the effects of electron-phonon coupling – another frontier for theoretical spectroscopy. A highlight was also the talk of Xavier Andrade – a former ETSF PhD student – who was one of the five contestants for the Volker Heine Prize. *(contributed by Patrick Rinke, FHI)*

## 4 A bit of everything else...

**Olle Eriksson (Department of Physics and Astronomy, Uppsala University, Sweden):**  
*Computational materials science applied to magnetism of bulk and nano-scale materials.*

Olle reviewed in his talk [this was one of the plenary talks of the DPG meeting, and the only computational one] three topics: the description of magneto crystalline anisotropy, the description of strongly correlated electrons, and magnetization dynamics.

Magneto-crystalline anisotropy is of great importance in order to increase the recording density in hard disk drives. A magnetic anisotropic material develops a spontaneous orientation of its magnetic moment, even without the presence of an external magnetic field, therefore allowing persistency in the stored data. The effect can be simulated by means of density functional theory, and he shows the test case of FeCo alloys [Phys. Rev. Lett. 93, 27203 (2004)]. He explores a phase space constituting of the composition of the binary compound, and an applied compression that induces a tetragonal distortion. Efficient hard disk can be obtained by having a large magnetic anisotropy energy (MAE) and a large saturation magnetic moment. The two properties can be optimized for compositions of about 50% Fe and Co and for a tetragonal distortion of 20%. Experimental data have later verified the DFT predictions [Phys. Rev. B 80, 64415 (2009)], confirming the quality DFT calculations.

In the second part of his talk, he introduced the use Dynamical Mean-Field Theory (DMFT), a method to deal with the electronic structure of strongly correlated materials. In these scenarios, the picture of independent electrons of standard DFT breaks down and the system is not well described. DMFT maps the many-body Hubbard model into an Anderson impurity model, in such a way that is exact in the limit of infinite nearest neighbors to the impurity. As a consequence of the presence of a Hubbard correction, electrons can become strongly localized, grasping the correct physics of strongly correlated systems. An implementation of DMFT has been developed on top of a full-potential linear muffin-tin orbital approach [Comp. Mat. Sci.

55, 295 (2012)]. As an example, an application on the electronic structure of an intermediate-valent materials like  $\text{YbInCu}_4$  [Phys. Rev. B 79, 165104 (2009)] was shown. In this system, the presence of strongly correlated f-electrons make simple DFT approximations like the LDA or LDA+U, the static limit of the DMFT, fail in the description of the partial density of states. Instead DMFT allows to correctly reproduce the experimental spectrum. Analogously for Mn doped GaAs, the presence of the Mn dopant is described only addressing the problem of strong correlations.

As a third topic to overview, he addressed the problem of magnetism dynamics. The time- and length-scale of the phenomenon varies from the nano to the macroscopic level. Accurate techniques like time-dependent density functional theory can be very accurate, but are too expensive to be carried on to scales larger than the nanometer. The atomistic approach that he chose instead allows the description of magnetism dynamics for dimensions that can even reach 100 microns. The magnetic moments of each atom are discretized and by means of the Landau-Lifshitz-Gilbert equations, the time evolution at finite temperatures of the system can be simulated, with parameters fitted on ab-initio data. The model is applied to the case of Co deposited on the Cu(001) surface, showing how spin wave modes are suppressed, confirming and explaining the experimental observations [Phys. Rev. Lett. 107, 37202 (2011)]. (*contributed by Andrea Cepellotti, EPFL*)

**Andre Geim (School of Physics and Astronomy and Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, UK):** *Beyond Graphene: Electronic Properties of Van der Waals Heterostructures.*

Committed to 2D, but not just to graphene. In this plenary talk, the 2010 Nobel prize winner Andre Geim discussed the challenges in many-body physics and materials design brought about by the rise of graphene and the extension of graphene layering scotch-tape technology to the production of multi-layered hybrid 2D structures. The individual atomic planes composing these structures range from graphene to Boron Nitride, to Silicon Dioxide, to Molybdenum Disulfide, to Tungsten Disulfide and Niobium Diselenide. Although the scotch-tape procedure leaves the atomic planes covered with sparse polymer waste, the multi-layered hybrid graphene structures appear to be of remarkably high quality. This happens since polymer impurities cluster in bubbles between the layers, leaving a large surface of the heterostructure perfectly clean. The clustering is peculiar result of the van-der-Waals inter-layer binding force. The above-mentioned 2D materials are all, apart from doped graphene, insulating and are therefore useful both as a substrate for supporting graphene layers during electronic structure measurements, and as a building block of graphene-based transistors and other circuitry elements. Among these, the graphene-BN transistor is mentioned, in comparison with the graphene- $\text{WS}_2$  or graphene- $\text{MoS}_2$  vertical layered transistors [1]. The more or less sizable lattice mismatch between graphene and the other atomically thin crystals is a feature which can be exploited to change the in-plane spectrum of stacked heterostructures. The so-called Moiré lattice patterns caused by this mismatch can be tuned changing the angular orientation of graphene layers on BN or  $\text{SiO}_2$ . The presence of Moiré patterns causes the appearance of a fractally complex set of supplementary Dirac points, whose location in phase space can be investigated by means of Quantum Hall measurements [2]. In this talk Andre Geim discussed also another exciting physical effect which

