The Abdus Salam
International Centre
for Theoretical Physics

Density Functional Theory and Beyond: Computational Materials Science for Real Materials

A Hands-on Workshop and Tutorial

6 - 15 August 2013
Venue: ICTP Adriatico Guest House, Kastler Lecture Hall

Organizers:
Volker Blum, Carsten Baldauf, Matthias Scheffler - Fritz Haber Institute (FHI), Berlin, Germany
Ralph Gebauer - the Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy

Co-sponsors:

Workshop websites at ICTP and FHI:
http://agenda.ictp.it/smr.php?2475 and *http://th.fhi-berlin.mpg.de/sitesub/meetings/DFT-workshop-2013/*

PRELIMINARY PROGRAMME & POSTER ABSTRACTS

DAY 1, TUESDAY - The Big Picture: Electronic Structure Theory (Room:Adriatico Guest House Kastler Lecture Hall)

6 August 2013

09:00 - 11:30 --- REGISTRATION ---
Registration of participants outside the Kastler Lecture Hall, and administrative matters.

14:30 - 14:45 **Volker Blum, Ralph Gebauer**
Introductory remarks

14:45 - 15:45 **Matthias Scheffler**
Electronic Structure Overview

15:45 - 16:45 **Stefano Baroni**
Challenges Beyond Ground State Electronic Structure Theory

16:45 - 17:15 --- Break ---

17:15 - 19:00 **Poster Parade**
Short oral presentations by all participants

19:00 - 21:30 --- Welcome reception ---
at the Adriatico Guest House Cafeteria, Terrace

DAY 2, WEDNESDAY - The Basics of DFT (Room:Adriatico Guest House Kastler Lecture Hall)

7 August 2013

09:00 - 10:00	**Mark Casida** **Exchange and Correlation**
10:00 - 11:00	**Volker Blum** **Electronic Sructure Theory in Practice I**
11:00 - 11:30	--- Coffee break ---
11:30 - 12:30	**Oliver Hofmann** **Electronic Structure Theory in Practice II**
12:30 - 14:00	--- Lunch break ---
14:00 - 18:00	(Room: Adriatico Guest House Informatics Lab.) **Lydia Nemec, Oliver Hofmann** **Practical Session 1: The Basics of Electronic Structure Theory**
18:00 - 19:00	--- Break ---
19:00 - 22:00	**Poster Session** drinks and food will be available during the poster session

DAY 3, THURSDAY - Periodic Systems: Basic Concepts for Solids and Surfaces (Room:Adriatico Guest House Kastler Lecture Hall)

8 August 2013

09:00 - 10:00	**Nikolaj Moll** **Periodic Systems: Concepts**
10:00 - 11:00	**Ralph Gebauer** **The Plane-Wave Pseudopotential Method**
11:00 - 11:30	--- Coffee break ---
11:30 - 12:30	**Claudia Draxl** **The Augmented Plane Wave Method**
12:30 - 14:00	--- Lunch break ---
14:00 - 18:00	(Room: Adriatico Guest House Informatics Lab.) **Franz Knuth, Sergey Levchenko** **Practical Session 2: Periodic Systems: Bulk Materials, Band Structures, and Densities of States**
18:00 - 20:30	--- Dinner break ---
20:30 - 22:00	(Room: Adriatico Guest House Informatics Lab.) **Extra computer time with tutors on hand**

DAY 4, FRIDAY - Beyond LDA and GGA, Correlation and Bringing Back the Nuclei (I) (Room:Adriatico Guest House Kastler Lecture Hall)

9 August 2013

09:00 - 10:00	**Sergey Levchenko** **Beyond DFT for Extended Systems**
10:00 - 11:00	**Frank Neese** **Electron Correlation: State of the Art in Quantum Chemistry**
11:00 - 11:30	--- Coffee break ---
11:30 - 12:30	**Jörg Neugebauer** **"Real Materials": Ab Initio Thermodynamics**
12:30 - 14:00	--- Lunch break ---
14:00 - 15:00	**Mariana Rossi** **Ab Initio Molecular Dynamics**
15:00 - 18:00	(Room: Adriatico Guest House Informatics Lab.) **Practical Session 3: Ab initio Molecular Dynamics**
18:00 - 20:30	**Dinner break**
20:30 - 22:00	(Room: Adriatico Guest House Informatics Lab.) **Extra computer time with tutors on hand**

DAY 5, SATURDAY (Room:Adriatico Guest House Informatics Lab.) (**Saturday**)

