The Abdus Salam
International Centre
for Theoretical Physics

17th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

15 - 17 January 2015
Trieste - Italy
Cosponsor(s) CECAM, Consorzio per la Fisica di Trieste, Psi-k and SISSA

POSTER SESSION II

FRIDAY, 16 JANUARY 2015

In alphabetical order of presenting author (underlined)

Atomistic simulations of multicaloric effects in ferroelectrics

S. Lisenkov and I. Ponomareva
Department of Physics, University of South Florida, Tampa, FL 33620, USA

Structural defects in P3HT-polymer chains probed in the ballistic transport regime

A. Lücke1, E. Rauls1, F. Ortmann2, W. G. Schmidt1, and U. Gerstmann1
1. Department of physics, University of Paderborn
2. Institute for Materials Science, Dresden University of Technology

Substrate doping: A strategy for enhancing reactivity of gold nanocatalyst by tuning the sp-bands

Nisha Mammen1, Stefano de Gironcoli2, Shobhana Narasimhan1
1. Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064 India
2. SISSA, via Bonomea 265, 34136 Trieste, Italy

πAg nanoclusters: An ab-initio vibrational dynamics Study

Venu H. Mankad1, Sanjeev K. Gupta2, Prafulla K. Jha3
1. Central Institute of Plastic Engineering and Technology, Ahmedabad-382 445, India
2. Department of Physics, St. Xavier’s College, Navrangpura, Ahmedabad-380009, India
3. Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara-390002, India

Thermal properties of bismuth calculated from first principles

Maxime Markov1, Jelena Sjakste1 , Giorgia Fugallo1, Lorenzo Paulatto2, Francesco Mauri2, Michele Lazzeri2, Nathalie Vast1
1 Laboratoire des Solides Irradies, Ecole Polytechnique - CEA - DSM - IRAMIS - CNRS UMR 7642, 91128 Palaiseau cedex, France
2 IMPMC, Universite Pierre et Marie Curie, CNRS 4 place Jussieu, F-75005 Paris, France

The Mixed (L-Threoninato)(L-Aasparaginato)Copper(II) System - Conformational Analysis of an Isolated Complex

Marijana Marković1,2, Michael Ramek2, Jasmina Sabolović1
1. Institute for Medical Research and Occupational Health, Ksaverska cesta 2, P. O. Box 291, HR-10001 Zagreb, Croatia, mmarkov@imi.hr, jasmina.sabolovic@imi.hr
2. Institut für Physikalische und Theoretische Chemie, Technische Universität Graz (NAWI Graz), Stremayrgasse 9, A-8010 Graz, Austria, michael.ramek@tugraz.at

Ultra-fast transient absorption of monolayer MoS2 from first principles

Margherita Marsili1, Deborah Prezzi1, Davide Sangalli2, Andrea Marini2
1. CNR, Istituto di Nanoscienze S3 – Modena (Italy)
2. CNR, ISM – Montelibretti (Italy)

Projector Augmented-wave formulation of response to strain and electric field perturbation within the density-functional perturbation theory

Alexandre Martin1, Marc Torrent1, Razvan Carracas2
1. CEA, DAM, DIF, F-91297 Arpajon, France
2. ENS de Lyon, UCBL Lyon 1, Université de Lyon

Electronic and magnetic structures of semimagnetic semiconductors investigated by first principle, mean field and series expansions calculations

R. Masrour1,2
1Laboratory of Materials, Processes, Environment and Quality, Cady Ayyed University, National School of Applied Sciences, 63 46000, Safi, Morocco
2LMPHE (URAC 12), Faculty of Science, Mohammed V-Agdal University, Rabat, Morocco

Surface Adsorbates and Defects on the Subsurface Cation Vacancy Stabilized Surface of Magnetite (001)

Eamon McDermott1, Roland Bliem2, Gareth Parkinson2, Ulrike Diebold2, Peter Blaha1
1. Institute for Material Chemistry, TU Wien, Vienna, Austria
2. Institute of Applied Physics, TU Wien, Vienna, Austria

A multiscale computational method for fluid dynamics simulation: application of nanoscience to enhanced oil recovery process

Aline O. Pereira1, Lucas Stori de Lara1, Raphael S. Alvim1, and Caetano R. Miranda1
1. NanoPetro Research Group , Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, 09210-580, Brazil

Stable and Efficient Linear Scaling First-Principles Molecular Dynamics for 10,000+ atoms

Michiaki Arita1,2, David R. Bowler3,4,5 and Tsuyoshi Miyazaki1,2
1. Computational Materials Science Unit, National Institute for Materials Science (NIMS), Japan
2. Graduate School of Science and Technology, Tokyo University of Science, Japan
3. Department of Physics & Astronomy, University College London (UCL), UK
4. London Centre for Nanotechnology (LCN), UCL, UK
5. International Materials Nanoarchitectonics (MANA), NIMS, Japan

Ab Initio Simulation of Enhanced Phosphorus-based Nano-composite Materials

Glenn Moynihan1, David O'Regan2
1. CRANN Institute, Trinity College Dublin
2. School of Physics, Trinity College Dublin

An investigation of quantum transport properties in silicon nanotube

Ebrahim Nadimi1, S. Ahmad Etghani2,3
1. Electrical Engineering Department, KN Toosi University of Technology, Tehran
2. Electrical Engineering Department, KN Toosi University of Technology, Tehran
3. Electrical Engineering Department, University of Tehran (current affiliation)

Efficient optimization of local orbitals and eigenstate calculations in linear-scaling DFT code CONQUEST

Ayako Nakata1, David R. Bowler2, Y. Futamura3, T. Sakurai3 and Tsuyoshi Miyazaki1
1. National Institute for Materials Science (NIMS), Japan
2. Department of Physics & Astronomy, University College London (UCL), U. K.
3. Department of Computer Science, University of Tsukuba, Japan

Native defects and impurities in single-layer MoS2 and shallow level formation with dielectric environments

Ji-Young Noh1,2, Hanchul Kim1, Yong-Sung Kim2
1. Department of Physics, Sookmyung Women's University, Seoul, Korea 2. Korea Research Institute of Standards and Science, Daejeon, Korea

Quantum Confinement in Silicon Quantum-Slabs

NOURBAKHSH Zahra
Institute for Research in Fundamental Science 'IPM', Niavaran Square, 11369 Tehran, ISLAMIC REPUBLIC OF IRAN

First-Principles Calculation for Thermal Oxidation Process of SiC

Tomoya Ono1
1. Center for Computational Sciences

First Principle Simulation of Optical Spectra in Gold-based Alloys

Okan K. Orhan and David D. O'Regan
School of Physics, Trinity College Dublin, Ireland

Enhancement of superconductivity with low doping in two-dimensional multivalley semiconductors

Betül Pamuk1, Matteo Calandra1, Francesco Mauri1
1. IMPMC, UMR CNRS 7590, Sorbonne Universités - UPMC

Jastrow correlations for solids

Martin Panholzer1
1. Center for Surface and Nanoanalytics, Johannes Kepler University Linz

Efficient conformational sampling of complex adsorbates with Basin Hopping in curvilinear coordinates

Konstantin Krautgasser1, Chiara Panosetti1, Dennis Palagin2, Karsten Reuter1, and Reinhard J. Maurer3
1. Technische Universitaet Muenchen, Germany
2. University of Oxford, United Kingdom
3. Yale University, USA

Surface phase transition driven by deprotonation reaction

Andrea Floris1, Chiara Paris1, Lev Kantorovich1
1. Department of Physics, King's College London, Strand, London WC2R 2LS, UK

Exchange-correlation kernels in adiabatic-connection fluctuationdissipation DFT – the renormalized ALDA and other kernels from the electron gas

Christopher E. Patrick1 and Kristian S. Thygesen1
1. Centre for Atomic-Scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

First principle calculation of anharmonic effect on phonon frequency and spectral functions

Lorenzo Paulatto1, Ion Errea2,3, Matteo Calandra1 and Francesco Mauri1
1. Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC), Université Pierre et Marie Curie (Paris VI), CNRS UMR 7590, IRD UMR 206, Case 115, 4 place Jussieu, 75252 Paris Cedex 05, France
2. Donostia International Physics Center (DIPC), Manuel de Lardizabal pasealekua 4, 20018 Donostia-San Sebastián, Basque Country, Spain
3. IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Spain

Seeding, nucleation and reactivity of alumina/Ni3Al(111) supported metallic nanoclusters: an ab-initio investigation

Jimena A. Olmos-Asar1, Erik Vesselli2,3, Alfonso Baldereschi1 and Maria Peressi1,4
1 Physics Department, University of Trieste, Strada Costiera 11, I-34151 Trieste, Italy
2 Physics Department and CENMAT, University of Trieste, via Valerio 2, I-34127 Trieste, Italy
3 IOM-CNR Laboratorio TASC, Area Science Park, S.S. 14 km 163.5, I-34149 Trieste, Italy
4 IOM-CNR DEMOCRITOS, Trieste, Italy

Low energy polymorphs of glycine from automated crystal structure prediction including vdW-aware functionals

Cong-Huy Pham1, Emine Kucukbenli2, Stefano de Gironcoli1
1. International School for Advanced Studies (SISSA), Trieste (Italy)
2. Ecole Polytechnique federele de Lausanne (EPFL), Lausanne (Switzerland)

Theophylline self-assembled structures on gold surfaces

Marco Pividori1, Carlo Dri1,2, Elena Orselli3, Maria Peressi1,2, Giovanni Comelli1,2
1. Department of Physics, University of Trieste
2. IOM-CNR Laboratorio TASC, Trieste
3. Department of Physics, University of Milan

Optical nonlinear properties for solids and nanostructures: theory and numerical simulations

Lucie Prussel, Valérie Véniard
Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA/DSM , 91128 Palaiseau, France and European Theoretical Spectroscopy Facility (ETSF)

Adsorption of pyridine on graphene

Abhilash R.1, H. Lin1, G. Fratesi1,2, G.P. Brivio1
1. Dipartimento di Scienza dei Materiali, Università di Milano - Bicocca, Via Cozzi 53 - 20125 Milano, Italy
2. Dipartimento di Fisica, Università di Milano, Via Celoria, 16 - 20133 Milano, Italy

Spin-Orbit interactions in single layer and nanoribbons of NiSe2

J. A. Reyes Retana1, G. G Naumis2, F. Cervantes-Sodi1
1.Departamento de Física y Matemáticas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880, Lomas de Santa Fe, 01219, DF, México
2. Departamento de Física-Química, Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Apartado Postal 20-364, 01000 México, Distrito Federal, México

Thermoelectric properties of AgSbTe2 from first-principles calculations

Nafiseh Rezaei1, S. Javad Hashemifar1,2 and Hadi Akbarzadeh1
1 Department of Physics, Isfahan University of Technology, 84156-83111 Isfahan, Iran
2 Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, 84156-83111 Isfahan, Iran

Density functional investigation of spin polarization in bulk and thin films of nitrogen intercalated Cu3N

Seyed Mojtaba Rezaei Sani1, Masoud Karimipour2, Marzieh Ghoohestani3, Seyed Javad Hashemifar4
1. Computational Physical Sciences Research Laboratory, School of Nano-Science, Institute for Research in Fundamental Sciences (IPM), Tehran, Iran
2. Department of Physics, Vali-E-Asr University of Rafsanjan,77139-36417 Rafsanjan, Iran
3. Nano research center, Department of Physics, Malek Ashtar University of Technology, Shahin Shahr, Isfahan, Iran
4. Department of Physics, Isfahan University of Technology, Isfahan, 84156-83111, Iran

Feasible and reliable ab initio calculations of materials relevant for nuclear waste management

Jose Jorge Rios Ramirez, George Beridze, Yan Li, Ariadna Blanca Romero and *Piotr M. Kowalski
Institut für Energie- und Klimaforschung (IEK-6) Nukleare Entsorgung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany; *contact: p.kowalski@fzjuelich.de

Dielectric matrix formulation of correlation energies within the Random Phase Approximation: Inclusion of (screened) exchange effects

Dario Rocca1,2, Bastien Mussard1,2, Georg Jansen3, János G. Ángyán2,1
1. University of Lorraine, Nancy (France)
2. CNRS, Nancy (France)
3. University of Duisburg-Essen (Germany)

A multi-scale protocol for simulating the optical properties of natural dyes in solution

Marta Rosa1, Marco Micciarelli1, Stefano Baroni1,2, Alessandro Laio1
1 Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Beirut 2-4, I-34014 Trieste, Italy
2 CNR-INFM DEMOCRITOS Theory@Elettra Group, I-34014 Trieste, Italy

Latent heat of magnetization for MnFeSi0.33P0.66

Prasenjit Roy1, R. A. de Groot1
1. Theoretical chemistry group, Institute of molecules and materials, Radboud University, Nijmegen, Netherlands

A real-time DFT scheme for electronic transport

Philipp Schaffhauser1, Stephan Kümmel 1
1. Theoretical Physics IV, University of Bayreuth, Germany

Exploring a non-local correlation functional: One-electron selfinteraction, potential asymptotics, and localized states

Tobias Schmidt1, Stephan Kümmel1
1. Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, Germany

First-principles based descriptor for intrinsic charge carrier mobility in organic devices

Christoph Schober 1, Karsten Reuter1, Harald Oberhofer1
1. Lehrstuhl für Theoretische Chemie, Technische Universität München

Blue phosphorene - metal interface study from first principles

Devina Sharma1 and Shobhana Narasimhan1
1. Theoretical Science Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore 560064 India

On the orbital ordering transition in KCuF3

Hunter Sims1, Eva Pavarini2, Erik Koch1
1. Dept. of Computational Materials Science, German Research School for Simulation Sciences, 52428 Jülich, Germany
2. Institute for Advanced Simulation, Forschungszentrum Jülich, 52428 Jülich, Germany

First-principles methods for 2D materials: electron-phonon interaction, strain-induced fields and screening in graphene

Thibault Sohier1
1. Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR 206, 4 Place Jussieu, F-75005 Paris, France

A theoretical analysis of the role of defects and doping in hexagonal boron nitride sheets

Himadri R. Soni1, Prafulla K. Jha2
1. Lehrstuhl für Theoretische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Universitat Erlangen- Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany
2. Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, India

Physical Factors Influencing Excited State Charge Transfer at the Perylene – Titanium Oxide Interface

O.A. Syzgantseva1,2), K. Laasonen2), M. Puska1)
1. COMP, Department of Applied Physics, Aalto University, P.O. Box 11100 FI-00076 Aalto, Finland
2. COMP, Department of Chemistry, Aalto University, P.O. Box 16100 FI-00076 Aalto, Finland

Self-Consistent Continuum Solvation model for the optical properties of complex molecular systems in solution

Iurii Timrov1, Oliviero Andreussi2, Alessandro Biancardi1, Nicola Marzari3, and Stefano Baroni1
1. SISSA - Scuola Internazionale Superiore di Studi Avantazi, Trieste, Italy
2. Department of Chemistry, University of Pisa, Pisa, Italy
3. EPFL - Ecole Polytechnique Federale de Lausanne (THEOS), Lausanne, Switzerland