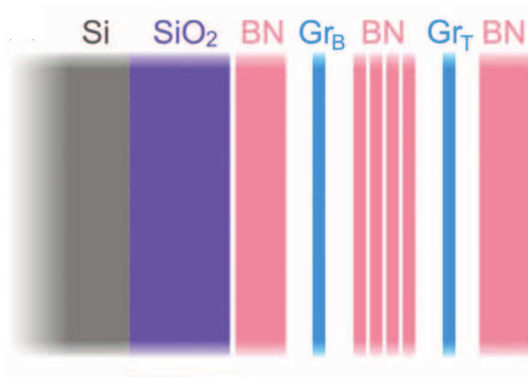


Figure 1: Schematic representation of a prototype graphene-BN field-effect transistor, from Ref. [1].

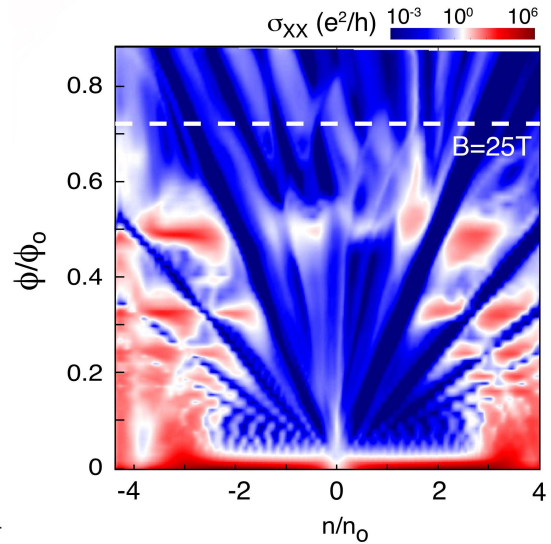


Figure 2: Longitudinal Hall conductivity as a function of graphene-layer doping and magnetic field flux, from Ref. [2].

can be investigated with great precision in this type of heterostructures, which is Coulomb drag [3]. Two graphene layers isolated by a BN layer in-between build a perfect example of strongly-coupled bilayer (for which the inter-layer distance is smaller than the Fermi wavelength). In such a system, cross-layer electron-electron interaction plays a crucial role in determining electronic structure and transport properties, so that a current flow or a charge fluctuation in the above layer can induce charge modulations and influence the resistivity in the other one. To summarize this talk in a few lines: graphene has undoubtedly proven itself to be promising and challenging for experimentalists, many-body physicists and electronic engineers, but professor Geim succeeds in making it appear very nice also to materials scientists, presenting for their joy a brand new box of LEGO which they can use for their games. *(contributed by Giovanni Borghi, EPFL)*

[1] Georgiou *et al.*, Nature Nanotechnology 8, 100 (2013)

[2] Dean *et al.*, arXiv:1212.4783

[3] Gorbachev *et al.*, Nature Physics 8, 896 (2012)

**Joerg Behler (Ruhr-Universitaet, Bochum):** *Interatomic potentials for molecules, solids, and surfaces based on interatomic potentials.*

Joerg described the challenges in accurate descriptions of complex systems - some examples being solid-liquid interfaces, catalysts, active sites in enzymes, metal-organic frameworks. Of course, for every system in principle there exists a functional that gives the energy of the system as a function of all the nuclear coordinates - its just that it is extremely challenging to approximate it with an analytic function. Some of the requirements of non-quantum mechanical, classical approaches is that the potential functional should have high accuracy, be systematically improvable, of general functional form, should be reactive (breaking and making bonds), high-dimensional, and should be easy to obtain, transferable, and efficient. Joerg described neural networks as high-quality interpolators of quantum mechanical potential energy surfaces. What