10 August 2013

09:00 - 12:30	**Weekend research project with tutors on hand**
12:30 - 14:30	--- Lunch break ---
14:30 - 21:30	--- Excursion, and social dinner ---

DAY 6, SATURDAY (Room:Adriatico Guest House Informatics Lab.) (**Sunday**)

11 August 2013

09:00 - 09:00	**Weekend Research Project with Tutors** All day long

DAY 7, MONDAY - Spectroscopy and Transport (Room:Adriatico Guest House Kastler Lecture Hall)

12 August 2013

09:00 - 10:00	**Ferdinand Evers** **Electronic Transport**

10:00 - 11:00	**Patrick Rinke** **Many-Body and GW**
11:00 - 11:30	--- Coffee break ---
11:30 - 12:30	**Heiko Appel** **TDDFT and Optical Properties**
12:30 - 14:00	--- Lunch break ---
14:00 - 15:00	**Christian Carbogno** **Charge and Heat Transport in Solids**
15:00 - 18:00	(Room: Adriatico Guest House Informatics Lab.) **Karsten Rasim, Christian Carbogno** **Practical Session 4: Charge Transport in Solids at Finite Temperatures**
18:00 - 20:30	--- Dinner Break ---
20:30 - 21:00	**Summary of the Weekend Research project**
21:00 - 22:00	(Room: Adriatico Guest House Informatics Lab.) **Extra computer time with tutors on hand**

DAY 8, TUESDAY - Beyond LDA and GGA, Correlation and Bringing Back the Nuclei (II) (Room:Adriatico Guest House Kastler Lecture Hall)

13 August 2013

09:00 - 10:00	**Luca Ghiringhelli** **From Ab Initio Molecular Dynamics to Statistical Mechanics**
10:00 - 11:00	**Alexandre Tkatchenko** **Practical Approach to Dispersion Interactions**
11:00 - 11:30	--- Coffee break ---
11:30 - 12:30	**Roberto Car** **Quantum Nuclei**
12:30 - 14:00	--- Lunch break ---
14:00 - 18:00	(Room: Adriatico Guest House Informatics Lab.) **Fabio Caruso, Heiko Appel, Patrick Rinke** **Practical Session 5: Excited State Formalisms**
18:00 - 20:30	--- Dinner break ---
20:30 - 22:00	(Room: Adriatico Guest House Informatics Lab.) **Extra computer time with tutors on hand**

DAY 9, WEDNESDAY - Large Scale and Multiscale (Room:Adriatico Guest House Kastler Lecture Hall)

14 August 2013

09:00 - 10:00 **Peter Haynes**
Linear Scaling DFT

10:00 - 11:00 **Jörg Behler**
Coarse-graining potential energy surfaces from ab initio data using artificial neural networks

11:00 - 11:30 --- Coffee break ---

11:30 - 12:30 **Peter Kratzer**
Coarse-Graining Time and Space: Kinetic Monte Carlo

12:30 - 14:00 --- Lunch break ---

14:00 - 18:00 (Room: Adriatico Guest House Informatics Lab.)
Björn Bieniek, Volker Blum, Gus Hart
Practical Session 6: Multiscale

18:00 - 20:30 --- Dinner break ---

20:30 - 22:00 (Room: Adriatico Guest House Informatics Lab.)
Extra computer time with tutors on hand

DAY 10, THURSDAY - Towards Real-World Application (Room:Adriatico Guest House Kastler Lecture Hall)

15 August 2013

09:00 - 10:00 **Gus Hart**
Deciphering the Materials Genome

10:00 - 11:00 **Michael Rieger**
Computational Materials Science at BASF

11:00 - 11:30 --- Coffee break ---

11:30 - 12:30 **Ellen D. Williams**
Frontiers for Basic Science (and Modelling) in Industry

12:30 - 12:40 **Closing remarks**

Contents

P 1

Tuning the knobs - Towards a Better Understanding of Energy Transfer Efficiency in Photosynthetic Systems

Florian Altvater
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Energy transfer within natural photosynthetic systems occurs at incredibly high efficiencies. How this is possible under ambient conditions is still debated and hard to tease out due to the complexity of the systems. The tobacco mosaic virus protein coat provides an ideal template to attach natural or artificial chromophores in a circular array [1] and thus decouple the energy transfer process from the biological environment.

Before looking at the system in whole I will first study vibrational effects on the photophysics of chromophores using DFT and TDDFT. Furthermore we will look at chromophore dimers at different gometries, also comparing the results to predictions based on the Förster theory. Using DFT/GW/BSE we will extend the research to linear arrays of chromophores and ultimately to the full system with chromophore-protein interactions combining quantum and statistical mechanics methods. Systematically varying the geometric parameters of the arrays as well as the nature of the chromophores will eventually enable us to understand the underlying principles of energy transfer efficiency.