Spin asymmetric band gap opening in graphene by Fe adsorption

E. del Castillo1,2, F. Cargnoni1,2, S. Achilli1,2, M.I. Trioni 1,2
1. Chemistry Department, University of Milan, via Golgi 19, 20133 Milano, Italy
2. CNR, National Research Council of Italy, ISTM, via Golgi 19, 20133 Milano, Italy

Modelling Cancellation Effects in the Optical Response of Many-Electron Systems

Marilena Tzavala12, Claudia Rödl12, Lucia Reining12
1. Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA, CNRS, 91128 Palaiseau cedex, France
2. European Theoretical Spectroscopy Facility (ETSF)

Tuning spin transport properties and molecular magnetoresistance through contact geometry

Ulman

Ab initio study of structural and vibrational properties of energetic solids

G. Vaitheeswaran*
Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Prof. C. R. Rao Road, Gachibowli, Hyderabad-500046, India

Protein field effects on electronic excitations of biological chromophores: a QMC and GW/BSE approach in QM/MM environment

Daniele Varsano1, Emanuele Coccia2, Olivia Pulci2, Adriano Mosca Conte3, Leonardo Guidoni2
1. S3 Center, CNR Institute of Nanoscience, via Campi 213/A, 41125 Modena, Italy
2. Dipartimento di Scienze Fisiche e Chimiche, Universitá degli Studi dell'Aquila, via Vetoio, 67100 Coppito, L'Aquila, Italy
3. ETSF, Dipartimento di Fisica, Universitá di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

Adsorption and dissociative adsorption of Nitric Oxide (NO) on Rh cluster over MgO(001) surface

Vasudevan M V 1, Bulumoni Kalita1, Prasenjit Ghosh2 and Shobhana Narasimhan1
1 Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064
2 Departments of Chemistry and Physics, Indian Institute of Science Education and Research-Pune, Pune 411021

Electron and Optical Spectroscopies of Graphene Nanoribbons on Au(111): Insights from Ab-Initio Calculations

Shudong Wang1, Deborah Prezzi1, Andrea Ferretti1, Alice Ruini1,2, Elisa Molinari1,2
1. CNR-Nanoscience Institute, S3 Center, 41125 Modena, Italy
2. Department of Physics, Mathematics, and Informatics, University of Modena and Reggio Emilia, 41125 Modena, Italy

Ab-initio modeling of peroxy bridge defect in amorphous silica

B. Winkler1, L. Martin-Samos1, N. Richard2, S. Girard3
1) Materials Research Laboratory, University of Nova Gorica, Vipavska 11c, 5270-Ajdovščina, Slovenia
2) CEA, DAM, DIF, Bruyères-le-Châtel, F-91297 Arpajon Cedex, France
3) Laboratirie Hubert Curien, Université de St-Etienne, UMR-CNRS 5516, Bâtiment F, 18 Rue du Professeur Benoît Lauras, F-42000 St-Etienne, France

Ab-initio studies of geometric and electronic properties of group VI-B transition metal dichalcogenides monolayers

Tomasz Woźniak1, Paweł Scharoch1
1. Departament of Theoretical Physics, Wroclaw University of Technology, Poland

Atomistic simulations of multicaloric effects in ferroelectrics

S. Lisenkov and I. Ponomareva
Department of Physics, University of South Florida, Tampa, FL 33620, USA

The materials that exhibit large caloric effects have emerged as promising candidates for solid-state refrigeration which is an energy-efficient and environmentally friendly alternative to the conventional refrigeration technology. However, despite recent ground breaking discoveries of giant caloric effects in some materials they appear to remain one of nature's rarities. Here we use atomistic simulations to study electrocaloric and elastocaloric effects in $Ba_{0.5}Sr_{0.5}TiO_3$ and $PbTiO_3$ ferroelectrics. Our study reveals the intrinsic features of such caloric effects in ferroelectrics and their potential to exhibit giant caloric effects. Some of the findings include the coexistence of negative and positive electrocaloric effects in one material and an unusual field-driven transition between them as well as the coexistence of multiple giant caloric effects in $Ba_{0.5}Sr_{0.5}TiO_3$ alloys. These findings could potentially lead to new paradigms for cooling devices.

This work is partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award DE-SC0005245.

Structural defects in P3HT-polymer chains probed in the ballistic transport regime

A. Lücke[1], E. Rauls[1], F. Ortmann[2], W. G. Schmidt[1], and U. Gerstmann[1]

1. Department of physics, University of Paderborn
2. Institute for Materials Science, Dresden University of Technology

The polymer P3HT is widely applied as photoactive layer in organic solar cells and for semiconducting layers in organic field effect transistors. In particular the crystalline region-regular modification offers large mobilities up to 0.1 $cm^2/(Vs)$ [1] which makes this material of high interest for organic semiconductor devices. As there are several orders of magnitude between the mobilities of crystalline and amorphous P3HT, we aim at microscopic insight into the influence of common kinds of conformal defects in regioregular P3HT using the framework of the ballistic transport regime.

A sophisticated theoretical *ab initio* investigation of a *complete network* of arbitrary distributed polymer chains require the treatment of several thousands atoms and is, thus, still today out of reach for density functional theory (DFT) in particular if interested in the predictive calculations of transport properties. In this work, we show that a direct multi-scattering approach as implemented in the Quantum Espresso Package [2] provides an physically transparent and efficient alternative to Green's functions based approachs that allows to investigate the influence of local structural defects onto the global transport properties of the polymer network. These structural defects encompass isomerism, torsional and bending defects as well as dislocations. By this, we gain further insight into the ballistic transport of P3HT. In particular, it becomes possible to explain why crystalline (rr)-HT-P3HT polymers are superior to other modifications.

[1] H. Sirringhaus et al., Nature, vol. 401, no. 6754, pp. 685-688 (1999).

[2] P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);
URL http://www.quantum-espresso.org

Substrate doping: A strategy for enhancing reactivity of gold nanocatalyst by tuning the *sp*-bands

Nisha Mammen[1], Stefano de Gironcoli[2], Shobhana Narasimhan[1]

1. Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064 India
2. SISSA, via Bonomea 265, 34136 Trieste, Italy

Abstract:
Catalytic Nanoscopic Au particles have been a widely studied subject of research in the recent years for their low temperature catalytic activity for reactions like CO oxidation. In this study we have attempted to investigate the interplay between the charge, the geometry and the catalytic activity of the Au clusters when supported over an oxide substrate.

We have chosen to study a model system of Au_{20} supported over an MgO substrate doped with Al atoms, by performing spin-polarized density functional theory calculations. The Au_{20} cluster is known to have a three-dimensional tetrahedral structure in gas phase as well as on pristine MgO. We show that doping the substrate with an electron donor switches the morphology of the cluster from its stable three-dimensional tetrahedral form to a two-dimensional planar form, and more interestingly, this also leads to a significant lowering of oxygen dissociation barriers on these clusters. The barriers are lowered by an amount proportional to the doping concentration. We attribute both the change in morphology and the enhanced reactivity of the cluster to charge transfer from the doped substrate to the Au cluster.

The *d*-band model explains trends in the reactivity of transition metals. This model claims that the higher in energy the *d*-band center of the metal, the greater its reactivity. However, the lowering of dissociation barriers observed in our study cannot be explained by the behavior of the *d*-band center of the Au atoms, which moves downwards, away from the Fermi energy upon substrate doping. We instead show that the charge transfer from the substrate to the Au cluster leads to an increased filling in the *s*- and *p*-bands of Au atoms, which leads to a lowering of energies of Au electrons in the *s*- and *p*-bands. We propose that this lowering in energy of the *sp*-bands explains our results on the enhanced reactivity of Au clusters.

πAg nanoclusters: An ab-initio vibrational dynamics Study

Venu H. Mankad[1], Sanjeev K. Gupta[2], Prafulla K. Jha[3]

[1] *Central Institute of Plastic Engineering and Technology, Ahmedabad- 382 445, India*
[2] *Department of Physics, St. Xavier's College, Navrangpura, Ahmedabad-380009, India*
[3] *Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara-390002, India*

Abstract. The size dependent structural, electronic and vibrational properties of silver metal clusters along with its bulk counterparts have been studied using the first principles calculations within density functional theory. The size effect was studied by calculating a series of clusters discussed in terms of the increase in band gap when going from the bulk to cluster. The phonon calculations show that the clusters with smaller size are dynamically stable. Our findings will give some reference to the insight understanding of the electronic and vibrational properties of size orientation dependent Ag metal cluster.

Keywords: Ag Cluster, Electronic Structure, Phonon.

Thermal properties of bismuth calculated from first principles.

Maxime Markov[1], *Jelena Sjakste*[1] , *Giorgia Fugallo*[1], *Lorenzo Paulatto*[2],
Francesco Mauri[2], *Michele Lazzeri*[2], *Nathalie Vast*[1]

[1] Laboratoire des Solides Irradies, Ecole Polytechnique - CEA - DSM - IRAMIS - CNRS UMR 7642, 91128 Palaiseau cedex, France
[2] IMPMC, Universite Pierre et Marie Curie, CNRS 4 place Jussieu, F-75005 Paris, France

A microscopic description of the thermal properties of materials based on the Boltzmann transport equation (BTE) coupled to fully ab initio data is quite a challenging task. Recently a new robust numerical approach for solving exactly the linearized BTE using the variational principle and the conjugate gradient scheme has been proposed in Refs. [1-2]. To describe the anharmonic scattering one needs to calculate the phonon-phonon matrix elements. A new beyond the state-of-the-art method based on density functional perturbation theory (DFPT) and the "2n+1" theorem has been recently implemented as an extension of the Quantum Espresso suite and applied to diamond [2], graphite and graphene [1].

Bismuth is an excellent model substance for the study of thermoelectricity. The bismuth-based compounds such as Bi2Te3 and Bi2Se3 are widely used thermoelectric materials in industrial applications. Recently in our laboratory significant progress has been achieved in the description of electronic and vibrational properties of bismuth, and in the determination of the magnitude of the electron-phonon coupling, both experimentally and theoretically [3-5].

In this poster I will present our results of the ab initio calculations of thermal transport properties in bismuth. We employ the recently developed methods [1,2] of the solution of BTE and phonon-phonon matrix elements calculation. We have obtained the temperature dependence of the lattice thermal conductivity which is in excellent agreement with experiment. Moreover we are able to predict the lattice thermal conductivity at temperatures where it has not been measured.

Our approach allows us to study how different phonons contribute to the lattice thermal conductivity and the impact of spin-orbit interaction on heat transfer in bismuth. We have found that the acoustic phonons give the main contribution which is uniform over the Brillouin zone. We have shown that the spin-orbit coupling interaction plays a crucial role in the heat transfer in bismuth.

The calculations were performed using the Quantum ESPRESSO package [6]. Computer time was granted by GENCI (Project No. 2210).

References:

[1] G. Fugallo, M. Lazzeri, L. Paulatto and F. Mauri, Phys. Rev. B **88**, 045430 (2013).

[2] L. Paulatto, F. Mauri and M. Lazzeri, Phys. Rev. B **87**, 214303 (2013).

[3] I. Timrov et al., Phys. Rev. B **85**, 155139 (2012).

[4] E. Papalazarou et al., Phys. Rev. Lett. **108**, 256808 (2012).

[5] J. Faure et al., Phys. Rev. B **88**, 075120 (2013)

[6] P. Giannozzi et al., J. Phys.: Condens. Matter **21**, 395502 (2009)

THE MIXED (L-THREONINATO)(L-ASPARAGINATO)COPPER(II) SYSTEM - CONFORMATIONAL ANALYSIS OF AN ISOLATED COMPLEX

Marijana Marković[1,2], **Michael Ramek**[2], **Jasmina Sabolović**[1]

[1]*Institute for Medical Research and Occupational Health, Ksaverska cesta 2,*
P. O. Box 291, HR-10001 Zagreb, Croatia, mmarkov@imi.hr, jasmina.sabolovic@imi.hr
[2]*Institut für Physikalische und Theoretische Chemie, Technische Universität Graz (NAWI Graz),*
Stremayrgasse 9, A-8010 Graz, Austria, michael.ramek@tugraz.at

Of the 23 amino acids that are known to exist in human serum, a substantial number were shown to compete effectively with albumin for the binding of copper. [1] Besides the albumin-bound copper, it was suggested that 5-10% of copper in serum exists in the form of mixed amino acid copper complexes. Under normal conditions, histidine was found as primarily being involved in forming these mixed amino acid-copper complexes. Other amino acids, which were shown most likely to be part of these mixed complexes, are threonine, glutamine, and asparagine. [1-3] It was proposed that the amino acid-bound fraction of copper in serum may have a physiological role in the biological transport of copper. Moreover, the copper(II) complexes of amino acids, small peptides and other low-molecular-weight ligands are used as valuable model systems that mimic copper-binding sites existing in biological systems. [4]

The exact molecular conformations of the (L-threoninato)(L-asparaginato)copper(II) complex, Cu(L-Thr)(L-Asn), both in vacuum and in solution are still unknown. To get a first glance into their molecular geometries in the gas phase, a full conformational analysis of this compound was performed by using the density functional theory (DFT) method and the unrestricted B3LYP functional with the LanL2DZ double-ζ basis set, to which a set of polarisation functions and diffuse functions was added. Both L-Thr and L-Asn are supposed to maintain their "glycinato-like" coordination mode, *i.e.* the configuration in which they are bound to Cu(II) via the amino nitrogen and carboxylato oxygen atoms.

The goal of this study is to examine the possibility of forming intramolecular hydrogen bonds in the title complex. We gained a total of 75 different equilibrium geometries of Cu(L-Thr)(L-Asn). Generally, the *trans* conformers are energetically more stable than the *cis* ones. The global minimum, labelled as *trans* Thr(e1)-Asn(e2), is 38.7 kJ mol^{-1} more stable than the corresponding *cis* minimum. A similarity for the most stable *trans* and *cis* conformer of the complex is a strong intramolecular hydrogen bond in the Asn-residue between the carbonyl atom of its amide group and its amino nitrogen. Likewise, in the Thr-residue an intramolecular hydrogen bond is generated between its hydroxyl group and its carboxyl oxygen atom. Regarding the Asn-residue, all conformations calculated are among those of the isolated $\mathrm{Cu(L\text{-}Asn)_2}$. [5] It should be specifically mentioned that we found new conformations that had not been detected in the isolated $\mathrm{Cu(L\text{-}Thr)_2}$ complex. [6] In the two new Cu(L-Thr) conformations an intramolecular hydrogen bond is formed between the hydroxyl group of the Thr-residue and the oxygen atom of the amido group in the Asn-residue. The trend of forming hydrogen bonds is more pronounced in *trans* than in *cis* complexes due to stereochemical reasons.