are neural networks? Well, they were described as Massively parallel interconnected networks of simple, adaptive elements and their hierarchical organizations (T. Kohonen, *Neural Networks*, 1, 3 (1998)). Artificial neural networks have hidden layers between the input (structure) and output (energy) layers - each inner layer node being a linear combination of the input variables, shifted, and with a functional form (activation function) applied to it. This is iterated across hidden layers and towards the output (the activation function for the output is typically linear). A review is given e.g. in Behler *PCCP* 13, 17930 (2011). While extremely flexible, neural networks struggle with high dimensionality, and cannot deal with atom permutations. A solution to this (Behler and Parrinello, *PRL* 98 146401 (2007) has been suggested where the total energy is represented as a sum of atomic energies - so a neural network potential would have a first inner layer (symmetry functions applied to atomic positions), second layer of atomic subnets, and third later giving atomic energies. Long-range terms are also dealt with neural networks, with atomic charges instead of atomic energies as third layer. Metadynamics on the 6 collective variables of a unit cell allowed to generate and span many phases of silicon, and a neural network for silicon was developed that represents essentially perfectly e.g. the energy-volume curve for each of the 9 lowest-energy phases (Behler et al, *PRL* 100, 2008). A second case study discussed was of copper particles on zinc oxide - with first a fit of separate potentials for Cu and ZnO, before obtaining a potential for the combined, ternary system. The potential obtained was of the same quality of the elemental cases, and early Monte Carlo results on cluster growth were shown. The last system discussed was water, with early cluster calculations presented, but already able to reproduce at least 5 phases of ice. In addition to these extensive successes (that can be summarized by the typical accuracy of 5 meV/atom or better in reproducing very complex potential energy surfaces), Joerg reminded some of the challenges or drawbacks: neural networks require large training sets, are restricted to 3-4 chemical elements, and their non-physical functional forms give limited extrapolation capabilities. (*contributed by Nicola Marzari, EPFL*)

**Hari Manoharan (Department of Physics, Stanford University):** *Designer Dirac Fermions, Topological Phases, and Gauge Fields in Molecular Graphene.*

At the heart of the very peculiar properties of graphene lies its honeycomb lattice of carbon atoms. Then it should be possible to mimic graphene's behavior in an artificial system, provided that electrons are constrained to move on a honeycomb lattice. This is the idea behind the original work by the group of Hari Manoharan at Stanford University, presented on Tuesday during the focus session on correlation in topological bands (TT18). The breakthrough to achieve their goal has been to use the tip of a scanning tunneling microscope (STM) to grab carbon monoxide (CO) molecules and move them on top of a copper surface. These molecules act on the surface electrons of copper as a local repulsive potential, which can be adopted as the building block to induce a periodic potential. Apparently, this is very different from graphene, where the building blocks are carbon ions that provide an attractive potential for electrons. Nonetheless, a triangular lattice of CO molecules would repel electrons, forcing them in the interstitial area with a honeycomb shape (see Fig. 3). Manoharan's group exploited such a duality between triangular and honeycomb lattices and managed to position CO molecules in a perfect triangular pattern. During his talk, Manoharan has shown maps of the local density of states (LDOS) on the copper surface, measured using the same STM tip. Electrons are indeed constrained in a honeycomb

shape, with maximum probability on the hexagonal lattice sites. By looking at the LDOS as a function of energy, clear signatures of graphene-like electronic properties appear: a distinct V shape close to the Dirac point and two van Hove singularities at the two sides of the Dirac point. Furthermore, the experimental results are in very good agreement with second-nearest-neighbors tight-binding theory. By fitting to the theoretical predictions, it is possible to extract information such as the Fermi velocity, which turned out to be around  $\sim 3 \times 10^5$  m/s (a factor of 3 smaller than in real graphene). Owing to the presence of these graphene-like spectral features, the authors dubbed this novel system molecular graphene. Although displaying many similarities with real graphene, this molecular version has an important advantage: tunability. Indeed CO molecules can be displaced at will, opening the possibility to design the underlying hamiltonian and even test theoretical predictions that have never been investigated in graphene. For instance, by increasing the lattice parameter the carrier density increases and can be even switched from p- to n-type. In this way, Manoharan and coworkers have been able to realize pnp junctions with atomically sharp interfaces. In addition, by tuning the distance between CO molecules, it is possible to modify the hopping energy between neighboring sites. This paves the way for very interesting scenarios. For instance, the authors have distorted the perfect triangular lattice of CO molecules in order to simulate a strained graphene sample according to the theoretical prescription by Guinea, Katsnelson, and Geim [Nat. Phys. 6, 30 (2010)]. This distortion gives rise to a uniform pseudo-magnetic field and Manoharan and his group have observed clear signatures of the emergence of Landau levels. Many other interesting phenomena have been investigated and new challenges for Manoharan and his group are now associated with the simulation of gauge fields and topological models in these artificial molecular lattices. *(contributed by Marco Gibertini, EPFL)*

**Paul Koenraad (Eindhoven University of Technology): *Single Impurities in Semiconductors Studied by STM***

In this invited talk, Prof. Koenraad introduced the emerging field of solotronics, where a solitary impurity can be exploited to examine fundamental physics or used as a functionalization agent to tap into novel optoelectronic device potential of standard semiconductors, by using recent developments in the area of scanning tunneling microscopy (STM), specifically, cross sectional (X-) STM.

Often in STM experiments, the bending of the band structure at the surface due to the electric field applied to the tip is considered as an unwanted feature that adds noise to the imaging results. X-STM is a technique that exactly utilizes this faulty nature of the experiments to examine and manipulate single impurities on the semiconductor surface. In this talk, Prof. Koenraad demonstrated the new possibilities in this approach through an example, one of the most popular semiconductor-dopant pairs: Silicon impurity on GaAs surface.