[1] Dedeo M.T., Duderstadt K.E., Berger J.M., Francis M.B. *Nano Lett.* **2010**, *10*, 181–186.

P 2

Photo-induced chemical reactions on metal nanoparticles

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The possibility of utilizing solar energy to execute photocatalytic chemical transformations in excited states, which cannot be performed in the ground state using typical thermo-catalytic processes, is extremely enticing. Unique photocatalytic, excited state, reactions have been demonstrated utilizing femtosecond lasers to excite adsorbate covered single crystal metal surfaces. These results have sparked an interest in utilizing metals to drive photochemical transformations, but the low efficiencies and high intensities required to drive these chemistries are significant barriers that must be overcome. Recent experimental work has shown that Pt nanoparticles, diameter < 5 nm, and plasmonic Ag nanoparticles, diameter < 100 nm, are able to efficiently drive photocatalytic reactions through resonant energy transfer processes. This work aims to address unanswered mechanistic questions regarding nanoparticle mediated photochemical processes. An extended two-temperature model (ETTM) is used to describe the temporal evolution of non-equilibrium electron distributions in photo-excited metal nanoparticles. The addition of adsorbates to metal nanoparticle surfaces is hypothesized to play a significant role in enhancing the efficiency of photocatalytic processes. These effects are incorporated by inputting DFT calculated adsorbate-induced changes in the electronic structure of metal surfaces into the ETTM. By coupling the ETTM and DFT calculated adsorbate induced changes in metal electronic structure we analyze the effect of adsorbate coverage and composition on the distribution and temporal evolution of energetic electrons in photo-excited metal nanoparticles. Our results will be presented in the context of the possibility for state-selected bond activation of adsorbates on metal nanoparticles under low-intensity visible light illumination.

P 3

Study of X-ray absorption and emission spectra of Li_xFePO_4 using first-principles methods

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Li-ion batteries are very promising power source for electric vehicles and they are capable of reducing the dependence on fossil oil and decreasing the carbon footprint. Olivine-structured lithium iron phosphate offers a safe operation based on the fundamental electronic structure of the Fe 3d and O 2p states as well as the high interfacial and thermal stability [1,2]. We provide an in-depth and systematic study of the phase transformation and (de)lithiation effect on electronic structure in Li_xFePO_4 single crystals using first-principles method. The x-ray absorption and emission spectra for O K-edge, Fe K- and L-edge are simulated using *ab initio* methods. Using these spectra we analyze the (de)lithiation process in terms of Li distribution, valency, spin states, and crystal field.

[1] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough J. Electrochem. Soc. 1997, 144, 1188.
[2] A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada, J. B. Goodenough J. Electrochem. Soc. 1997, 144, 1609.

P 4

Pressure induced structural phase transformation in TiN: A first-principles study

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Titanium nitride (TiN), which is widely used for hard coatings, reportedly undergoes a pressure-induced structural phase transformation, from the relatively open NaCl (coordination-6) to more dense CsCl structure (coordination-8). The pressure required for the structural transformation of TiN predicted by the theoretical results (above 300 GPa) is much higher than the experimentally observed pressure (approximately 7 GPa). To fill this gap between the theory and experiment, we studied the structural phase transformation of TiN using first-principles calculations based on density functional theory (DFT) as implemented in the Quantum Espresso package.

New transformation path from NaCl structure to CsCl structure has been established. Our results show that the stress required for this structural transformation is much lower when it is deviatoric in nature vis--vis that under hydrostatic pressure. Structural stability of TiN has been investigated using phonon calculations which disclose the instability of the CsCl phase as formed after the transformation. Structural distortions of the ideal CsCl structure of TiN do not eliminate its instabilities. On examining the possible stability of CsCl structure of TiN using phonon dispersion curves at different pressures, we predict that it can be stabilized by an additional pressure (to that of 347 GPa required for transforming TiN from NaCl to CsCl structure) of 99 GPa. From the electronic structure calculations, we estimate the electrical conductivity of TiN in the CsCl structure to be about 5 times of that in NaCl structure, which could be useful in experimental characterization of the NaCl to CsCl structural phase transformation.