[1] P.Z. Neumann, A. Sass-Kortsak, J. Clin. Invest. 46 (1967) 646–658.
[2] P. S. Hallman, D. D. Perrin, A. E. Watt, Biochem. J. 121 (1971) 549–555.
[3] V. Brumas, N. Alliey, G. A. Berthon, J. Inorg. Biochem. 52 (1993) 287–296.
[4] H. C. Freeman, Adv. Protein Chem. 22 (1967) 257–424.
[5] M. Marković, M. Ramek, J. Sabolović, 50th Symposium on Theoretical Chemistry, Vienna 2014, poster.
[6] M. Marković, M. Ramek, J. Sabolović, Brijuni Conference, Brijuni 2014, poster.

Ultra-fast transient absorption of monolayer MoS_2 from first principles

Margherita Marsili[1], *Deborah Prezzi*[1]
Davide Sangalli[2], *Andrea Marini*[2]

1. CNR, Istituto di Nanoscienze S3 – Modena (Italy)
2. CNR, ISM – Montelibretti (Italy)

Among transition-metal dichalcogenides monolayers, MoS_2 is one of the most studied thanks to extremely promising features, such as a direct band-gap in the visible range, a very high luminescence quantum efficiency, high electron mobility, high room-temperature current on/off ratio, and potential for valleytronics applications [1-4].

In this work we compute ultrafast transient absorption spectra of MoS_2 monolayers. We employ a novel approach which combines density-functional and non-equilibrium Green's function theories [6], as implemented in the Yambo code [7]. This approach allows the description of pump-probe optical experiments where the system is excited by an ultrashort laser pulse, and the variation of the optical response is probed at different time delays, thus providing a wealth of information on the fundamental physics of the relaxation processes. This method was recently applied to the case of bulk Si [8]. The extension of the study to the case of monolayer MoS_2 is extremely challenging due to the interplay of excitonic, electron-phonon and spin-orbit coupling effects that govern the physics of the excited states of this material. We thus describe the excitation of the MoS_2 electronic system and follow the subsequent dynamics using a fully non-collinear spin formulation of the theory, including excitonic effects. The results are compared with experimental pump-probe data.

[1] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010)

[2] A. Splendiani, L. Sun, Yu. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Lett. 10, 1271 (2010)

[3] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat. Nanotech. 6, 147 (2011)

[4] K. F. Mak, K. L. McGill, J. Park, and P. L. McEuen Science 344, 1489 (2014)

[6] A. Marini, J. Phys.: Conf. Ser. 427 012003 (2013)

[7] A. Marini, C. Hogan, M Grüning, and D. Varsano, Comp. Phys. Comm. 180, 1392 (2009)

[8] D. Sangalli and A. Marini, arXiv:1409.1706 (2014)

Projector Augmented-wave formulation of response to strain and electric field perturbation within the density-functional perturbation theory.

Alexandre Martin[1], Marc Torrent[1], Razvan Carracas[2]

1. CEA, DAM, DIF, F-91297 Arpajon, France
2. ENS de Lyon, UCBL Lyon 1, Université de Lyon

A formulation of the response of a system to strain and electric field perturbations in the pseudopotential-based density functional perturbation theory (DFPT) has been proposed by D.R Hamman and co-workers. It uses an elegant formalism based on the expression of DFT total energy in reduced coordinates, the key quantity being the metric tensor and its first and second derivatives. We propose to extend this formulation to the Projector Augmented-Wave approach (PAW). In this context, we express the full elastic tensor including the clamped-atom tensor, the atomic-relaxation contributions (internal stresses)and the response to electric field change (piezoelectric tensor and effective charges). With this we are able to compute the elastic tensor for all materials (metals and insulators) within a fully analytical formulation. The comparison with finite differences calculations on simple systems shows an excellent agreement. This formalism has been implemented in the plane wave DFT ABINIT code and applied to the computation properties of materials present in the inner core of the earth.

Electronic and magnetic structures of semimagnetic semiconductors investigated by first principle, mean field and series expansions calculations

R. Masrour[1,2*]

[1]Laboratory of Materials, Processes, Environment and Quality,
Cady Ayyed University, National School of Applied Sciences, 63 46000, Safi, Morocco.
[2]LMPHE (URAC 12), Faculty of Science, Mohammed V-Agdal University, Rabat, Morocco

Keywords : Electronic and magnetic structure, Magnetic moment, Néel temperature, Exchange interactions.

PACS: 71.15.-m, 67.80.dk, 71.45.Gm.

*~~~~***corresponding author: rachidmasrour@hotmail.com***

Abstract:

The Self-consistent *ab initio* calculations, based on DFT (Density Functional Theory) approach and using FLAPW (Full potential Linear Augmented Plane Wave) method, are

performed to investigate both electronic and magnetic properties of the Mn(Fe)A(A=Se, Ge, S, ..) compounds. Polarized spin and spin-orbit coupling are included in calculations within the framework of the ferromagnetic state between two adjacent Mn atoms. The ferromagnetic and antiferromagnetic energies of MnA systems are obtained. Magnetic moment considered to lie along (001) axes are computed**.** Obtained data from *ab initio* calculations are used as input for the high temperature series expansions (HTSEs) calculations to compute other magnetic parameters. The exchange interactions between the magnetic atoms Mn-Mn in MnA are given using the mean field theory. The High Temperature Series Expansions (HTSEs) of the magnetic susceptibility of with the magnetic moments in MnAs ($m_{\text{Mn or Fe}}$) through Ising model is given up to *ten*th order series in ($x=J_1(\text{Mn-Mn})/k_BT$). The Néel temperature T_C is obtained by HTSEs of the magnetic susceptibility series combined with the *Padé* approximant method. The critical exponent γ associated with the magnetic susceptibility is deduced as well.

Surface Adsorbates and Defects on the Subsurface Cation Vacancy Stabilized Surface of Magnetite (001)

Eamon McDermott[1], *Roland Bliem*[2], *Gareth Parkinson*[2], *Ulrike Diebold*[2],
Peter Blaha[1]

1. Institute for Material Chemistry, TU Wien, Vienna, Austria
2. Institute of Applied Physics, TU Wien, Vienna, Austria

Having proposed a new surface reconstruction for the magnetite (001) surface which is stabilized by a subsurface cation vacancy[i], we are now studying the extended properties of this reconstruction, including its preferred adsorption sites for various metals, the properties of oxygen vacancies at the structure and the adsorption of CO and OH groups. The surface structure has interesting chemistry, due to the presence of an oxygen site with a +1 oxidation state. In particular, we are interested in understanding our database of known magnetite surface defects as observed by STM. Progress on several ongoing investigations will be reported.

---

[i] Bliem, R., McDermott E. J,. et al, Subsurface Cation Vacancy Stabilization of the Magnetite (001) Surface, Science. in press (2014).

A multiscale computational method for fluid dynamics simulation: application of nanoscience to enhanced oil recovery process.

Aline O. Pereira[1], Lucas Stori de Lara[1], Raphael S. Alvim[1], and Caetano R. Miranda[1]

1. NanoPetro Research Group , Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, 09210-580, Brazil

contact: caetano.miranda@ufabc.edu.br

Dispersed nanoparticles solutions have shown the ability to control and modify the interfacial and wetting properties of liquid-liquid and liquid-solid interfaces. Although the recent advances in experimental techniques, the determination of the interfacial tension and wetting properties at nanoscale continues to be a challenge. Molecular dynamics simulations (MD) are a good alternative to determine the interfacial properties of a system. However, atomistic simulations have key limitations. For instance, the accuracy of the interatomic potentials and how to scale-up the fluid information at nanoscale to larger ones, where industrial processes may take place. Here, we propose an integrated multiscale computational protocol ranging from first principles calculations, molecular dynamics and Lattice Boltzmann method (LBM) to explore potential applications of nanoscience in Enhanced Oil Recovery (EOR) processes. More specifically, we study the role of functionalized SiO2 nanoparticles into oil displacement process in clay pore structures. At first, the montmorillonite (MMT) surface with functionalized Si probe tip model was investigated within density functional theory (DFT) with the generalized gradient approximation (GGA) revPBE functional with van der Waals density functional (vdW-DF). These results were benchmarked with classical MD calculations. Our MD calculations indicate that the addition of nanoparticles to the brine solution considerably reduces the interfacial tension between oil and brine. Also, a small reduction in oil viscosity and an increase of the contact angle is observed. By mapping the MD results into LBM parameters and simulating the injection of NP solution into porous structures at microscale, we observed that the inclusion of nanoparticles indeed improve the oil displacement process in realistic pore network models. The proposed multiscale approach can be a useful tool to explore potential chemical additives for EOR and investigate the effects of the interfacial tension and wetting properties on fluid behavior at both nano and micro scales.

Stable and Efficient Linear Scaling First-Principles Molecular Dynamics for 10,000+ atoms

Michiaki Arita[1,2], *David R. Bowler*[3,4,5] *and* *Tsuyoshi Miyazaki*[1,2]

1. Computational Materials Science Unit, National Institute for Materials Science (NIMS), Japan.
2. Graduate School of Science and Technology, Tokyo University of Science, Japan.
3. Department of Physics & Astronomy, University College London (UCL), UK.
4. London Centre for Nanotechnology (LCN), UCL, UK.
5. International Materials Nanoarchitectonics (MANA), NIMS, Japan.

The recent progress of linear-scaling or O(N) methods in the density functional theory (DFT) is remarkable. [1] We expect that first-principles molecular dynamics (FPMD) simulations based on DFT can now treat more realistic and complex systems using the O(N) technique. However, very few examples of O(N) FPMD simulations exist so far and the information for the accuracy or reliability of the simulations is very limited. In this paper, [2] we show that efficient and robust O(N) FPMD simulations are now possible by the combination of the extended Lagrangian Born-Oppenheimer molecular dynamics method, which was recently proposed by Niklasson *et al.*, [3] and the density matrix minimization method as an O(N) technique. Using our linear-scaling DFT code CONQUEST, we investigate the reliable calculation conditions for the accurate O(N) FPMD and demonstrate that we are now able to do actual and reliable self-consistent FPMD simulation of a very large system containing 32,768 atoms using about 1000 CPUs of K-computer or Fujitsu FX10. Since CONQUEST has almost ideal parallel efficiency even when we use more than 10,000 CPUs, [4] we can conclude that FPMD simulations on million-atom systems are now possible.

[1] D. R. Bowler and T. Miyazaki, Rep. Prog. Phys. **75**, 036503 (2012).

[2] M. Arita, D. R. Bowler and T. Miyazaki, J. Chem. Theor. Comput., in press. (DOI: 10.1021/ct500847y)

[3] A. M. N. Niklasson, Phys. Rev. Lett. **100**, 123004 (2008).

[4] M. Arita, S. Arapan, D. R. Bowler and T. Miyazaki, Journal of Advanced Simulation in Science and Engineering, **1**, 87 (2014).

Ab Initio Simulation of Enhanced Phosphorus-based Nano-composite Materials

Glenn Moynihan[1], *David O'Regan*[2]

1. CRANN Institute, Trinity College Dublin

2. School of Physics, Trinity College Dublin

Composite materials, comprising a polymer matrix doped with low volume fractions of relatively strong nano-flakes, have demonstrated significant improvement of their mechanical properties over their pure form [1-4]. Yet, despite the decrease in cost for producing high quality nano-flakes, cost-effective, highly-functional nano-composite materials have remained elusive in industry. Achieving optimum dispersion of the flakes within the material and maximumising the inter-facial interaction on the molecular level remain the most arduous obstacles yet to be overcome.

In this study, the mechanical properties of neat PVC are shown to be reinforced by the presence of nano-flakes of Black Phosphorus (BP). Two-dimensional BP, or *phosphorene*, has recently emerged as a promising material in electronic and mechanical applications, displaying high electron mobility and mechanical flexibility. The presence of a band-gap (tuned via the number of layers) is also an attractive feature that makes phosphorene a potential rival for graphene in the emerging, low-dimensional market.

A variety of models were investigated to account for the underlying reinforcing effects evident in the experimental data, most notably the Halpin-Tsai model [5] and Voigt-Reuss-Hill model[6], which is needed due to the high anisotrop of BP. At the time of writing no clear mechanism has been identified to account for the improvement.

We performed the calculations of the bulk and two-dimensional BP phases with Quantum Espresso, using an Ultrasoft pseudo-potential and implemented the van der Waals interaction via the Grimme potential.

[1] S-K. Kim,J.J. Wie, W. Mahmood, H.S. Park, *Nanoscale*, 2014, **6**, 7430

[2] Y. Yang, W. Rigdon, X. Huang, X. Li, *Scientific Reports*, **3**, 2086

[3] J. Liang, Y. Huang,L. Zhang, Y. Wang, Y. Ma, T. Guo, Y. Chen, *Adv. Funct. Mater.* **2009**, 19, 2297-2302

[4] J.A. King, D.R. Klimek, I. Miskioglu, G.M. Odegard, *J. Appl. Polym. Sci.* **2013**, 4217-4223

[5] J.C. Halpin, J.L. Kardos, *Polym. Eng. And Sci.,* **May 1976**, Vol 16, No 5

[6] R. Hill, Proc. Phys. Soc. A 65 349

An investigation of quantum transport properties in silicon nanotube

Ebrahim Nadimi[1], *S. Ahmad Etghani*[2,3]

1. Electrical Engineering Department, KN Toosi University of Technology, Tehran
2. Electrical Engineering Department, KN Toosi University of Technology, Tehran
3. Electrical Engineering Department, University of Tehran (current affiliation)

Recent exciting researches on fabrication of silicon nanotubes motivate us to characterize different suggested SiNTs structures by means of first principles calculations based on density functional theory. In contrary to their counterparts (CNTs) SiNTs have stable structures with both sp2 as well as sp3 hybridized bonding. Tubular configurations consist of 4, 5 and 6 silicon atoms in each ring have been considered in our investigations. The structural stability and electronic density of states have been compared in different structures, which show interesting quantization effects. The electronic transport properties of these SiNTs are also studied based on a combination of density functional theory and non-equilibrium Green's function formalism. The quantization effects lead to novel current-voltage characteristics of the studied SiNTs.

Efficient optimization of local orbitals and eigenstate calculations in linear-scaling DFT code CONQUEST

Ayako Nakata[1], *David R. Bowler*[2], *Y. Futamura*[3], *T. Sakurai*[3] *and Tsuyoshi Miyazaki*[1]

1. National Institute for Materials Science (NIMS), Japan
2. Department of Physics & Astronomy, University College London (UCL), U. K.
3. Department of Computer Science, University of Tsukuba, Japan

CONQUEST[1] is a linear-scaling (O(N)) DFT code developed jointly by UCL and NIMS. CONQUEST achieves O(N) by using the locality of density matrices with the density matrix minimization method. Local orbitals which are called support functions are used to express the locality of density matrices. We have introduced multisite support functions[2], which are the linear combinations of pseudo-atomic orbitals from a target atom and its neighbor atoms. Multisite support functions correspond to local molecular orbitals so that the number of required support functions can be the minimal. The multisite support functions are determined by using the localized filter diagonalization method[3]. The double cutoff method and the smoothing method are introduced to improve efficiency and stability of calculations.