In this example, X-STM is performed on the cleaved edge of GaAs neutral (110) surface. The local tip induced band bending causes the impurity levels to approach the bent valance band maximum of the surface so that electrons at the impurity level can be freed, leaving behind an ionized impurity. Using different voltage values for the tip, Silicon impurities at different layers below the surface could be ionized. Furthermore, different direction in ionization can be obtained by changing the sign of the applied voltage. Using the STM images obtained, one

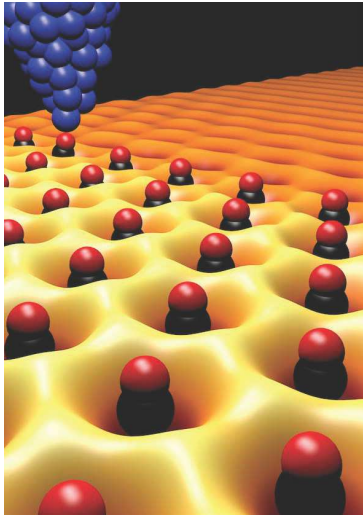


Figure 3: Carbon monoxide molecules (black/red) can be moved and positioned at will on top of a copper surface using a scanning tunneling microscope (dark blue). Such molecules produce a repulsive potential that repels surface electrons. When the pattern of carbon monoxide molecules is triangular, electrons are constrained to reside in the interstitial regions with honeycomb shape. Thus, electrons in such an artificial lattice behave like in graphene, but with a much higher degree of tunability. Figure from <https://news.slac.stanford.edu/features/molecular-graphene-heralds-new-era-designer-electrons>.

can then determine the binding energy for single impurities and even inter-impurity interaction, mainly, screen coulomb interaction between charged pairs.

By examining the binding energies of silicon at different layers below the surface, this example reveals a counter intuitive relationship between impurity depth vs binding energy: the deeper is the impurity, the more loosely it is bound! Prof Koenraad posed this issue as an open question to the theoreticians in the audience, which emphasized the importance of gatherings such as DPG, where different research groups can communicate the open questions in respective fields, kickstarting a collaborative effort in solving them.

Prof Koenraad continued his talk with a device-oriented feature of Si impurities on GaAs surface. In a 2011 study they have shown that Si impurities demonstrate random switching of the charge state, between +1 and -1, at a distinct STM tip voltage about 1V, where higher voltages result in a bright STM signal, characteristic of positively charged Si, and lower voltages give a dark signal that indicate a negatively charged impurity. Based on a statistical analysis of the XSTM images of the same impurity site over an extended period of time and at different temperature, Koenraad group was able to model this switching with a two-level model and Boltzmann distribution, and deduce the energy difference between these configurations,  $12 \pm 5$  meV, which is not in agreement with the theoretical suggestion of about 0.8 eV. This was another issue open to further investigation. Nevertheless, the Koenraad group was able to envision a memory device, using different applied voltage and photoexcitation of the impurity level, in combination with the switching mechanism of the impurity.

Prof Koenraad concluded his talk by sharing a glimpse of his research groups future plans to deepen their understanding of the switching dynamics and to utilize its full potential in

applications. (*contributed by Emine Kucukbenli, EPFL*)

**Chris Van de Walle (Materials Department, University of California, Santa Barbara, USA):** *Complex oxides for next-generation electronics.*

Chris Van de Walle started summarizing the well-known formation of a 2D electron gas (2DEG) layer at the interface between  $\text{LaAlO}_3$  (LAO) and  $\text{SrTiO}_3$  (STO). He discussed the microscopic origin of this effect, emphasizing also the difference with the “standard” 2DEG that forms at e.g.  $\text{AlGaN}/\text{GaN}$  interfaces (where the structure has to be doped in order to show a 2DEG), while in the case of LAO/STO the interface charge has an intrinsic origin.

He then pointed out that there is an apparent discrepancy with experiments. A simple calculation in which we assign 0.5 electrons per unit cell tells us that the interface can in principle sustain a charge density of  $3 \cdot 10^{14} \text{ cm}^{-2}$  (a quite large value for a 2DEG electron gas), but experiments observe instead a surface charge density that is about one order of magnitude smaller.

Where does this discrepancy arise from? Van de Walle showed how the ideal charge of  $3 \cdot 10^{14} \text{ cm}^{-2}$  arises only if the LAO layer is sandwiched between two identical STO layers, forming therefore a symmetrical structure with two identical LAO/STO interfaces. In experiments, instead, thin LAO layers are grown on top of a STO substrate, but one cannot coherently regrow a thick STO layer on top of LAO. As a consequence, due to the asymmetrical nature of the structure, a strong dipole and thus an electrostatic potential build up, draining electrons away from the 2DEG.