P 5

Computational and NMR Studies of β-Lactam Hydrolysis

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Due to their potent antibacterial activity and low toxicity, β-lactams have been the most effective chemotherapeutic agents for the treatment of bacterial infections since their discovery in 1920s. In this work the mechanisms of hydrolysis of β-lactams from three different families are studied using computational quantum chemistry calculations and NMR spectroscopic experiments. The computational studies considered several alternative pathways and were performed with density functional theory (DFT) methods in implicit solvent using a triple-ζ polarization basis set and the B3LYP and BP86 functionals. The results with the different functionals are similar and show that the mechanism and energetics of the hydrolysis reaction depends upon the strength of the nucleophile. Small, but notable, differences are also observed for the hydrolysis reactions of β-lactams from different families for a given nucleophile. The theoretical results are validated experimentally by NMR studies of the same hydrolysis reactions.

P 6

Dopant Selection Guided by Sabatier's Principle: The Example of Doped Ceria for Promoting the Two-Step Water Dissociation

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Use of *ab-initio* methodologies, based on Density Functional Theory, in describing surface science phenomenon has allowed for an increasing predictive ability of materials. In the case of H_2 synthesis, cerium based oxides have garnered significant interest given their oxygen buffering capability that facilitates the creation of active surface defect sites (vacancies). Tailoring the activity and selectivity of these materials towards low temperatures is paramount to improving reactivity. We started investigating the fundamentals governing the surface phases of cerium (IV) oxide under a range of environments. In the case of a pure ceria system in an O_2 environment, it was found that T $>$ 1500 K or $P_{O_2} < 10^{-13}$ atm are required for any appreciable surface reduction. However, exposing the surface to a highly reducing environment such as CO or H_2 could help circumvent these harsh conditions. Given the aforementioned observations we sought to alter surface reducibility by doping with various alkali and transition metal elements. Doping ceria had an effect on the surface vacancy formation; low valence dopants favor defect formation, whilst high valence dopants suppress it. Armed with the insight dopants have on surface vacancy formation, their corresponding impact on the consecutive dissociation of water at these sites was studied. Using a carefully strategized multi-step screening approach abiding with the Sabatiers Principle, we were able to identify a subset of dopants that would promote surface reactivity towards H_2 synthesis. Dopants such as Sc, Au, Co, Pd, La, Y, Hg, Mn, Zr, Cr, and Fe possesed a critical balance in improving surface reducibility while sustaining the dissociation of water, hence are promising candidates in enhancing the two-step water dissociation process.

P 7

Structure Solution and Prediction for Complex Modular Materials

K. A. Bradley, C. Collins, M. S. Dyer, J. B. Claridge, G. R. Darling and M. J. Rosseinsky

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Complex functional transition metal oxides can generally be described in terms of layers or modules containing elements in particular chemical environments. This observation has led to the development of the Extended Module Materials Assembly (EMMA)[1] approach for the generation of plausible candidate structures of particular compositions. Combining the modular description with classical lattice dynamics and finalising candidate structures by optimization with DFT, the EMMA method has been extended in this project to examine interfaces in layered materials[2] and novel hexagonal perovskite structures[3].

[1] Dyer, M.S. et al., *Science* [preprint], DOI:10.1126/science.1226558, (2013)
[2] Dyer, M. S. et al., *Angew. Chem. Int. Ed.*, **51**, 3418-3422, (2012)
[3] Mallinson, P.S. et al., *Angew. Chem. Int. Ed.*, **44**, 7733-7736, (2005)

P 8

Optical engineering of metal oxides: 3*d* impurities in Al_2O_3 and ZnO

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We have performed a systematic investigation of the chemical processes due to the presence of transition metal impurities in the structure of corundum (Al_2O_3) and zincite (ZnO), in particular those that give rise to colour.

One major result concerns the blue colour of sapphire ($\alpha - Al_2O_3$ with Fe and Ti impurities), the origin of which is at the centre of a long-standing debate. The mechanism has been analysed at different levels of theory (Born ionic potentials, Hartree-Fock, and Density Functional Theory). We identify that nearest neighbour Ti and Fe pairs exist in a Ti^{III}/Fe^{III} ground-state configuration. The charge transfer from Ti to Al (*i.e.* from Ti^{III}/Fe^{III} to Ti^{IV}/Fe^{II}) is responsible for the blue colour of sapphire. In contrast to the general assumption, the Ti^{IV}/Fe^{II} configuration is a metastable state that occurs due to optical excitation.

We have also considered more complex defect configurations involving three species. We propose that a tri-cluster between $Ti^{III} - (Ti^{IV}/Fe^{II})$ in which the titanium cations are edge-sharing and the Ti^{IV}/Fe^{II} pairs are face-sharing, could exist. This defect aggregate leaves the charge transfer energies unchanged, potentially increasing the stability of the Ti^{IV}/Fe^{II} pairs. Intravalence d-d transitions and intervalence Fe to Fe charge transfer cannot occur at the appropriate wavelengths for colouration. All predictions are consistent with available spectroscopic measurements.