The accuracy and computational efficiency of the present method are demonstrated by investigating the energetic and geometrical properties of several systems. Fig. 1 shows the calculated density of states around HOMO-LUMO gap of a hydrated DNA system. The present method has succeeded in providing the band-gap energy with the error less than 0.01 eV from the conventional method while reducing the computational time to about 1/10.

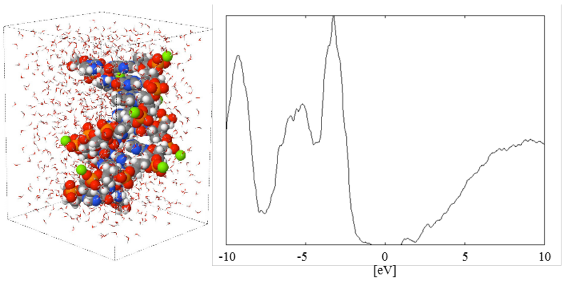


Fig. 1. Density of states of hydrated DNA.

We have also employed an efficient projection method to obtain the eigenstates in specific energy ranges proposed by Sakurai and Sugiura[4] with the sparse matrices constructed by CONQUEST. It enables us to obtain efficiently band energies and charge densities in the specific energy ranges. The results and efficiency of this method has been compared with those of the conventional exact diagonalization method in CONQUEST.

[1] http://www.order-n.org/ [2] A. Nakata, D. R. Bowler, T. Miyazaki, J. Chem. Theory Comput., 10, 4813-4822 (2014). [3] M. J. Rayson and P. R. Briddon, Phys. Rev. B, 80, 205104 (2009). [4] T. Sakurai and H. Sugiura, J. Comp. Appl. Math., 159, 119 (2003).

Native defects and impurities in single-layer MoS_2 and shallow level formation with dielectric environments

Ji-Young Noh[1,2], *Hanchul Kim*[1], *Yong-Sung Kim*[2]

1. Department of Physics, Sookmyung Women's University, Seoul, Korea
2. Korea Research Institute of Standards and Science, Daejeon, Korea

We investigate the atomic and electronic structures of various native point defects and substitutional dopants in the single-layer (SL) MoS_2, based on density functional theory calculations. To understand the stability and doping ability of the native defects in a SL MoS_2, we calculate formation energies and transition levels of the native defects in various charge states. For the charged states, spurious electrostatic interaction between image charges in supercell is rigorously treated and eliminated. For native defects, we find that V_S and the S_i (in the form of a S-adatom) hold low formation energies among the native defects. The S_i is found to be a neutral defect, while the V_S is a deep single acceptor. In contrast, the Mo-related native defects of V_{Mo} and Mo_i are found to be high in formation energy. The V_{Mo} is a deep single acceptor and the Mo_i is a deep single donor. Based on these results, we conclude that the native defects act as deep trap centers for electrons and holes rather than efficient dopants in a SL MoS_2. [1] We also investigate Re and Nb impurities in a SL MoS2, which have been considered to be present in natural molybdenites. The Re and Nb are found to have deep transition levels in SL MoS_2, however, the transition levels are changed, and even show deep to shallow level transition by the dielectric screening effects. Therefore, the substrate and encapsulation layer should strongly affect the doping ability and carrier concentration in MoS_2-based thin film transistors.

*This work was supported by the Future-based Technology Development Program(Nano Fields) (No. 2009-0082490) through the National Research Foundation of Korea(NRF).

[1] J. –Y. Noh et al., Phys. Rev. B 89, 205417 (2014).

Title: Quantum Confinement in Silicon Quantum-Slabs

Abstract:

The quantum confinement (QC) attracts many attentions in photovoltaics (PV) field recently, because of the special optoelectronic properties, which can possibly increase the efficiency of the solar cells significantly. On the basis of density functional-pseudopotential calculations, we predict the occurrence of quantum confinement in quantum slabs of silicon embedded in hydrogenated amorphous-Si. We show and clarify that only holes in the valence states are confined effectively within the quantum-slabs of a-Si. QC in silicon slabs, which are confined only in one dimensional, proves QC in quantum wires and quantum dots of nc-Si:H, which are confined in two and three dimensional, respectively. According to this study, we find that nc-Si:H is a promising material for oxygen-free optoelectronics and photovoltaics.

First-Principles Calculation for Thermal Oxidation Process of SiC

Tomoya Ono[1]

1. Center for Computational Sciences

Silicon carbide (SiC) is attracted much attention due to its high breakdown strength. To fabricate a SiC-based metal-oxide-semiconductor field-effect-transistors, a high-quality SiC/SiO_2 interface is required. Unlike Si/SiO_2 interfaces, SiC/SiO_2 interfaces suffer from a large amount of interface traps such as C interstitials, C-C dimers, and so on. The experimental study using secondary ion-microprobe mass spectrometer (SIMS) indirectly proves that the most of C atoms do not remain at the interface after the thermal oxidation since the C signal near the interface is under the detection limit of the SIMS measurement [1]. On the other contrary, high-resolution transmission electron microscopy (HRTEM) observed the certain amount of C-atom rich layers at the SiC/SiO_2 interface [2]. Thus there are controversial reports regarding the interfacial atomic structure of the SiC/SiO_2 interface.

In this study, the oxidation process as well as the CO desorption of the 4H-SiC(0001) surface and 4H-SiC(0001)/SiO_2 interface are examined by first-principles total energy calculations. The calculation is carried out using RSPACE code [3]. 4H-SiC(0001) surface model and 4H-SiC(0001)/SiO_2 interface model are employed to imitate initial and middle stages of oxidation, respectively. Oxygen atoms are sequentially inserted between Si-C bond and the energies of the CO desorption is calculated by removing the C atom as a form of CO from the surface and interface models. It is found that the CO desorption becomes preferable when the number of inserted O atoms is three because the stress is relaxed by removing the CO molecule from the SiC/SiO_2 interface.

When C atoms are not removed as CO molecules at the SiC/SiO_2 interface, the unoxized Si-C bond will remain in SiO_2. I also calculate the effect of the Si-C bond in SiO_2 and the CO desorption from SiO_2. The Si-C dimer in SiO_2 can be modeled by replacing one Si atom with one C atom, and removing one O atom between the C atom and the neighboring Si atom in SiO_2. The energy of the CO desorption is -3.59 eV, indicating that the CO desorption is unfavorable. Therefore C atoms are immediately emitted from the interface as CO molecules and not kicked out from SiO_2, which agrees with the conclusion obtained by SIMS [1] and disagree with that by HRTEM [2].

[1]K. Chatty *et al.*, J. Electron. Mater. **28**, 161 (1999).
[2]T. Zheleva *et al.*, Appl. Phys. Lett. **93**, 022108 (2008).
[3]K. Hirose *et al.*, *First Principles Calculations in Real-Space Formalism,* (Imperial College, London, 2005).

First Principle Simulation of Optical Spectra in Gold-based Alloys

Okan K. Orhan and David D. O'Regan

School of Physics, Trinity College Dublin, Ireland

The particular optical and plasmonic properties of noble metals, their nanostructures and nanoclusters give rise to their widespread utility in technologies such as medical imaging, sensing at the nanoscale [1], and heat-assisted magnetic data storage [2]. The macroscopic dielectric function is the central physical quantity describing the optical properties of extended materials, both experimentally and theoretically. First principles calculations of this quantity, particularly if they may be integrated in recently-developed high-throughput approaches [3], offer a fresh approach to simulating the feasibility of optimizing optical properties for particular optical requirements, by alloying, superlatticing, or by the synthesis of hitherto unknown crystalline phases. Such calculations are challenging, however, due to the demands of intraband transitions at the Fermi level, both local and non-local electron-electron interactions, and relativistic effects.

In this study, we perform first principles calculations, using the Quantum Espresso package [4] in combination with the Yambo code [5], of the optical spectra yielded by various levels of theories applied to bulk Au and Au_6AgCu alloys. The convergence of the optical spectra with respect to Brillouin zone sampling finesse, the choice of the excitation damping scheme, and the possibility of reducing the number of bands and plane-waves used in optical calculations, for a fixed target excitation energy window, are separately investigated. The commutator-like term in the electron velocity due to the presence of non-local potentials is found to be the dominant term in the predicted optical spectra in bulk Au; its inclusion is essential. Relativistic effects are also found to be too large to be reliably neglected. An approach to accelerating the convergence of spectra in random alloys with respect to supercell size, making use of Boltzmann factor computed on a larger number of smaller cells, is proposed, and preliminary results on the random Au_6AgCu alloy are demonstrated.

[1] Jain, P. K., Huang, X., El-Sayed, I. H., & El-Sayed, M. A., *Accounts of Chemical Research*,*41*(12), 1578-1586 (2008).

[2] Black, C. T., Gates, S. M., Murray, C. B., & Sun, S., *U.S. Patent No. 6,162,532*. Washington, DC: U.S. Patent and Trademark Office (2000).

[3] Curtarolo, S., Hart, G. L., Nardelli, M. B., Mingo, N., Sanvito, S., & Levy, O., *Nature Materials*, *12*(3), 191-201 (2013).

[4] Giannozzi, P., et al., *Journal of Physics: Condensed Matter*, *21*(39), 395502 (2009).

[5] Marini, A., Hogan, C., Grüning, M., & Varsano, D., *Computer Physics Communications*, *180*(8), 1392-1403 (2009).

Enhancement of superconductivity with low doping in two-dimensional multivalley semiconductors

<u>Betül Pamuk</u>[1], Matteo Calandra[1], Francesco Mauri[1]

1. IMPMC, UMR CNRS 7590, Sorbonne Universités - UPMC

The superconductivity emerges at low doping of two-dimensional (2D) multivalley semiconductors. Against expectations, both the magnetic susceptibility and the superconducting transition temperature, T_c of nitride halides, MNCl, with M=Zr, Hf, decreases upon weak Li-doping. In order to understand this behavior, first, we investigate the electronic structure of these systems under different Li-doping. Furthermore, we analyze the magnetic properties of the doped semiconductors by obtaining the spin susceptibility, χ_s. We evaluate χ_s using first principles density functional theory. In addition to semi-local PBE functional, we utilize hybrid functionals with several levels of exchange and the RPA approximation. This approach allows us to understand the effect the of the exchange energy on the enhancement of the spin susceptibility (χ_s / χ_{0s}).

This work is supported by the Graphene Flagship and by Agence Nationale de la Recherche under reference ANR-13-IS10-0003-01.

Jastrow correlations for solids

Martin Panholzer[1]

1. Center for Surface and Nanoanalytics, Johannes Kepler University Linz

DFT is the most widely used method to solve the many body Schrödinger equation for the ground state. However the band structure is not well described by the Kohn-Sham eigenvalues alone. In order to improve upon that one has to employ other methods, like GW, in order to obtain the self energy, which corrects the Kohn-Sham band structure. Most of the time this works reasonably well, if self consistency is used [1], but in some cases this is not enough [2]. A possible improvement could be the use of a Jastrow correlated wave function.

Jastrow correlations are well established for strongly correlated homogeneous systems like Helium, Nuclear matter or the Jellium model. Krotscheck and Kohn [3] showed that for a Jellium slab, Jastrow correlations are important for the correct description of surface energies. Their main conclusion is: "*The local density approximation for the particle hole interaction is inadequate to calculate the surface energy of simple metals.*" To get an estimate for the importance of correlations in realistic systems, the FHNC (Fermi Hyper Netted Chain) method will be implemented for periodic structures and the result, a screened particle hole irreducible interaction, will be used to calculate the self energy in a correlated GW approximation.

The resulting Euler Lagrange equations for the optimal correlation function are solved by diagonalizing a related eigenvalue problem. The numerical cost of such an approach is comparable to the inversion of the screening function for one frequency in ordinary GW calculations.

1. Mark van Schilfgaarde, Takao Kotani, and S. Faleev. Quasiparticle Self-Consistent GW Theory. Phys. Rev. Lett., 96(22):226402, June 2006.

2. Stephan Lany. Band-structure calculations for the 3d transition metal oxides in GW. Phys. Rev. B, 87(8):085112, February 2013.

3. E. Krotscheck and W. Kohn. Nonlocal Screening in Metal Surfaces. Phys. Rev. Lett., 57(7), 1986.

Efficient conformational sampling of complex adsorbates with Basin Hopping in curvilinear coordinates.

Konstantin Krautgasser[1], *Chiara Panosetti*[1], *Dennis Palagin*[2], *Karsten Reuter*[1], *and Reinhard J. Maurer*[3]

[1]Technische Universität München, Germany
[2]University of Oxford, United Kingdom
[3]Yale University, USA

Continuous computational and methodological advances provide first-principles access to ever larger and more complex adsorbate molecules. The vastly increasing configurational spaces of such molecules nevertheless pose an enormous challenge. Local geometry optimizations of a few chemically motivated adsorption modes are inadequate to sample these spaces and need to be replaced by rigorous global optimization techniques. In those, a crucial role is played by the choice of coordinates representing geometries and trial moves. When aiming for sampling in chemically motivated subspaces the most popular, but physically blind choice of Cartesians is often inefficient. Rather than e.g. testing for adsorption modes of the intact adsorbate, Cartesian trial moves may quickly lead to dissociated structures. We address this by presenting a Basin Hopping (BH) scheme employing Delocalized Internal Coordinates (DICs) suitable for covalently bound systems. In the application to two rather diverse systems we indeed find that such DIC trial moves significantly reduce the sampling efficiency: Retinoic Acid on Au(111) and $Si_{16}H_{16}$ clusters in gas-phase and on Si(001).

Surface phase transition driven by deprotonation reaction

Andrea Floris[1], *Chiara Paris*[1], *Lev Kantorovich*[1]

1. Department of Physics, King's College London, Strand, London WC2R 2LS, UK

Molecular self-assembly on surfaces is of great interest due to large number of applications such as catalysis [1] and fabrication of new functional materials [2,3]. Up to now, a great effort has been given mainly to metallic surfaces [4,5],while comparatively little is known about molecule-surface interaction and chemical reactivity of organic molecules on insulating surfaces. However, for many applications such as molecular electronics, or molecular optics, the replacement of metallic materials with insulators may improve the performance of such devices or be even crucial in some cases (e.g. to eliminate leaking currents).

In collaboration with the experimental group of Prof. A. Kühnle at Mainz University, we aim to understand the reactivity of 2,5-dihydroxybenzoic acid (DHBA), an organic molecule deposited on an insulating substrate of calcite. Non-contact AFM experiments show that DHBA molecules deposited at room temperature initially form two different molecular structures: (i) a striped phase, which consists of hydrogen-bonded molecular dimers and (ii) a dense, highly packed phase of de-protonated molecules covalently bonded to the calcite surface. Interestingly, after several hours of observation the striped phase gradually transforms into the dense one, which then remains the only one present [6]. We have investigated this phase transition by performing DFT calculations in conjunction with kinetics modeling (KMC) and molecular dynamic simulations.

In the present communication, we will show our theoretical results in comparison with most recent experimental measurements.