To prove and quantify this effect, in Ref. [1] Van de Walle and coworkers have performed Schrödinger-Poisson simulations, where parameters (as the valence and conduction band offsets, and the effective masses) have been obtained from ab-initio DFT calculations with a HSE hybrid functional, which gives a good description for both materials. Using this model, they showed that the measured charge density can be explained if the two interfaces are different, as it happens in the experiment. Moreover, he also discussed how it is possible to prevent electron transfer to the surface by passivating it with hydrogen, or depositing a metal layer on top of LAO, as discussed in e.g. Ref. [2].

Are there materials in which electrons are not transferred to the surface, even without the need of passivating the second interface? Van de Walle showed that in the case of a STO/ $\text{GdTiO}_3$  system ( $\text{GdTiO}_3$  is a Mott insulator), there is no charge buildup and the full expected charge density is obtained, because STO can be grown with high quality on top of  $\text{GdTiO}_3$  and therefore the two interfaces are symmetric. He also pointed out that in the specific case of GTO, even without a STO regrowth the system maintains the full 2DEG density at the STO/ $\text{GdTiO}_3$  interface. Indeed, the STO/ $\text{GdTiO}_3$  interface has been realized experimentally [3] and the expected full charge density of  $3 \cdot 10^{14} \text{ cm}^{-2}$  has been measured. (*contributed by Giovanni Pizzi, EPFL*)

[1] Janotti et al., Phys. Rev. B 86, 241108(R) (2012)

[2] Arras et al., Phys. Rev. B 85, 125404 (2012)

[3] Moetakef et al., APL 99, 232116(2011)

**Fritz Körmann (Max-Planck-Institut für Eisenforschung, Düsseldorf):** *First-principles*

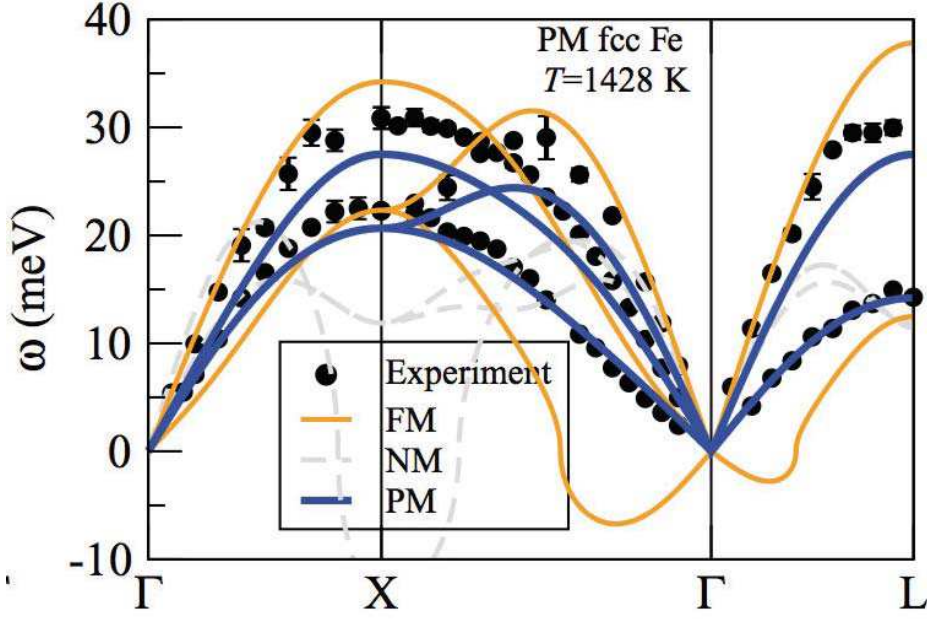


Figure 4: Phonon spectra for paramagnetic fcc iron (blue line) in comparison with experimental data. FM (yellow line) and NM (grey line) results are also included. Figure from Phys. Rev. B 85, 125104 (2012).

#### *thermodynamics of paramagnetic iron*

In this talk, directly related to Neugebauer’s invited talk on fully ab-initio determination of the free energies, the author describes the approach they have introduced to account explicitly for the paramagnetic character of the high temperature  $\gamma$ -phase of iron. He shows how this approach is able to give a correct description of the softening of the phonon dispersion and of the characteristic antiinvar effects.

A spin-average over different quasi-random spin configurations calculated via ab-initio is used to effectively describe the spin fluctuations in the paramagnetic system. Due to their different time-scales, spin and vibrational degrees of freedom are adiabatically decoupled to build a magnetic partition function from which it is possible to get the “true paramagnetic forces acting on the frozen nuclei as well as the associated free energy of the system.

As a first application it is discussed how, contrary to what happen in the NM/FM limits, the corresponding dynamical matrix displays real eigenvalues at  $\sim 1400$  K (see Fig. 4). The mechanical stabilization of the fcc phase in the ab-initio framework is a first good indicator to highlight the relevance of this method.