[1] J. K. Bristow, Stephen C. Parker, C. Richard A. Catlow, Scott M. Woodley and Aron Walsh, Angew. Chemie, 2013, Under Review

P 9

Ab-initio study of the surface modification effects on the electronic band structure of Porous 3C-SiC

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Cubic porous SiC (3C-PSiC) is a semiconductor which can be synthesized in various nanostructures like pores, this kind of nanostructure have enormous surface area, which offer interesting possibilities for band gap engineering. In this work we performed a study of the effects of different surface passivation species on the structure and electronic properties of 3C-PSiC. The porous structures were modeled by removing atoms of an otherwise perfect SiC crystal in the [001] direction producing two different surface chemistries which exhibit a surface exclusively composed of Si or C atoms. The changes in the electronic states of the porous structures with both surface chemistries were studied using different passivation agents: Hydrogen, Fluorine, Oxygen and Hydroxyl. We performed the electronic band structure and density of states calculations on 3C-PSiC by means of Density Functional Theory, based on the generalized gradient approximation. In particular, we have used a revised version of Perdew, Burke, and Enzerhof exchange-correlation functional, based on the pseudopotential plane-wave approach. Our results show that the pore surface chemistry greatly influences the behavior of the electronic properties of these structures; for instance, in the hydrogenated case a C-rich configuration creates larger electronic band gaps than the Si-rich case. The Fluorine passivation creates greater band gaps than the Hydroxyl passivation in the C-rich case; additionally the O passivation reduces the band gap energy compared to the H passivated case [1]. The changes of the band gap that arise due to surface pore chemistries leads to the possibility of band gap engineering.

[1] A. Trejo, M. Calvino, A. E. Ramos and M. Cruz-Irisson, Nanoscale Res. Lett. 7, 471(2012).

Acknowledgments

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P 10

Ab initio simulations of Magnesium Oxide under extreme conditions

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A large number of Super Earths, i.e. planets in the mass range 1-10 M_E, have been discovered during the CoRoT and Kepler mission. The state of matter inside those planets (e.g. temperatures and pressures) is much more extreme that in the interior of the Earth due to their greater mass.

In order to improve the understanding of the interior of exoplanets and their physical properties [1], *ab initio* calculations for the planetary materials are needed. A possible representative is MgO, which is an abundant material in the Earth mantle. Therefore, it is expected to be also important for the mantle of exoplanets, as well as for giant gas planets with rocky cores (e.g. Jupiter [2]).

Using *ab initio* molecular dynamic simulations (VASP [3]), we have determined the phase diagram for MgO up to 20000 K and 8 TPa. In particular, the transition from the solid to the molten salt phase has been studied using diffusion analyses and pair distribution functions. The transition from the NaCl- (B1) to the CsCl- (B2) structure in solid MgO is determined by calculating the respective free enthalpies. To figure the entropy for both solid phases computations within the harmonic approximation with the PHONOPY code [4] as well as thermodynamic integration are performed.

With the resulting simulation data the phase diagram of MgO is constructed, the equation of state (EOS) is calculated, and the Hugoniot curve is determined. The B1-to-B2 and the liquid-solid transition line are compared with earlier simulation and experimental results.

[1] V. Stamenković, D. Breuer, T. Spohn, *Icarus*, **216**, 2 (2011)
[2] H.F. Wilson, B. Militzer, *Phys. Rev. Lett.*, **108**, 11 (2012)
[3] G. Kresse, J. Hafner, *Phys. Rev. B*, **48**, 17 (1993)
[4] A. Togo, F. Oba, I. Tanaka, *Phys. Rev. B*, **78**, 134106 (2008)

P 11

A first-principles investigation of the atomic and electronic structure of Pt_n, Cu_n and $(PtCu)_n$ (n=2-14) clusters