[1] Nilius N., Risse T., Schauermann S., Shaikhutdinov S., Sterrer M., Freund H. , J. Top.Catal. 54 (2011) 4–12.
[2] Forrest, S. R., Chem. Rev. 97 (1997) 1793–1896.
[3] Umbach, E., Glockler, K. Sokolowsk, Surf. Sci. 402-404 (1998) 20–31.
[4] Rosei, F. Schunack, M. Naitoh, Y. Jiang, P. Gourdon, A. Lægsgaard, E. Stensgaard, I. Joachim, C. Besenbacher, F. Prog. , Surf. Sci. 71 (2003) 95–146.
[5] Barth J. V., Surf. Sci. Rep. 40 (2000) 75–149.
[6] Kittelmann M., Rahe P., Gourdon A., Kühnle, ACS NANO 6 (2012) 7406-7411.

Exchange-correlation kernels in adiabatic-connection fluctuation-dissipation DFT – the renormalized ALDA and other kernels from the electron gas

Christopher E. Patrick[1] *and Kristian S. Thygesen*[1]

1. Centre for Atomic-Scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Although the exchange-correlation kernel is usually associated with excited-state properties through time-dependent DFT, the kernel also presents a pathway to beyond-RPA calculations of ground-state correlation energies via the adiabatic-connection fluctuation-dissipation (ACFD) formalism. Although the adiabatic local-density approximation (ALDA) is known to perform poorly in ACFD-DFT, a number of model kernels have been developed which improve the RPA's description of correlation energy in the homogeneous electron gas (HEG) [1]. Here we present the application of these model HEG kernels to inhomogeneous systems through the calculation of the structural properties of a test set of solids. We assess the importance of the long and short-wavelength limiting behavior of the kernels, compare exchange-only kernels to their full exchange-correlation counterparts, and also consider a simple dynamical kernel. We also place the recently-introduced renormalized ALDA [2] into the context of other HEG kernels and identify promising directions for future study.

[1] M. Lein, E. K. U. Gross and J. P. Perdew, Phys. Rev. B 61, 13431 (2000)

[2] T. Olsen and K. S. Thygesen, Phys. Rev. B 88, 115131 (2013)

Research supported by the Danish Council for Independent Research’s Sapere Aude Program, Grant No. 11-1051390.

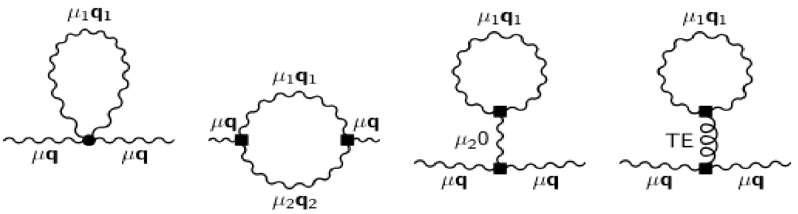
First principle calculation of anharmonic effect on phonon frequency and spectral functions

Lorenzo Paulatto[1], Ion Errea[2,3], Matteo Calandra[1] and Francesco Mauri[1]

1. Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC), Université Pierre et Marie Curie (Paris VI), CNRS UMR 7590, IRD UMR 206, Case 115, 4 place Jussieu, 75252 Paris Cedex 05, France
2. Donostia International Physics Center (DIPC), Manuel de Lardizabal pasealekua 4, 20018 Donostia-San Sebastián, Basque Country, Spain
3. IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Spain

Anharmonic effects can be treated perturbatively as long as they are weak. At lowest order, the harmonic phonon self-energy should be corrected by the four Feynman self-energy diagrams represented in figure. The real part of the diagrams contributes to the phonon lineshift, i.e., to a change of the phonon frequency, while the imaginary part of the diagrams is responsible for the broadening of phonon lines. The three phonon process described by the bubble diagram (B) contributes to both the linewidth and the lineshift, while the loop diagram (L) has a two-phonon fourth-order vertex which contributes exclusively to the lineshift. We have finally decomposed the tadpole diagram in an optical part (TO), which contributes to the relaxation of internal coordinates, and an acoustical part (TA), where the line of zero energy and momentum can be associated to the elastic constants of the material and accounts for the thermal expansion.

The tadpole diagrams reduce to the quasi-harmonic approximation (QHA) under certain conditions.



(L) (B) $(\mathrm{T_O})$ $(\mathrm{T_A})$

The summation of these diagrams *ab initio* requires the knowledge of third- and fourth-order derivative of Born-Oppenheimer total energy. We have developed a method and a chain of computational tools to compute the effect of the four diagrams in the most computationally efficient way. The third order term is computed via the "2n+1" theorem[1]; the fourth order, is treated with the stochastic self-consistent harmonic approximation method[2]. The combination of the two methods allows us to simulate the phonon spectral function, at any energy and momentum; even in the presence of strong anharmonicity, where the density functional perturbation theory breaks down[3].

1. L.Paulatto, F. Mauri, M. Lazzeri. Phys. Rev. B 87, 214303 (2013)
2. I. Errea, M. Calandra, and F. Mauri. Phys. Rev. Lett. 111, 177002 (2013)
3. L. Paulatto, I. Errea, M. Calandra, F. Mauri. *Submitted Phys. Rev. B.*

Seeding, nucleation and reactivity of alumina/$Ni_3Al(111)$ supported metallic nanoclusters: an ab-initio investigation

Jimena A. Olmos-Asar[1], *Erik Vesselli*[2,3], *Alfonso Baldereschi*[1] *and Maria Peressi*[1,4]

[1] Physics Department, University of Trieste, Strada Costiera 11, I-34151 Trieste, Italy
[2] Physics Department and CENMAT, University of Trieste, via Valerio 2, I-34127 Trieste, Italy
[3] IOM-CNR Laboratorio TASC, Area Science Park, S.S. 14 km 163.5, I-34149 Trieste, Italy
[4] IOM-CNR DEMOCRITOS, Trieste, Italy

We investigate the mechanisms of seeding and nucleation of metallic nanoclusters onto an ultrathin alumina template supported on Ni3Al(111) by means of ab-initio density functional theory calculations. Many atoms (Fe, Co, Ni, Cu, Pd, Ag and Au) show preferential occupation of the defective sites of the ordered so-called “dot” structure of the oxide film, where the adsorption is stronger than in the “network” or any other surface site. The relative strength varies with the atomic species, going from the large values of Pd and Ni to the low value of Ag. These results rationalize the experimental evidence showing that some metals such as Pd and Ni create highly ordered patterns of seeds and further nucleation of nanoclusters, whereas others, such as Ag, give rise to less ordered superstructures at room temperature [1].

We study then the interaction of carbon monoxide with a self-seeded ordered array of Cu nanoclusters, comparing simulations with in situ X-Ray Photoelectron Spectroscopy measurements. Adsorption and dissociation of carbon monoxide occur at the copper clusters. The involved mechanisms are investigated at the atomic level, unveiling the effects of cluster finite size, reconstruction, support, and of local CO coverage. It is found that the high coverage of CO at the cluster surface, which considerably exceeds that achievable on single crystal surfaces, facilitates the metal restructuring and the reaction, yielding carbon incorporation into the bulk of the particles [2,3].

[1] J. A. Olmos-Asar, E. Vesselli, A. Baldereschi and M. Peressi, in preparation

[2] J. A. Olmos-Asar, E. Vesselli, A. Baldereschi, and M. Peressi, Self-seeded nucleation of Cu nanoclusters on $Al_2O_3/Ni_3Al(111)$: an ab-initio investigation, Physical Chemistry Chemical Physics 16 (2014) 23134-23142.

[3] J. A. Olmos-Asar, E. Monachino, C. Dri, A. Peronio, C. Africh, P. Lacovig, G. Comelli, A. Baldereschi, M. Peressi, and E. Vesselli, CO on supported Cu nanoclusters: coverage and finite size contributions to the formation of carbide via the Boudouard process, submitted

Low energy polymorphs of glycine from automated crystal structure prediction including vdW-aware functionals.

Cong-Huy Pham[1]*, Emine Kucukbenli*[2]*, Stefano de Gironcoli*[1]

1. International School for Advanced Studies (SISSA), Trieste (Italy)
2. Ecole Polytechnique federele de Lausanne (EPFL), Lausanne (Switzerland)

Accurate ab initio crystal structure prediction of even small organic compounds have been extremely challenging, not only due to polymorphism and molecular flexibility but also due to difficulties in addressing the intra-molecular vdW correlation from first principles [1]. We have recently implemented an accurate description of vdW-aware functionals within Quantum Espresso open source simulation package [2] and demonstrated their success in predicting the right energy ordering of small organic crystals [3]. In this work we combine this development with the recent tools in the field of evolutionary structure prediction for molecular crystals [1] and asses the applicability, strengths and weaknesses of this combination to address real world problems in molecular crystal discovery, using glycine crystals as a test case. The crystal structure of amino acid glycine, with its five stable polymorphs lying very close in energy and its two known phase transitions under pressure, constitutes an excellent testbed for both crystal structure prediction methods and vdW functionals. Here we report on the performance of evolutionary structure discovery algorithms within USPEX and vdW-DF and rVV10 functionals in predicting the phase space of glycine by studying the stability of all experimentally resolved structures up to 20 GPa. We also predict several new glycine crystal structures some of which are energetically more stable than known polymorphs.

[1] Zhu et al. Acta Cryst B68, 215 (2012)
[2] Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009)
[3] Sabatini et al., J. Phys.:Condens. Matter 24, 424209 (2012)

Theophylline self-assembled structures on gold surfaces

Marco Pividori[1], *Carlo Dri*[1,2], *Elena Orselli*[3], *Maria Peressi*[1,2], *Giovanni Comelli*[1,2]

1. Department of Physics, University of Trieste
2. IOM-CNR Laboratorio TASC, Trieste
3. Department of Physics, University of Milan

Theophylline molecule is an alkaloid, a natural nitrogen compound of the xanthine group and plays an important role in several biochemical processes. It has structural and pharmacological properties similar to caffeine and to nucleobases such as adenine and guanine and for this reason the study of this molecule can give us very important information on very simple bio-systems [1,2]. Moreover, since theophylline is also used as a drug to treat respiratory diseases, the knowledge of interactions between the molecules and with the metallic surface may be relevant to the development of specific sensor devices devoted to molecular recognition.

By combining ab initio density functional theory (DFT) calculations and high-resolution scanning tunneling microscopy performed at liquid helium temperature (LT-STM) we characterized at the atomic scale the adsorption structures of theophylline molecules over Au(111) surface. Analogously to other molecules of the xanthine family [3], we have observed that theophylline molecules adsorb on gold surfaces in periodically self-assembled ordered structures. STM images show evidence of two dominant self-assembled periodic structures that are stable even at room or higher temperature, and of homochiral domain boundaries within the racemic self-assembled structures. For each structure, we extracted the starting configurations from the STM data and we performed DFT calculations including van der Waals interactions to find the minimum energy configurations. By comparing experimental and simulated STM images, we characterized the microscopic arrangement of the adsorbed structures, the chirality of the individual molecules and their mutual interactions, obtaining relevant informations about the strength and the nature of the inter-molecular bonds. The self-assembly configurations are dominated by hydrogen bonds and are only weakly interacting with the substrate. We also confirmed the homochirality of the boundary region.

[1] J. Cleaves et al., Chem. Soc. Rev., 2012, **41**, 5502–5525
[2] I. Johnson et al., PLoS ONE, 2012, **7** (12), e50019.
[3] M. Yu et al., ACS Nano, 2011, **5**, 6651

Optical nonlinear properties for solids and nanostructures: theory and numerical simulations

Lucie Prussel, Valérie Véniard

Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA/DSM , 91128
Palaiseau, France and European Theoretical Spectroscopy Facility (ETSF).

A comprehensive understanding of the optical properties of solids is crucial for the improvement of non-linear materials and devices. It offers the opportunity to search for new materials with very specific properties. One particularly important process is second harmonic generation, where two photons are absorbed by the material and a photon, at twice the energy of the incoming photon, is emitted. This process, due to its sensitivity to the symmetry of the system is often used as a probe for studying surfaces and interfaces.

However, the presence of a static electric field inside a material also enables second harmonic generation, through a third order process, named EFISH (Electric Field Induced Second Harmonic). The second harmonic spectroscopy in structures where electric fields are present becomes tricky, since we have to separate the contributions of the second order from those of the EFISH.

We develop theoretical approaches to study this type of non-linear properties in the context of Time-dependent Density Functional Theory (TDDFT) and associated numerical tools for the calculation of second harmonic in the presence of a static electric field (EFISH).

Adsorption of pyridine on graphene

Abhilash R.[1], *H. Lin*[1], *G. Fratesi*[1,2], *G.P. Brivio*[1]

1. Dipartimento di Scienza dei Materiali, Università di Milano- Bicocca, Via Cozzi 53 - 20125 Milano, Italy.

2. Dipartimento di Fisica, Università di Milano, Via Celoria, 16- 20133 Milano, Italy.

Graphene is a two dimensional allotrope of carbon with a honeycomb lattice structure and several unique electronic and optical properties. Our study deals with understanding the interaction of an organic adsorbate on a graphene sheet. Pyridine, C_5H_5N, a basic heterocyclic compound structurally related to benzene is adsorbed on graphene.

The stable configurations of pyridine on graphene are determined by density functional theory considering van der Waals correction including translational as well as rotational degrees of freedom. The most stable configuration of this system is when the nitrogen atom of pyridine is at the center of the graphene ring, with an adsorption energy of -0.60 eV but other cases show similar values pointing to high molecular diffusivity. It is found that neglecting van der Waals interactions underestimates the adsorption strength by one order of magnitude and seriously overestimates the adsorption bond length as well.

The electronic band structure and the density of states of the system reveal minimal interaction of the molecule with the substrate also shown by Löwdin population analysis. Further we examine the near-edge X-ray absorption fine structure (NEXAFS) spectrum of the system using the transition-potential approach.

Spin-Orbit interactions in single layer and nanoribbons of $NiSe_2$.

J. A. Reyes Retana[1], G. G Naumis[2], F. Cervantes-Sodi[1]

1.Departamento de Física y Matemáticas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880, Lomas de Santa Fe, 01219, DF, México.

2. Departamento de Física-Química, Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Apartado Postal 20-364, 01000 México, Distrito Federal, México,

The spin-orbit interaction effect in the two-dimensional $NiSe_2$ centered honeycomb is presented. Also, the effect in their corresponding six different zigzag nanoribbons and two armchair nanoribbons are described. By means of density functional theory and fully relativistic psedupotentials, the electronic properties of these quasi-one dimensional materials are analyzed to investigate the effect of the spin-orbit interaction. All *ab initio* calculations were performed with the Quantum ESPRESSO plane wave DFT and density functional perturbation theory (DFPT) code, available under the GNU Public License. The inclusion of the spin-orbit interaction leads to a metallic behavior in 2D-$NiSe_2$ while without such interaction the system is a semiconductor with a bandgap of 0.11 eV. The effect of the spin-orbit interaction in the nanoribbons is about 0.10 eV. As a result of the reconstruction, all zigzag nanoribbons are metallic, but when they are passivated, only two of them became semiconductors. In the case of armchair nanoribbons, the two families bare and passivated are semiconductors. The highest bandgap value is for the passivated armchair with a energy of ~0.6 eV. Also, the study of the bandgap as a function of the zigzag- and armchair nanoribbons widths are discussed.