The thermal expansion coefficient of the  $\gamma$ -phase is also calculated in the paramagnetic QH approximation. The extra magnetic contributions affect the temperature dependence of the expansion coefficient mainly at low temperature where a peak appears. At high temperatures, in the window of thermodynamic stability of the fcc phase, the characteristic antiinvar effects are recovered. The author relates this effect to an “anomalous” decrease displayed by the Gruneisen parameter, emphasizing again the differences with respect to other metallic systems like Cu, Pd, Pt (see Ref. [1]) where vibrational + electronic contributions are dominant and where such a

strong frequency dependence is not observed. (*contributed by Daniele Dragoni, EPFL*)

[1] B. Graboswki et. al., Phys. Rev. B 76, 024309 (2007)

**Roser Valentí (Institut für Theoretische Physik, Goethe Universität Frankfurt, Frankfurt, Germany):** *Correlation Effects in Organic Superconductors, Focused Session: Dynamical Mean-Field Approach to Correlated Electron Materials.*

Organic charge-transfer salts are fascinating correlated-electron materials exhibiting rich phase diagrams, including both coherent and “bad” metallic behaviour, Mott insulation, magnetic ordering, and superconductivity, which may be explored by chemical doping or relatively moderate pressures. Prof. R. Valentí of Goethe Universität Frankfurt gave a very engaging Topical Talk on this class of materials, in which she described their recent investigation by her group using density-functional theory + dynamical mean-field theory (DFT+DMFT), within the full potential linearized augmented plane wave formalism. These studies are all the more interesting for being, to date, among the spatially largest realistic applications of the DFT+DMFT method.

The layered salt  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, studied in Refs. [1,2] and discussed in detail in this talk, crystallises such that the BEDT-TTF molecules form dimers at the vertices of well-separated triangular lattices. A single hole resides on each dimer, in analogy to the Hubbard model at half-filling, necessitating the refinement of the DFT(LDA) description using a method such as DMFT in order to accurately describe the degenerate, half-filled bands crossing the Fermi level, and their satellite Hubbard bands.

An important outcome of this talk was that first-principles based evidence was demonstrated for the origin of the two peaks clearly seen in the optical spectra of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, computed by decomposing the DFT+DMFT optical conductivity into its contributions from intra-band (due to the formation of Hubbard bands, and scaling with  $U$ ) and inter-band (due to charge-transfer within a dimer) transitions. The strong suppression of the Drude peak, observed in experiment, was very nicely reconciled with theory in terms of the strong transfer of spectral weight from the bands at the Fermi level to the upper and lower Hubbard bands. The effects of varying temperature on observed properties were also discussed in detail, via the temperature-dependence on structural properties and the consequent variation of the Coulomb repulsion to bandwidth ratio.

In the final section of this very interesting and well-attended Topical Talk, Prof. Valentí described DFT+DMFT calculations carried out on multiply potassium doped picene crystals, K<sub>x</sub>picene, which have attracted attention due to a recent experimental report of superconductivity. Picene in its non-doped form is a wide-bandgap semiconductor, but states close to the Fermi level may be introduced by intercalation with potassium clusters of between one and three atoms. In this latter section of the talk, and in Ref. [3], it was demonstrated that DFT+DMFT locates a Mott insulating solution at integer doping, in agreement with photoemission spectra measured as part of the same study, and does not support superconductivity. Possible resolutions of this discrepancy between theory and previous experiment were offered, including superconductivity at grain boundaries or the formation of an alternative picene crystal structure under pressure.

In conclusion, this talk offered a very promising picture of the current state of the art of ap-