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Transition metal clusters have attracted great attention due to quantum confinement effects fostering the potential for many applications[1]. Moreover, the study of clusters can provide insights about the nanoparticles (NPs) formation. In particular, bimetallic NPs can present optimized properties, for example, PtCu NPs present enhanced oxygen reduction reaction activity when compared to pure Pt NPs[2]. However, this improvement is not well understood. Thus, an in-depth understanding of the compositional structure as well as growth mechanism of PtCu clusters arises as extreme importance to understand the improved catalytic activity of PtCu NPs. In this work, using first-principles calculations based on density functional theory within the generalized gradient approximation in the formulation PBE as implemented in the FHI-aims code[3], we investigate the atomic structure and electronic properties of anionic, cationic and neutral Pt_n, Cu_n and $(PtCu)_n$ clusters (n=2-14 atoms) for all compositions. The results show that Cu_n clusters are very influenced by shell effects and properties present an oscillatory-like behaviour. For Pt_n clusters, three structures were found more stable than in literature, for n=7, 8, and 12 atoms. In general, these clusters present higher magnetic moments and smaller ECN and HOMO-LUMO gaps than Cu_n ones. Moreover, all magic Pt_n clusters (neutral and charged Pt_6, Pt_{10}, and Pt_{14} were accompanied by an enhanced s-d hybridization. Our Excess energy analysis for $(PtCu)_n$ binary clusters show that the alloy formation is favorable for most cases. In particular, Pt(Cu)-rich binary clusters present almost the same properties as $Pt_n(Cu_n)$-clusters. For systems that shell closure is not satisfied, we found that the primary mechanisms for stabilization of these binary clusters are based on both: maximum number of hetero bonding and strain effects. Indeed, our atomic radial distribution analysis show that, in general, for the majority of most stable binary clusters, there are more Cu atoms closer to the gravity center in order to release strain energy. These results form a basis to understand the formation of greater particles such as 55-atoms core-shell PtCu NPs as well as basis to investigate ligand and support effects in these systems.

[1] Y. LU; W. CHEN; Chem. Soc. Rev., v.41, p.3594, 2012. [2] P. STRASSER et.al.; Nature Chem., v.2, p.454, 2010. [3] V. BLUM et.al.; Comp Phys Commun, v.180, p.2175, 2009.

P 12

Low-temperature metallic liquid hydrogen: an ab-initio path-integral molecular dynamics perspective

Ji Chen[1,2], Xin-Zheng Li[2], Qianfan Zhang[1,2], Matthew I. J. Probert[3], Chris J. Pickard[4], Richard J. Needs[5], Angelos Michaelides[6], Enge Wang[1,2]

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Experiments and computer simulations have shown that the melting temperature of solid hydrogen drops with pressure above about 65 GPa, suggesting that a liquid state might exist at low temperatures. It has also been suggested that this low temperature liquid state might be non-molecular and metallic, although evidence for such behaviour is lacking. Here, we report results for hydrogen at high pressures using *ab initio* path-integral molecular dynamics methods, which include a description of the quantum motion of the protons at finite temperatures. We have determined the melting temperature as a function of pressure by direct simulation of the coexistence of the solid and liquid phases, and have found an atomic solid phase from 500 to 800 GPa which melts at a temperature below 200 K. Beyond this and up to pressures of 1,200 GPa a metallic atomic liquid is stable at temperatures as low as 50 K. The quantum motion of the protons is critical to the low melting temperature in this system as ab initio simulations with classical nuclei lead to a considerably higher melting temperature of 300 K across the entire pressure range considered.

[1] Ji Chen, Xin-Zheng Li, Qianfan Zhang, Matthew I. J. Probert, Chris J. Pickard, Richard J. Needs, Angelos Michaelides and Enge Wang. Submitted.

P 13

Energetic and structural study of LDH MgAl-x (x = O(1-), Cl(1-))

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Layered double hydroxides (LDHs) are a group of laminar compounds with brucite-like structure. The layers are composed of hydroxide groups coordinated to divalent and trivalent metal cations and the interlayer space accommodates anions that compensate the layer charge. LDHs are good catalyst. In some reactions the catalyzer effect depends upon the molar ratio R=divalent/trivalent of the cations and the ion present in the interlayer region. For example in the reaction of cyanoethylation of methanol catalyzed with LDH MgAl-OH the highest activity is displayed when R=Mg/Al=3[1]. This reactivity reduces dramatically if Cl(1-) is present as interlayer anion. In this work we have studied the LDH MgAl-x (x=Cl(1-), OH(1-)) in which R=3 to get a deeper insight into the factors governing the catalytic activity of LDHs. We have used Density Functional Theory (DFT) in the Kohn-Sham formulation with the PBE[2] approximation to the functional for exchange and correlation, plane waves as basis set functions and the PAW[3] formalism as implemented in the VASP code.

A geometric and energetic analysis of the optimized structures indicates that anion-layer interactions are stronger (by 0.59 eV or larger) for Cl(1-) anion. Also the energetic barriers between absorption sites are larger for Cl(1-) than for OH(1-). It is shown that latter is connected to the formation of strong hydrogen bonds between the OH(-1) anion and the layer. Therefore it expected that OH(1-) presents a larger mobility than Cl(1-) along the interlayer region. A discussion about the connection of our results with the reactivity of these catalizers is presented.