Thermoelectric properties of AgSbTe2 from first-principles calculations

Nafiseh Rezaei[1], S. Javad Hashemifar[1,2] and Hadi Akbarzadeh[1]

1 Department of Physics, Isfahan University of Technology, 84156-83111 Isfahan, Iran
2 Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, 84156-83111 Isfahan, Iran

The structural, electronic, and transport properties of AgSbTe2 are studied by using full-relativistic first-principles electronic structure calculation and semiclassical description of transport parameters. The results indicate that, within various exchange-correlation functionals, the cubic $Fd\bar{3}m$ and trigonal $R\bar{3}m$ structures of AgSbTe2 are more stable than two other considered structures. The computed Seebeck coefficients at different values of the band gap and carrier concentration are accurately compared with the available experimental data to speculate a band gap of about 0.1–0.35 eV for AgSbTe2 compound, in agreement with our calculated electronic structure within the hybrid HSE (Heyd-Scuseria-Ernzerhof) functional. By calculating the semiclassical Seebeck coefficient, electrical conductivity, and electronic part of thermal conductivity, we present the theoretical upper limit of the thermoelectric figure of merit of AgSbTe2 as a function of temperature and carrier concentration.

Density functional investigation of spin polarization in bulk and thin films of nitrogen intercalated Cu_3N

Seyed Mojtaba Rezaei Sani[1], *Masoud Karimipour*[2], *Marzieh Ghoohestani*[3], *Seyed Javad Hashemifar*[4]

1. Computational Physical Sciences Research Laboratory, School of Nano-Science, Institute for Research in Fundamental Sciences (IPM), Tehran, Iran

2. Department of Physics, Vali-E-Asr University of Rafsanjan,77139-36417 Rafsanjan, Iran

3. Nano research center, Department of Physics, Malek Ashtar University of Technology, Shahin Shahr, Isfahan, Iran

4. Department of Physics, Isfahan University of Technology, Isfahan, 84156-83111, Iran

It has been reported theoretically that the intercalation of nitrogen in the voids of the rather open cubic structure of bulk Cu_3N build up a magnetic structure. In an extended effort to study this system, we have investigated spin polarization in bulk and thin films of nitrogen intercalated Cu_3N (Cu_3N_2) structure by means of first-principles calculations based on Kohn-Sham density functional theory and ultrasoft pseudopotentials technique. Contrary to the previous studies, the results show that after an accurate structural relaxation of the system, magnetism in the bulk structure vanishes. This effect is due to the migration of the intercalated nitrogen atom from the body center of the cell to the nearness of one of the cell faces. Similar study for the thin films of 5, 7, 9 and 11 monolayers thickness was performed and it was found that initial relaxation of structures with 7 and 11 monolayers show a net magnetic moment of 2.6 μ_B. By a more extended survey of the energy surfaces, the film with 7 monolayers loses its magnetic moment similar to the bulk structure but the film with 11 monolayers maintains its magnetic moment. It is possibly a new quantum size effect that keeps the intercalated nitrogen atom of the middlemost cell at the body center site. Electron density map of this film clearly confirms the spin polarization upon the intercalated atom.

Feasible and reliable *ab initio* calculations of materials relevant for nuclear waste management

Jose Jorge Rios Ramirez, George Beridze, Yan Li, Ariadna Blanca Romero and *Piotr M. Kowalski

Institut für Energie- und Klimaforschung (IEK-6) Nukleare Entsorgung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany; *contact: p.kowalski@fz-juelich.de

Safe nuclear waste management is a challenging problem faced by nuclear engineering utilizing societies. One of the major tasks is to find good materials capable to permanently immobilize radionuclides and improve the yet limited understand of the surface reactivities of the nuclear materials, such as spent nuclear fuel. One considered solution in management of nuclear waste is the immobilization of the radionuclides in ceramic materials, such as monazite and pyrochlore, that are known to resist the radiation damage. Around the World there exist several ongoing research projects devoted to understanding the interaction of actinide elements with such materials. In principle, with modern computational resources and the state-of-the-art ab initio quantum chemistry methods it should be possible to make a significant contribution to this research field by doing atomistic simulations. However, Density functional Theory (DFT), which is usually the only method of choice for *ab initio* simulation of chemically complex materials, often dramatically fails to describe systems containing strongly correlated *f*-electrons [1]. The resulting necessity of using hybrid-functionals or unfeasible post-Hartree-Fock techniques such as CCSD(T) significantly limits the size and complexity of materials that could be investigated [2, 3]. In this study we present an assessment of the performance of different, feasible DFT-based computational methods in prediction of the structural and thermodynamic properties of actinide- and lanthanide-bearing materials such as simple uranium-bearing compounds and solids, monazite-type orthophosphates ($LnPO_4$), pyrochlores ($Ln_2(Zr,Hf)_2O_7$) and water-covered PuO_2 surfaces. We show that properties of these materials can be reliably computed with DFT+U method, where Hubbard U value is derived *ab initio* [4], at the level of much more computationally demanding methods [5,6]. We also present the results of the systematic DFT+U investigation of structure of water adsorbed on PuO_2 surfaces. We will show and interpret the stability diagrams of such surfaces obtained with the methods of *ab initio* thermodynamics.

References:

[1] Weng *et al., Chem. Rev.*, **2013**, **113**, **1063** [2] G. A. Shamov, G. Schreckenbach, and T. N. Vo *Chem. Eur. J.* **2007**, **13**, **4932**. [3] C.Hattig, "Computational Nanoscience: Do It Yourself!", S. Blügel, D. Marx, John von Neumann Institute for Computing, Jülich, NIC Series, **2006**, **31**, **245**. [4] M. Cococcioni and S. de Gironcoli , *Phys. Rev. B*, **2005**, **71**, **035105**. [5] A. Blanca Romero *et al*., J. comput. Chem. **2014, 35, 1339.** [6] G. Beridze and P. M. Kowalski, *submitted to J. Phys. Chem. A*.

Dielectric matrix formulation of correlation energies within the Random Phase Approximation: Inclusion of (screened) exchange effects

Dario Rocca[1,2], *Bastien Mussard*[1,2], *Georg Jansen*[3], *János G. Ángyán*[2,1]

1. University of Lorraine, Nancy (France)
2. CNRS, Nancy (France)
3. University of Duisburg-Essen (Germany)

Starting from the general expression of the ground state correlation energy in the adiabatic connection fluctuation dissipation theorem (ACFDT) framework, it is shown that the dielectric matrix formulation, which is usually applied to calculate the random phase approximation (RPA) correlation energy, can also be used for alternative RPA expressions including exchange effects. Within this framework we derive equations for the correlation energy within the second order screened exchange (SOSEX), an approximate time-dependent Hartree-Fock (TDHF), and second order Moller-Plesset (MP2) levels of theory. The accuracy of these approaches can be further improved by introducing the effect of the screening to obtain an approximate formulation of the Bethe-Salpeter equation for correlation energies. The proposed formalism is particularly suitable for implementation in periodic boundary condition plane-wave codes, in particular by using a compact basis set to represent dielectric matrices [1]. To demonstrate the accuracy of these approaches the binding curves of several diatomic molecules will be shown.

[1] D. Rocca, J. Chem. Phys. 140, 18A501 (2014)

A multi-scale protocol for simulating the optical properties of natural dyes in solution

Marta Rosa[1], Marco Micciarelli[1], Stefano Baroni[1,2], Alessandro Laio[1]

1 Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Beirut 2-4, I-34014 Trieste, Italy
2 CNR-INFM DEMOCRITOS Theory@Elettra Group, I-34014 Trieste, Italy

The optical properties of natural dyes in solution result from the statistical average of the spectra arising from different molecular geometries. Sampling the relevant configuration space is hindered by the long time taken by the system to hop from one conformer to the next. Here we propose a multi-scale approach to cope with this problem, based on a combination of classical molecular dynamics (MD), ab initio (AI) MD, and advanced clustering techniques [1], to address configurational sampling, and time-dependent density-functional theory (TDDFT) [2] to address optical spectroscopy. The conformational free-energy landscape of the system is first sampled using classical MD and the relevant conformers identified and classified using a recently proposed clustering algorithm [1]. A first estimate of the conformers' free energies is obtained from a cluster population analysis. The bias introduced by the classical force field is then corrected with the differences between classical and ab-initio energies computed for selected configurations within a same conformer. The optical activity of different conformers is determined as the time average of the spectra computed on the fly over an AIMD trajectory within a same conformer [3], using the recently developed Liouville approach to TDDFT [2]. In order to enhance the statistics, while keeping the numerical labor at an acceptable level, TDDFT spectra are evaluated once every many MD time steps, and interpolated in-between using an empirical but well controlled relation between TDDFT and independent-electron spectra, the latter being much cheaper to compute. The overall optical activity is finally evaluated by averaging the contributions from different conformers, weighted with the free energies previously determined. This methodology is being benchmarked in the paradigmatic case of cyanin (cyanidin 3-glucoside), a natural dye whose derivatives are receiving great attention in the food and pharmaceutical industries, and some preliminary results will be reported.

[1] Rodriguez, Science 344 (6191), 1492-1496
[2] D. Rocca et al., J. Chem. Phys. 128, (2008); X. Ge, al. Computer Physics Communications 185.7 (2014)
[3] B.O. Malcioglu et al. JACS 133, (2011), X. Ge et al, DOI 10.1016/j.cplett2014.09.025

Latent heat of magnetization for $MnFeSi_{0.33}P_{0.66}$

Prasenjit Roy[1], *R. A. de Groot*[1]

1. Theoretical chemistry group, Institute of molecules and materials, Radboud University, Nijmegen, Netherlands

Magnetic refrigeration is a very promising environmental-friendly method to encounter the energy shortage of the world by implementing the magnetocaloric effect (MCE) [3]. Various materials were proposed in the last decade as the suitable candidate for magnetic refrigeration. MnFeSiP series of material is distinguishable among them for the use of non-toxic, inexpensive elements and also for very high efficiency. There are several ways to measure the efficiency of the MCE, viz.- measuring the adiabatic temperature change (ΔT_{ad}) or measuring the entropy change at the transition. MnFeSiP materials show a first order magneto-elastic phase transition at the Curie temperature (T_C). This simultaneous occurrence of the magnetic and elastic transition in this material account for a higher ΔT_{ad} (or high entropy change) [1], which is linearly proportional to the Latent heat (L) of magnetization.

$$L = \{| Q_{L\text{-}H} | - | Q_{H\text{-}L} |\}/ 2m$$

Where $Q = mC_P\Delta T_{ad}$, Q_{L-H} and $Q_{H\text{-}L}$ are the heat exchange during low to high and high to low temperature transition.

Experimentally L can be determined with techniques such as Differential Scanning Calorimetry (DSC). Heat flow is measured directly from the sample and that accounts for the latent heat of the system [2]. The calculation of L theoretically is not straightforward. In our study we use Viena Ab-initio Simulation Package (VASP) in addition to the Phonopy package, to determine the finite temperature properties of the system. Quasi Harmonic Approximation (QHA) was applied successfully to determine the Gibbs free energy (G) of $MnFeSi_{0.33}P_{0.66}$. Hence we show a phase transition around 425 K (close to the experimental T_C). From the temperature derivative of G , the specific heat (C_P) was obtained and finally the latent heat was calculated. Our calculated value matches well with the experiments.

References:

[1]. N. H. Dung et. al. Advanced Energy Materials, 1(6):1215–1219, 2011

[2]. Mohammadreza Ghahremani et al. J. Appl. Phys., 113:17A943, 2013

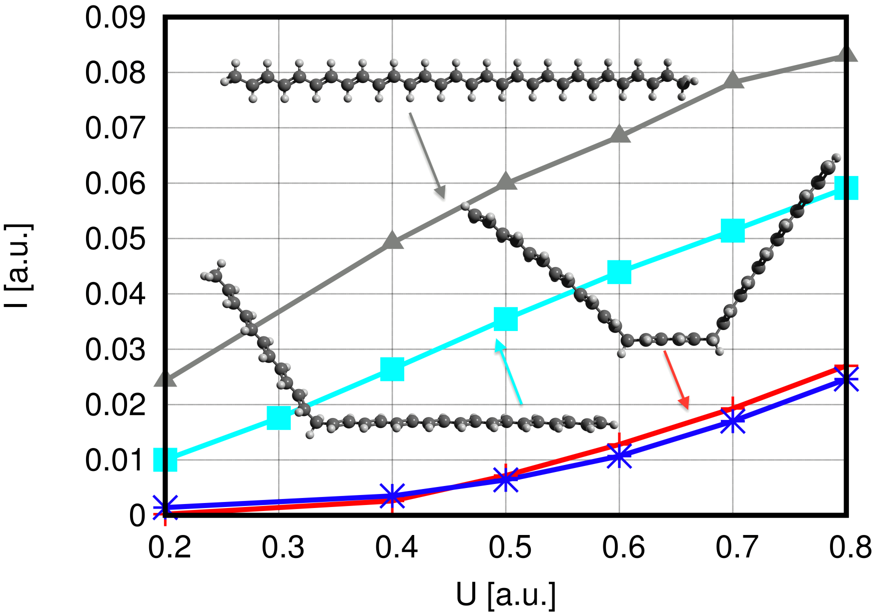
[3]. V. K. Pacharschy et al. Phys. Rev. B., 64:144406, 2001

A real-time DFT scheme for electronic transport

Philipp Schaffhauser[1], *Stephan Kümmel*[1]

1. Theoretical Physics IV, University of Bayreuth, Germany

We present an approach for calculating the charge transport through molecular systems that relies on solving the time-dependent Kohn-Sham equations in real-time and real-space. So far, propagation methods were mostly used for closed quantum systems and therefore did not allow for studying transport problems which involve a source and a drain. We resolve this problem by introducing absorbing and anti-absorbing boundary conditions. By comparing to established results we verify our computational scheme. Using the new formalism we examine how molecular distortions, and, e.g., breaks in the conjugation of organic systems, change the molecular conductivity. Furthermore we investigate the charge transport in a "molecular loop".



The figure shows first principle calculations of the current-voltage dependence for three molecules. The first molecule is Polyacetylen. In the second one the conjugation of Polyacetylen is interrupted by one CH_2 group and in the third one by two CH_2 groups, which leads to different numbers of kinks in the chain. Each kink reduces the conductivity of the chain by about a factor of two.

Exploring a non-local correlation functional: One-electron self-interaction, potential asymptotics, and localized states

Tobias Schmidt[1], *Stephan Kümmel*[1]

1. Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, Germany.