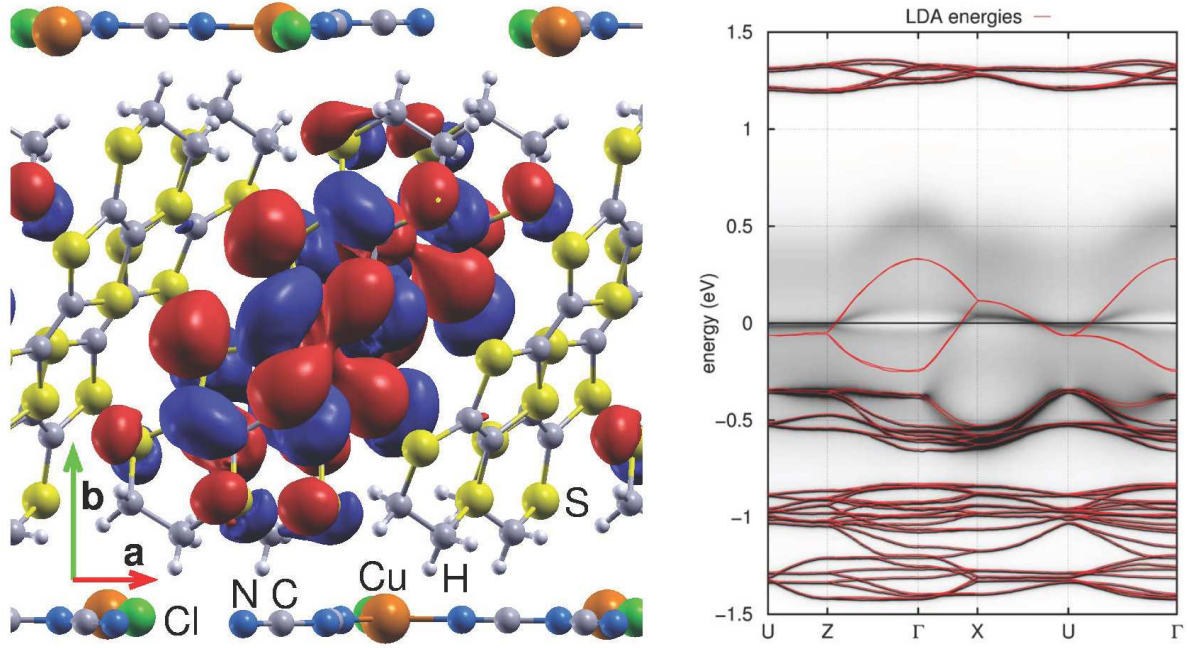


Figure 5: From Ref. [2] (left) The structure of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, shown with a Wannier function isosurface corresponding to the LDA bands crossing the Fermi level, and (right) the momentum-resolved spectral function for the same material, computed at the LDA (red lines) and LDA+DMFT@ $U = 0.6$  eV (grey contours) level of theory. The mass enhancement and suppression of the conductive bands and the formation of Hubbard quasiparticle satellites within LDA+DMFT is evident.

plication of DFT+DMFT and related methods to crystalline materials of relatively high spatial complexity and system size, and the practical applicability of such many-body techniques for low-energy states in general. (*contributed by David D. O'Regan, EPFL*)

- [1] J. Ferber, K. Foyevtsova, H.O. Jeschke, and R. Valentí, arXiv:1209.4466 (2012).
- [2] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. 103, 067004 (2009).
- [3] A. Ruff, M. Sing, R. Claessen, H. Lee, M. Tomić, H. O. Jeschke, and Roser Valentí, arXiv:1210.4065 (2012).

**Stefan Kurth (Univ. of the Basque Country UPV/EHU, San Sebastian, Spain and IKERBASQUE, Basque Foundation for Science, Bilbao, Spain):** *Lattice density functional theory at finite temperature with strongly density-dependent exchange-correlation potentials.*

The derivative discontinuity of the exchange-correlation energy as a functional of density is a crucial property of density functional theory (DFT), that allows to compute correctly the band gap in solids or the highest occupied molecular orbital and the lowest unoccupied molecular orbital energies of molecules. This property, however, is absent in the standard DFT with local and semi-local exchange and correlation functionals. In principle, with the lattice DFT method, the discontinuity of the exchange and correlation potentials with half-filling occupation

number can be guaranteed by some appropriate approximations for local Hartree and exchange-correlation potentials at the different lattice sites. However, due to convergence problems of the Kohn-Sham self-consistency cycle, the use of these functionals is mostly restricted to situations where the local density is away from the half-filling case. In this talk, Stefan has introduced a new way that has been published recently by him and his colleagues [1] to deal with this convergence problem as dealing with the local-approximations for the exchange-correlation potential which exhibit rapid variations as function of the density. In the first part of the talk, he has rephrased the search for the self-consistent Kohn-Sham potential in terms of finding the roots of a set of coupled nonlinear equations. Then, to find these solutions of the nonlinear equation, he suggested an iterative algorithm based on successive application of the bisection method in one dimension. The method has been applied for some modeled systems of electrons in a harmonic trap interacting via a Hubbard interaction. Moreover, based on the thermodynamic Bethe-ansatz solution of the uniform Hubbard model, Stefan has also proposed the newly designed local approximations for exchange correlation functionals. These functionals are dependent on temperature, and are parametrized to generalize the calculations of the lattice DFT at finite temperatures. Some results computed with these functionals for one-dimensional lattice model were also shown in the last part of the talk. (*contributed by Ngoc Linh Nguyen, EPFL*)

[1] Gao Xianlong, A-Hai Chen, I. V. Tokatly, and S. Kurth, PRB 86, 235139 (2012)