[1] J.S. Valente, H. Pfeiffer, E. Lima, J. Prince, J. Flores, *J.Catal.* 279:196-204 (2011)

[2] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77:3865-3868 (1996).

[3] P. E. Blöchl, *Phys. Rev. B.* 50:17953-17979 (1994)

P 14

Exact Non-Additive Kinetic Potentials in Realistic Chemical Systems

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Non-additive kinetic energy bifunctional $T_s^{nad}[\rho_A,\rho_B]$ is the key element of the Frozen Density Embedding Theory (FDET). Its functional derivative, the non-additive kinetic potential $\frac{\delta T_s^{nad}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})}$, is one of the components of the effective embedding potential. The exact form of the functional is not known, however, for a given pair of densities the corresponding potential $v_t^{nad}(\mathbf{r})$ can be constructed, in principle exactly, by means of inversion techniques. The analytic inversion is used to obtain the exact potentials for chemically relevant pairs of electron densities, representing: dissociating molecules, two parts of a molecule linked by a covalent bond, or valence and core electrons[1]. This strategy can be applied to systems, in which the target density ρ_A is a spin-compensated two-electron density, whereas the sum $\rho_A+\rho_B$ is not subject to any restrictions. The obtained potentials are analyzed to identify the qualitative features that should be taken into account when constructing an approximation to the corresponding bifunctional.

It is also shown that due to the LCAO approximation, the resulting Kohn-Sham densities may be not pure-state non-interacting *v*-representable[2]. This results in problems with interpretation of the inverted potentials, which are not reliable in some regions of space. The way how it affects the results is analyzed by comparing the exact Kohn-Sham potential for a given LCAO density with the actual potential used to compute it.

The form of $\frac{\delta T_s^{nad}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})} = v_t^{nad}[\rho_A,\rho_B](\mathbf{r})$ is known in the limit of $\rho_A \to 0$ and ρ_B being a spin-compensated two-electron density. In practice, this condition is approximately met in the vicinity of nuclei of the environment, where the most-inner shell is not much penetrated by the other electrons. Detecting these regions would possibly allow to improve locally the non-additive kinetic potential. This can be achieved with a help of the Single Exponential Decay Detector (SEDD)[3], which has been recently introduced as a density-based descriptor of bonding patterns in molecules.

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P 15

Silica-Based Materials In Pharmaceutical Formulations: An Insight From Quantum-Mechanical Simulations

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Amorphous silica has been commonly used as a solid additive in pharmaceutical dosage forms, primarily as a tableting, anti-caking excipient. The interest in the pharmaceutical employment of amorphous silica has rapidly grown in recent years following the development of silica-based mesoporous ordered materials and the discovery of their biomedical applications. Among silica-based mesoporous materials, MCM-41 is one of the most studied since it was proposed as a drug delivery system. Confinement in mesoporous materials has been studied to stabilize the amorphous phase of apolar drugs, so to improve their solubility in aqueous media. Notwithstanding the relevance of this topic, the atomistic details about the specific interactions between the surfaces of the above materials and drugs and the energetic of adsorption are almost unknown. We resort to a computational ab initio approach, based on periodic Density Functional Theory (DFT), to shed some light on this topic. We simulated[1] the adsorption of ibuprofen and aspirin, two popular non-steroidal anti-inflammatory drugs, on two realistic models of amorphous silica surfaces,[2] characterized by different hydrophilic/hydrophobic properties due to different SiOH surface groups density. Particular effort was devoted to understand the role of dispersive (vdW) interactions in the adsorption mechanism and their interplay with H-bond interactions. As a subsequent step, we directly simulated the interaction of ibuprofen with the pore walls of a full 3D atomistic model of this material.[3] The MCM-41 pore has been filled with increasing loading of ibuprofen to compute structure and energetic of adsorption in the material. All simulations revealed that adsorption of drugs on amorphous silica is a strongly exothermic process. In particular, our results can account for the experimental evidence of ibuprofen crystal amorphization induced by the contact with the mesoporous silica material. The different level of wettability of the surfaces and the heterogeneous chemical nature of the drugs unveiled that a variety of phenomena occur in these systems, all having a role in the adsorption mechanism. Dispersion interactions play a crucial role in dictating the features of the drug/silica system. Their role grows along the increasing hydrophobicity of both the adsorbed molecule and the surface. Our results can also provide a general scheme to rationalize the competition between the adsorption of ibuprofen either as a monomer or as a dimer on the MCM-41 walls.