The performance of Kohn-Sham density functional theory (KS DFT) in ground-state energy calculations depends strongly on how the one-electron self-interaction (SI) error is treated in the exchange-correlation (xc) functional approximation that is used. The SI-error in particular limits the interpretability of the KS eigenvalues, e.g., the quality of the results that one obtains with (semi-)local functionals for the density-of-states or ionization potentials (IPs). On the other hand, functionals with an inherent SI-error such as the LDA or Generalized Gradient Approximations can lead to reasonable accuracy for binding energies or geometries of molecules.

We here present a new, non-local correlation functional that is compatible with exact exchange [1]. The functional is of local hybrid form and aims at a good description of binding properties while at the same time yielding physically meaningful eigenvalues. We discuss resulting improvements, but also limitations in achieving this aim. Similar observations are made for almost any class of density functional approximation.

By analyzing the local multiplicative KS potential, we demonstrate that although the functional is SI free, its potential does not reach the correct form in the limit |r| → ∞ for finite systems (see Fig. 1) [2]. We therefore investigate the connection between SI and the potential asymptotics. Furthermore, we focus on the electronic structure of systems containing transition metals and the interpretation of their KS eigenvalues as a physical density-of-states. As such systems typically resist a satisfying description via standard DFT methods due to their localized *d*-states, using a novel functional with a non-local correlation part may open new applications in material sciences.

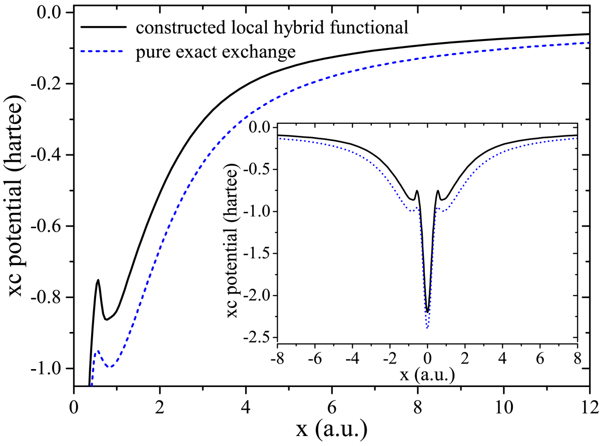


Fig. 1 The xc potential of the Carbon atom computed with the designed local hybrid functional in comparison to pure exact exchange along the numerical grid.

---

[1] T. Schmidt, E. Kraisler, A. Makmal, L. Kronik, and S. Kümmel, J. Chem. Phys. **140**, 18A510 (2014).

[2] T. Schmidt, E. Kraisler, L. Kronik, and S. Kümmel, Phys. Chem. Chem. Phys. **16**, 14357 (2014).

First-principles based descriptor for intrinsic charge carrier mobility in organic devices

Christoph Schober[1], *Karsten Reuter*[1], *Harald Oberhofer*[1]

1. Lehrstuhl für Theoretische Chemie, Technische Universität München

In organic electronics charge carrier mobility is a key performance parameter. Due to the complex manufacturing processes of e.g. organic field effect transistors (OFETs) measured mobilities are often heavily affected by the device preparation. This masks the intrinsic materials properties and therewith hampers the decision whether further device optimization for a given organic molecule is worthwhile or not. Within hopping models based e.g. on Marcus theory the intrinsic mobility can be reliably calculated from first principles. Using a perturbative approach to this theory we formulate a descriptor that can be efficiently calculated for a wide range of organic molecules. For this descriptor we obtain good correlations to fully calculated mobilities, as well as to highest-quality experimental data where device preparation uncertainties are minimized. This suggests the descriptor as a useful tool for materials screening and quick assessment of device-related influences in measured mobilities.

Blue phosphorene - metal interface study from first principles

Devina Sharma[1] *and Shobhana Narasimhan*[1]

1. Theoretical Science Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore 560064 India

Blue phosphorene (BP), a theoretically predicted stable allotrope of black phosphorene with a wide electronic band gap of ~2eV [1-2] is seen as a potential contender for next generation electronics. Fundamental study of metal-phosphorene contact is a prerequisite for its use in device fabrication. Therefore, we here present theoretical investigation of the interfacial properties of monolayer of blue phosphorene on metal substrates using density functional theory. The adsorption of BP on metal surfaces, having lattice mismatch less than 5% comprising of Zr and Sc (0001) and Ag, Au, Al, Pt and Cu (111) is studied. The interfacial properties for different metal substrates are studied by analyzing geometry, bonding, charge transfer, metal-phosphorene work function and electronic structure.

References:

[1] Zhen Zhu and David Tomanek, Phys. Rev. Lett. 112, 176802 (2014)

[2] Jiefeng Xie, M. S. Si, D. Z. Yang, Z. Y. Zhang and D. S. Xue, J. Appl. Phys. 116, 073704 (2014)

On the orbital ordering transition in $KCuF_3$

Hunter Sims[1], *Eva Pavarini*[2], *Erik Koch*[1]

1. Dept. of Computational Materials Science, German Research School for Simulation Sciences, 52428 Jülich, Germany
2. Institute for Advanced Simulation, Forschungszentrum Jülich, 52428 Jülich, Germany

The Mott insulating perovskite $KCuF_3$ is considered the paradigmatic system with long-ranged orbital order and a cooperative Jahn-Teller distortion of the F-octahedra. This broken symmetry state is usually understood as the result of the destabilization of the symmetric structure due to crystal-field splitting (Jahn-Teller effect) or to super-exchange between the orbitals (Kugel-Khomskii mechanism), which leads to a gain in energy with increasing distortion, which is counteracted by the quadratic deformation energy of the lattice. In this picture, it is expected that, as a consequence of the lattice entropy, with increasing temperature the distortions will be gradually reduced, eventually vanishing at the ordering temperature T_c. Such a transition is, however, not found experimentally. We explain its absence.

First-principles methods for 2D materials: electron-phonon interaction, strain-induced fields and screening in graphene.

Thibault Sohier[1]

1. *Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR 206, 4 Place Jussieu, F-75005 Paris, France*

We use first-principles calculations, at the density-functional-theory (DFT) and GW levels to study the electron-phonon interaction for acoustic phonons in graphene. This includes the so-called gauge field and deformation potential. We find that the main contribution is the unscreened acoustic gauge field, while the deformation potential is strongly screened and negligible [1,2].

We use the phonon package of Quantum ESPRESSO to verify and refine existing analytical models for the coupling of electrons to acoustic phonons. However, within this framework, GW corrections are inaccessible and the screening of the deformation potential is incorrect due to the presence of periodic images.

To calculate the coupling parameters within the GW approximation, we propose a method [2] based on band structure calculations in strained graphene. We interpret the zero-momentum limit of acoustic phonons as a strain of the crystal unit cell and link electron-acoustic phonon coupling to the strain-induced pseudomagnetic field. This "static strain" method also gives access to the bare deformation potential.

To evaluate the screening effects on the deformation potential, we evaluate the static 2D dielectric function within density functional perturbation theory (DFPT) [3]. The response of the electronic density to an external potential is calculated in a two-dimensional framework by a careful treatment of the long-range behavior of the Coulomb interaction. We then apply the resulting static dielectric function of single-layer graphene to the bare deformation potential to obtain the screened deformation potential.

The methods presented here can be applied to other 2D materials, and the results in the case of graphene suggest the importance of further developments in the field of DFT simulation of 2D materials in general.

[1] C.-H. Park, N. Bonini, T. Sohier, G. Samsonidze, B. Kozinsky, M. Calandra, F. Mauri, and N. Marzari, Nano Lett. **14**, 1113 (2014).

[2] T. Sohier, M. Calandra, C.-H. Park, N. Bonini, N. Marzari, and F. Mauri, Phys. Rev. B **90**, 125414 (2014).

[3] T. Sohier, M. Calandra, and F. Mauri, in preparation.

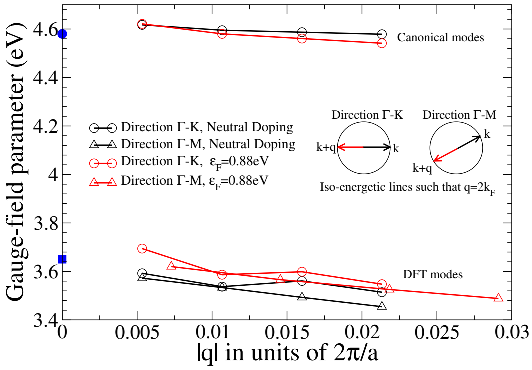


Fig. 1: Gauge field parameter of graphene calculated within DFPT and using the static strain method (dots at q=0).

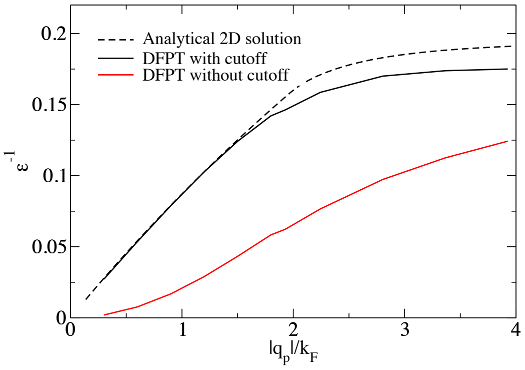


Fig. 2: Effects of interlayer interactions in DFPT calculations of the 2D inverse dielectric function of doped graphene.

A theoretical analysis of the role of defects and doping in hexagonal boron nitride sheets

Himadri R. Soni[1], *Prafulla K. Jha*[2]

1. Lehrstuhl für Theoretische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Universitat Erlangen- Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany.
2. Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, India

Density functional theory studies are reported namely to analyze the hexagonal boron nitride (*h*-BN) sheets, both pristine and doped with carbon. The electron-ion interactions have been modeled using ultrasoft pseudopotentials and the exchange-correlation energies have been approximated by the method of the Perdewu-Zunger for the local density approximation (LDA). In this work, we have studied pristine h-BN sheets, one carbon atom doped *h*-BN, four carbon atoms doped h-BN and defect induced h-BN sheets. The optimal geometries, binding energies, density of states (DOS), phonon dispersion curves (PDS) and phonon density of states were obtained. Phonon dispersion curves show that single carbon doped *h*-BN sheets are dynamically stable whereas four carbon atoms doped *h*-BN sheets are dynamically unstable. We also study the vacancy defect in *h*-BN sheets. We have also calculated the work function of pristine *h*-BN, carbon doped *h*-BN and defect induced *h*-BN and observed that the work function is directly related to the band gap and doping or defect in the structure.

Physical Factors Influencing Excited State Charge Transfer at the Perylene – Titanium Oxide Interface

O.A. Syzgantseva(1,2), K. Laasonen(2), M. Puska(1)

1. COMP, Department of Applied Physics, Aalto University, P.O. Box 11100 FI-00076 Aalto, Finland
2. COMP, Department of Chemistry, Aalto University, P.O. Box 16100 FI-00076 Aalto, Finland

Physical factors, affecting the amount and the rate of dynamical excited state charge transfer (CT) at the anchored perylene molecule – titanium oxide interface, are considered within Real-Time propagation Time-Dependent Density-Functional Theory (RT-TDDFT) and Ehrenfest Dynamics (ED) formalisms [1], implemented in the GPAW program [2]. The influence of ionic dynamics on the rate and amount of CT is analysed. The impact of the perylene anchor group (COO- or COOH) and the details of the initial excitation on the process dynamics is considered. By the increase of the size of the computational TiO_2 system the transferred charge saturates toward one electron, and electron injection rates become coherent with experimental and theoretical literature data [3].

[1] A.Ojanperä, V. Havu, L. Lehtovaara, M. Puska, J. Chem. Phys. 136, 144103 (2012)
[2] J. Enkovaara et al. J. Phys. Condensed Matter, 22, 253202 (2010)
[3] O.A. Syzgantseva, M. Puska, K. Laasonen, J. Phys. Chem. C, 118, 25310 (2014)

Self-Consistent Continuum Solvation model for the optical properties of complex molecular systems in solution

Iurii Timrov[1], Oliviero Andreussi[2], Alessandro Biancardi[1], Nicola Marzari[3], and Stefano Baroni[1]

1. SISSA - Scuola Internazionale Superiore di Studi Avantazi, Trieste, Italy
2. Department of Chemistry, University of Pisa, Pisa, Italy
3. EPFL - Ecole Polytechnique Federale de Lausanne (THEOS), Lausanne, Switzerland

We present a new method to compute the optical properties of complex molecular systems in solution, based on the Liouville-Lanczos approach [1] to Time-Dependent Density-Functional Theory [2], as implemented in the “turboTDDFT” component [3] of the Quantum ESPRESSO distribution [4], and the recently proposed revised self-consistent continuum solvation (SCCS) model [5], as implemented in the “Environ” component of Quantum ESPRESSO. In the spirit of the Polarizable Continuum Model (PCM) [6], the solvent is modelled by a continuous polarizable medium. At variance with it, however, the shape and size of the cavity hosting the solute is determined self-consistently depending on the molecular electron ground-state charge-density distribution. The new method, which has been implemented in the turboTDDFT component of Quantum ESPRESSO, has been benchmarked on the 4-Aminophthalimide molecule in water, resulting in a remarkable agreement with the results obtained from the implementation of the PCM in the Gaussian code [7].

[1] D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008).

[2] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[3] O.B. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni, CPC 182, 1744 (2011).

[4] P. Giannozzi et al., J. Phys.: Condens. Matter 21, 395502 (2009). www.quantum-espresso.org

[5] O. Andreussi, I. Dabo, and N. Marzari, J. Chem. Phys. 136, 064102 (2012).

[6] J. Tomasi, B Mennucci, and R. Cammi, Chem. Rev. 105, 2999 (2005).

[7] M.J. Frisch et al., Gaussian, Inc., Wallingford CT (2004). www.gaussian.com

Spin asymmetric band gap opening in graphene by Fe adsorption

E. del Castillo[1,2], *F. Cargnoni*[1,2], *S. Achilli*[1,2], *M.I. Trioni* [1,2]

1. Chemistry Department, University of Milan, via Golgi 19, 20133 Milano, Italy
2. CNR, National Research Council of Italy, ISTM, via Golgi 19, 20133 Milano, Italy

The adsorption of Fe atom on graphene is studied by first-principles density functional theory using the SIESTA code [1]. The structural, electronic, and magnetic properties are analyzed at different coverages, all preserving C_{6v} symmetry for the Fe adatom. We observed that binding energies, magnetic moments, and adsorption distances rapidly converge as the size of the supercell increases.
Among the considered supercells, those constituted by $3n$ graphene unit cells show a very peculiar behavior: the adsorption of a Fe atom induces the opening of a spin-dependent gap in the band structure. In particular, the gap amounts to tenths of eV in the majority spin component, while in the minority one it has a width of about 1~eV for the 3×3 supercell and remains significant even at very low coverages (0.25~eV for θ=2%).
The comparison with all the other $3d$ adsorbates (Sc-Ni) shows that these features are peculiar of Fe only. In fact all the other kind of adsorbate retains the metallic behavior also for the $3n$ family of coverages [2].