**Karsten Albe (TU Darmstadt):** *Challenges for first-principles based computation of properties of oxide materials.*

Multifunctional oxides are key materials for the development of new technologies because they exhibit a host of interesting properties such as ferroelectricity, piezoelectricity, pyroelectricity and they are also commonly used as ionic conductors. Karsten Albe gave a talk on the application of first-principles calculations to understand the properties of these materials. He pointed out the fact that interatomic potentials were not very accurate to model these ionically bonded oxides. However first-principles results may be used in combination with statistical averaging techniques to calculate macroscopically measurable values. He goes on to explain the application of this method in the specific case of transparent conductive oxides. Transparent conductive oxides (TCO) are one of the most important component materials in optoelectronic devices like thin film solar cells, organic light-emitting diodes and flat panel displays. Based on experimental observations, oxygen vacancies are thought to act as intrinsic donor defects thus explaining the large concentration of free electrons available in the system. However, LDA/GGA+U calculations show that these oxygen vacancies appear as deep color centers are hence unlikely to thermally provide the free electrons observed. As a result, a host of other models have been used to explain this phenomenon in these materials. To resolve the existing experiment-theory controversy, Karsten and his group investigated the validity of local DFT methods for calculating defect properties in TCOs, and calculated the formation energy of both the charged and neutral oxygen vacancies as a function of the Fermi energy using different functionals. The hybrid functionals show a charge transition closer to the conduction unlike the LDA/GGA+U. From their calculations they conclude that oxygen vacancies are capable of acting as shallow donors to account for the free electron concentration. In the last part of the talk, Karsten presented results on the diffusion of intrinsic charge carriers in Indium oxide. The first principle calculations were



performed using the nudged elastic band method and the activation energy for specific hopping processes was calculated. These activation energies were later used to calculate the mobility of these defects at different temperatures using a kinetic Monte Carlo method. (*contributed by Anand Chandrasekaran, EPFL*)

[1] Ágoston, Péter *et al.* “Intrinsic n-Type Behavior in Transparent Conducting Oxides: A Comparative Hybrid-Functional Study of In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and ZnO”, *Physical Review letters* 103, 245501 (2009).

[2] Ágoston, Péter, and Karsten Albe “Ab initio modeling of diffusion in indium oxide”, *Physical Review B* 81 195205 (2010).

**Vittoria Colizza (INSERM and Universite Pierre et Marie Curie, Paris, France) - ISI Foundation, Turin, Italy):** *Fighting infectious diseases in a complex world.*

During the twenty-nine different sections comprising hundreds of different talks, in DPG several prizes have been awarded to young scientists that in the last years gave significant contributions in their fields. One of them is the Young Scientist Award for Socio- and Econophysics that seeks to promote the work of young researchers and honors exceptional original contributions that use methods from physics to gain a better understanding of socio-economic problems.

This year the YSA has been given to Dr. Vittoria Colizza, a young Italian investigator working since several years on one of the most crucial social challenges: how to forecast of global epidemic spreading. After a short but somehow empathic presentation from the chairman, and the usual greetings to all the public and collaborators, Dr. Colizza starts an interesting overview on all her most recent achievements in the field, showing the audience how physics and social issues can really meet.

The focus of the talk was mainly about mathematical and computational models (MCMs) for real-time forecasting of epidemics diffusion on global scale. With other collaborators Dr. Colizza developed GLEAM, the Global Epidemic and Mobility model, a dynamical model that integrates high-resolution data on human demography and mobility in a metapopulation stochastic epidemic framework. Based on sophisticated approximations, the model relies anyway on a complex set of parameters that have to be fitted on some real case scenario, and here is where Dr. Colizza presents her work on H1N1.

The recent pandemics of H1N1 has been a unique opportunity to benchmark GLEAM and to understand if MCMs can become a real tool for public governance and governments. With this goal this Dr. Colizza and coworkers used the data on the pandemic invasion up to 18 June 2009, calibrating the GLEAM with a Monte Carlo Maximum Likelihood approach, forecasting the activity peak of the fall/ winter wave in the northern hemisphere and, for the first time, publishing the model results before the arrival of the peak, in September 2009.

Results presented are really impressive, showing the model's ability to forecast the epidemics spread both in the timing and in geographical diffusion. In fact, thanks to the data gathered from more than 50 countries about the 2009 H1N1 (a process that took more than three years) Dr. Colizza and coworkers could finally validate their work, with a great success. There is in fact a very significant correlation between the data and the prediction (Spearman coefficient 0.48,  $P = 0.0001$ ), with an error within 4 weeks for 95% of the countries.

Dr. Colizza's work demonstrates how critical MCMs can get in this field, offering robust predictions weeks ahead of an influenza peak, a buffer within key strategic decisions can be implemented by governments and public institutions. And even if lots of work is still needed to make this models complete, as Dr. Colizza pointed out, these techniques give some important new opportunities for physicist to test their skills on global challenges for humanity. (*contributed by Riccardo Sabatini, EPFL*)

[1] M. Tizzoni, P. Bajardi, C. Poletto, J. J. Ramasco, D. Balcan, B. Goncalves, N. Perra, V. Colizza, and A. Vespignani, *BMC Medicine* 10, 165 (2012).

[2] W. Van den Broeck, C. Gioannini, B. Goncalves, M. Quaggiotto, V. Colizza, and A. Vespignani, *BMC Infectious Diseases* 11, 37 (2011).