To explore the effects on the electronic transport properties we calculated the transmission coefficient T(E) and the electric current using the TranSIESTA code [3], which combines the non-equilibrium Green's function (NEGF) technique with density functional theory. The junction is constituted by two pure graphene semiinfinite electrodes with a Fe covered nano-dimensional graphene in between. Two different coverages are considered showing very different spin-polarization of the current.

References

[1] J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14,** (2002) 2745.
[2] E. del Castillo, F. Cargnoni, S. Achilli, G.F. Tantardini, M.I. Trioni, ”Spin asymmetric band gap opening in graphene by Fe adsorption”, *Surf. Sci.* (2014) in press.
[3] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, *Phys. Rev. B* **65,** (2002) 165401.

Modelling Cancellation Effects in the Optical Response of Many-Electron Systems

Marilena Tzavala[12]*, Claudia Rödl*[12]*, Lucia Reining*[12]

1. Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA, CNRS, 91128 Palaiseau cedex, France
2. European Theoretical Spectroscopy Facility (ETSF)

The state-of-the-art *ab initio* method to describe excitonic excitations in solids is the solution of the Bethe-Salpeter equation (BSE) based on a Kohn-Sham electronic structure with *GW* quasiparticle corrections for the energy eigenvalues. This approach is based on the idea to first create an electron and a hole in the system (*GW*) and describe their interaction in a second step (BSE). Indeed, in spectroscopies such as optical absorption or energy loss, the number of electrons does not change. Therefore, it seems more natural to calculate these spectra by means of time-dependent density-functional theory (TDDFT).

For many solids, ranging from *sp* semiconductors to correlated insulators with open *d* shells, strong cancellation effects between the *GW* quasiparticle corrections and the electron-hole attraction are found. This observation may guide the search for new exchange-correlation kernels that can capture also excitonic effects. In order to elucidate the mechanisms that govern this cancellation, we study simple model systems for the self-energy.

Poster Title: Tuning spin transport properties and molecular magnetoresistance through contact geometry.

Abstract:

Molecular spintronics seeks to unite the advantages of using organic molecules as nanoelectronic components, with the benefits of using spin as an additional degree of freedom. For technological applications, an important quantity is the molecular magnetoresistance. In this work, we show that this parameter is very sensitive to the contact geometry. To demonstrate this, we perform *ab initio* calculations, combining the non-equilibrium Green's function method with density functional theory, on a dithienylethene molecule placed between spin-polarized nickel leads of varying geometries. We find that, in general, the magnetoresistance is significantly higher when the contact is made to sharp tips than to flat surfaces. Interestingly, this holds true for both resonant and tunneling conduction regimes, i.e., when the molecule is in its "closed" and "open" conformations, respectively. We find that changing the lead geometry can increase the magnetoresistance by up to a factor of ~5. We also introduce a simple model that, despite requiring minimal computational time, can recapture our *ab initio* results for the behavior of magnetoresistance as a function of bias voltage. This model requires as its input only the density of states on the anchoring atoms, at zero bias voltage. We also find that the non-resonant conductance in the open conformation of the molecule is significantly impacted by the lead geometry. As a result, the ratio of the current in the closed and open conformations can also be tuned by varying the geometry of the leads, and increased by ~400%.

Reference:

1. "Tuning spin transport properties and molecular magnetoresistance through contact geometry", Kanchan Ulman, Shobhana Narasimhan, and Anna Delin, Journal of Chemical Physics, 140, 044716 (2014).

Ab initio study of structural and vibrational properties of energetic solids

G. Vaitheeswaran*

Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad,
Prof. C. R. Rao Road, Gachibowli, Hyderabad-500046, India.

Solid energetic materials play an important technological role as explosives and fuels. Inorganic azides, a class of energetic systems, are potential model systems to study fast reactions in solids because they are chemically and structurally simple among solids that can deflagrate or detonate. Most of the inorganic azides show variation in stability towards heat, light, and shock. They undergo decomposition into metal and nitrogen under the action of suitable wave length of light (ultra-violet light) and even detonation may result when the temperature is close to their melting point[1]. These metal azides can also be used as a parent compound to obtain polymeric nitrogen, an ultimate green high energy material[2,3]. To understand the decomposition phenomena, knowledge of electronic band structure and optical properties are essential. In this talk, I will present the results of density functional calculations on various metal azides and NH_4N_3 systems. Although the decomposition process is a non-adiabatic phenomenon, as a first level of understanding, we have used adiabatic approximation for the description of the structural, electronic, optical and vibrational properties of the systems. As these compounds are molecular solids, we also include the semi-empirical vander Waals interactions (vdW) in our calculations for the complete description of the crystal structures. The high pressure structural behavior of KN_3, RbN_3 will be discussed [4,5,6]. The results on structural, electronic, bonding and optical properties of orthorhombic ammonium azide (NH_4N_3) will also be presented [7].

***E-mail:** vaithee@uohyd.ac.in

References

1. Uddin, J.; Barone, V.; and Scuseria, G. E, Mol. Phys, **2006**, 104, 745.
2. Eremets, M. I.; Gavriliuk, Alexander G.; Trojan, I. A.;, Dzivenko Dymitro A.; Boehler, R, Nat. Mat, **2004**, 3, 558.
3. Eremets, M. I.; Popov, M. Yu.; Trojan, I. A.; Denisov, V. N.; and Boehler, R.; Hemley, R. J, J. Chem. Phys, **2004**, 120, 10618.
4. Ramesh Babu, K.; Bheema Lingam, Ch.; Tewari, S. P.; Vaitheeswaran, G, J. Phys. Chem A, **2011**, 115, 4521.
5. Ramesh Babu, K ; Vaitheeswaran, G, Chem. Phys. Lett, **2012**, 533, 35.
6. Vaitheeswaran. G and Ramesh Babu K, J. Chemical Sciences. **2012,** 124, 1391.
7. Yedukondalu, N.; Vikas D Ghule and G. Vaitheeswaran.; J. Phys. Chem. C. **2012**, 116, 16910.

Protein field effects on electronic excitations of biological chromophores: a QMC and GW/BSE approach in QM/MM environment.

Daniele Varsano[1] *, Emanuele Coccia*[2] *, Olivia Pulci*[2] *, Adriano Mosca Conte*[3] *,*
Leonardo Guidoni[2]

1. S3 Center, CNR Institute of Nanoscience, via Campi 213/A, 41125 Modena, Italy
2. Dipartimento di Scienze Fisiche e Chimiche, Universitá degli Studi dell'Aquila, via Vetoio, 67100 Coppito, L'Aquila, Italy
3. ETSF, Dipartimento di Fisica, Universitá di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

The accurate calculation of electronic excited states of large and electronically correlated biological chromophores in their complex protein environment still represents a challenge for quantum chemistry. Two ab initio techniques are recently emerging as candidates to correctly tackle this issue: Quantum Monte Carlo (QMC) calculations for the ground state geometry optimization, and Many Body Green's Function Theory (GW/BSE) for exited state energies. In the present work we use the Variational Monte Carlo (VMC) to carry out structural optimizations and we present an extension of MBGFT to complex environments, using a Quantum Mechanics/Molecular Mechanics framework. This technique is applied to evaluate the optical properties of the retinal protonated Schiff base (RPSB) chromophore in rhodopsin, the protein responsible for dim light vision in the vertebrates. The comparison between these excitation energies and that obtained for a gas phase calculation on a retinal geometry obtained in the protein environment reveals the essential role of the protein field in the spectral tuning of the molecule.

Adsorption and dissociative adsorption of Nitric Oxide (NO) on Rh cluster over MgO(001) surface

Vasudevan M V[1], Bulumoni Kalita[1], Prasenjit Ghosh[2] and Shobhana Narasimhan[1]

1 Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064
2 Departments of Chemistry and Physics, Indian Institute of Science Education and Research-Pune, Pune 411021

Abstract

Among various gases present in automobile exhaust Nitric oxide (NO) is an important and hazardous component for ecology and health. NO can cause acid rain, depletion in ozone layer and many more effects. So it is desirable to convert NO to other harmless forms like N_2[1]. This can be achieved through catalytic decomposition of NO as done in three way catalytic converters of automobiles. Dissociation of NO is the rate limiting step in this process [2]. Rhodium (Rh) has found to be an efficient catalyst which can adsorb and dissociate NO [3] and adsorption of NO over gas phase Rh clusters are studied previously[4] . In experimental scenario it is difficult to characterize a free standing cluster lacking a host support [5]. So in this work we have placed the Rh_n clusters ($n \leq 4$) over MgO(001) surface and studied the adsorption of NO gas and co-adsorption of N and O.

References

[1] S. Shetty et al., J. Phys. Chem. C. 113 (2009)
[2] E.H.G. Backus et al., J. Chem. Phys. 92 (1998)
[3] D. Loffreda, D. Simon & P. Sautet, J. Chem. Phys. 108 (1998)
[4] P. Ghosh, R. Pushpa, S. de Gironcoli & S. Narasimhan J. Chem. Phys. 128 (2008)
[5] M.B. Torres et al., J. Phys. Chem. A 115 (2011)

Electron and Optical Spectroscopies of Graphene Nanoribbons on Au(111): Insights from Ab-Initio Calculations

Shudong Wang[1], *Deborah Prezzi*[1], *Andrea Ferretti*[1], *Alice Ruini*[1,2], *Elisa Molinari*[1,2]

1. CNR-Nanoscience Institute, S3 Center, 41125 Modena, Italy
2. Department of Physics, Mathematics, and Informatics, University of Modena and Reggio Emilia, 41125 Modena, Italy

Graphene nanostructures have striking properties related to the lateral confinement that can open a band gap and induce semiconducting behavior with controlled quantum states and a variety of peculiar width- and edge-related phenomena depending on the details of the atomic structure. Radically new functionalities can thus be designed, far beyond those expected from extended graphene systems or conventional semiconductors. Key features connected to the tunability of electronic and optical properties as a function of structural parameters, e.g. width and edge structure of graphene nanoribbons (GNR), have been predicted theoretically (see e.g. [1]); however, only recently atomic control of GNR geometry (orientation, width and edge termination) was demonstrated by a novel approach based on depositing molecular precursors on appropriate substrates, which catalyze polymerization and ribbon formation [2]. These advancements in the fabrication procedure have thus allowed the first measurements of the band gap, dispersion and optical properties of atomically precise armchair GNRs [3,4].

In this work we perform ab initio calculations and compute quasiparticle energies and optical properties of GNRs within the so-called GW-BSE scheme. We focus on a specific armchair nanoribbon (7-AGNR). The presence of the substrate is accounted for by means of a classical image charge model for the screened Coulomb interaction. Our findings show that the metallic substrate induces a significant reduction of the energy gap as compared to the isolated 7-AGNR, bringing the GW gap from 3.7±0.1 eV to 2.3-2.7 eV on Au(111). On the contrary, the position of the optical peaks remains unaltered. Our results are in very good agreement with the experimental values obtained by STS, ARPES, and differential reflectance data [3,4], indicating that this scheme can provide quantitative predictions for electron and optical spectroscopies of nanoribbons on weakly coupled substrates such as Au.

[1] D. Prezzi et al., PRB, 77 (2008) 041404; D. Prezzi et al., PRB, 84 (2011) 041401; C. Cocchi et al., JPCC, 115 (2011) 2969; C. Cocchi et al., JPCL, 2 (2011) 1315.
[2] J. Cai et al., Nature, 466 (2010), 470.
[3] P. Ruffieux, J. Cai, N. C. Plumb, L. Patthey, D. Prezzi, A. Ferretti, E. Molinari, X. Feng, K. Mullen, C. A. Pignedoli, and R. Fasel,ACS Nano, 6 (2012) 6930.
[4] R. Denk, M. Hohage, P. Zeppenfeld, J. Cai, C. A. Pignedoli, H. Söde, R. Fasel, X. Feng, K. Müllen, S. Wang, D. Prezzi, A. Ferretti, A. Ruini, E. Molinari, and P. Ruffieux, Nat. Commun 5, (2014) 4253.

Ab-initio modeling of peroxy bridge defect in amorphous silica

B. Winkler[1], *L. Martin-Samos*[1], *N. Richard*[2], *S. Girard*[3]

1) Materials Research Laboratory, University of Nova Gorica, Vipavska 11c, 5270-Ajdovščina, Slovenia

2) CEA, DAM, DIF, Bruyères-le-Châtel, F-91297 Arpajon Cedex, France

3) Laboratirie Hubert Curien, Université de St-Etienne, UMR-CNRS 5516, Bâtiment F, 18 Rue du Professeur Benoît Lauras, F-42000 St-Etienne, France

A major motivation for study of point defects in silica is their role in the degradation of SiO_2based optoelectronic devices. One of the primary steps for understanding and controlling degradation processes is the one-to-one assignment between defect structure at the atomic scale and experimental signature (optical absorption bands, Electron Paramagnetic Resonance- EPR, Fermi contact/g-tensor, Photoluminescence bands, etc). Experimentally, bi-univocal assignments are not straightforward. Indeed, correlations have to be found between the results of different complementary spectroscopic techniques, such as Optical Absorption (OA), Photo-Luminescence spectra (PL) or (EPR combined with various treatments like irradiation, temperature, etc. Moreover, the sample itself contains always many different defects and impurities that make hard to detect and identify “single signals” against the background of other signals. In this context, ab-initio modelling plays a crucial role for calculating basic properties of defects.

Among other defects, the identification of the optical signature of Peroxy Linkage (POL) is still under debate. Experiments report values between 3.8 eV and 7 eV, while modelling, through mean-field theories, suggest absorption around 6 eV. In this work, electronic and optical properties have been modelled through what is nowadays considered the state-of-the-art approach, i.e. Density functional theory, GW approximation and solution of the Bethe-Salpeter equation. The DFT method provides good ground state configuration, GW approximation provides the quasi-particle band structure (N+1 and N-1 electronic excitations of the N electron gas), by properly including exchange and correlation effects. The Bethe-Salpeter Equation (BSE) takes into account electron-hole interactions through the diagonalization of an effective two-particle Hamiltonian (neutral excitations of the N electron gas) that contains parameter-free exchange and screening effects between holes and electrons.
This study shows presence of three bands assigned to POL. Very low calculated values of oscillator strengths mean it would be difficult to detect these transitions experimentally.

Ab-initio studies of geometric and electronic properties of group VI-B transition metal dichalcogenides monolayers

Tomasz Woźniak[1], *Paweł Scharoch*[1]

1. Departament of Theoretical Physics, Wroclaw University of Technology, Poland.

Recently, monolayers of group-VIB transition metal dichalcogenides attract significant interest due to their extraordinary electronic and optical properties. We have studied from first principles the geometry and the electronic structure of six MX2 monolayers (M=Mo, W; X=S, Se, Te), using various techniques. Basing on the obtained band structures we propose a parametrization for a three band tight binding model, which can accurately reproduce energy bands in the entire Brillouin zone.