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P 16

Optical properties of an organic dye from time dependent density functional theory with explicit solvent: The case of alizarin

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The influence of a water solvent on the optical absorption properties of alizarin is investigated using time-dependent density functional theory (TDDFT). The solvent is modeled at two different levels of theory: a structureless dielectric medium, using a polarizable continuum model, and the explicit inclusion of water molecules which are treated at the same level of theory as the solute. Thermal effects on the photoabsorption spectra are included by combining TDDFT with first principle molecular dynamics. The effect of molecular distortions on the excitation energies and oscillator strengths is analyzed, and a strong correlation between particular structural and optical properties is found.

P 17

Interactions and Reactivity of Organometallic Anticancer Complexes

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After the discovery of cisplatin as a potent cytostatic drug[1], compounds of platin and other transition metals become the first choice in the cancer treatment. The continuing research aims on higher specificity (and thus less side-effects), broader activity without eliciting resistance. Our goal is to use *ab-initio* methods to study substitution effects on the reactivity (hydrolysis rate) of benzene-Pt compounds (*trans*-$[Pt(NH_3)_2(C_6H_6)Cl]^+$).
In the second part of our work we will study the mechanisms of hydrolysis and DNA binding of Ru and Os analogs of RAPTA compounds[2].

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P 18

Engineering the Band Gap of Inorganic Nanotubes: A linear scaling density functional theory investigation.

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We report a linear scaling density functional theory (LSDFT) investigation of the structural and electronic effects introduced through the modification of Aluminosilicate (AlSi) nanotubes (NT) *via* both doping and chemical functionalization. Insulating AlSi NTs have attracted recent attention due to several factors; their ease of preparation, open ended and water soluble nature, permanent polarisation and localisation of the valence (VB) and conduction (CB) bands in real space [1]. These features support the idea that AlSi NTs could have applications in photocatalysis, where separation of photo-generated electron hole pairs may be stabilised by the NT permanent polarisation. Given that the AlSi NT primitive cell contains in excess of 300 atoms, we make use of the LSDFT code ONETEP [2], which has allowed us to study systems up to a few thousand atoms. Initially we consider selective chemical functionalization of the inner layer, specifically the substitution of inner surface hydroxyls by organic methyl groups as synthesised in [3]. The greater steric hindrance of the methyls affects the optimal NT diameter and thereby leads to a different curvature with respect to the pristine AlSi NT. We discuss how such functionalization and curvature affect the real space separation of the VB and CB edges. Secondly, we isolate and investigate an iron substitution point defect within the Aluminium Oxide sublayer. Leveraging on the linear scaling implementation of DFT+U in ONETEP [4], we study the electronic properties of Fe-doped AlSi NT as a function of the dopant concentration. Finally we quantify the effect of dopant concentration on the localisation of dopant states within the band gap region.

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P 19

Magnetic and Ferroelectric Properties of Multiferroic $TbMnO_3$

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Multiferroics, materials which are simultaneously magnetic and ferroelectric, have attracted a lot of attention during the last decade. Even though this is a quite broad class of compounds, only some of them are interesting from the point of view of practical applications, namely, the ones which have strong coupling between magnetic and ferroelectric orders and demonstrate gigantic magnetoelectric effects.

Perovskite $TbMnO_3$ is the typical example of such multiferroics. According to experimental data [1], its electric polarization (along *c*-axis) appears only together with the establishment of a specific magnetic ordering (incommensurate spin spiral confined in *bc*-plane) at low temperatures. Obviously, these orders are strongly coupled. Moreover, it was shown that the application of an external magnetic field can cause the spin-flop transition of the spiral from *bc*- to *ab*-plane, which results in the switching of the direction of electric polarization from *c*- to *a*-axis [2].

The generation of magnetic ordering in $TbMnO_3$ could be understood and explained by competing exchange interactions between nearest-neighboring and next-nearest-neighboring Mn^{3+} magnetic moments, but the source of electric polarization needs to be clarified. Basically, two mechanisms of generation of electric polarization should be taken into account: 1) purely electronic (in which spin-orbit interaction changes the hybridization of electronic orbitals and thus shifts the center of charge); and 2) ionic (due to magnetically-induced ionic displacements) [3-5].

The near-term aim of our work is to investigate the magnetic and ferroelectric properties of $TbMnO_3$ by first-principles calculations. At the first step we are going to evaluate nearest-neighbor and next-nearest-neighbor intra- and interplane exchange parameters for this compound and to define a magnetic ground state. Then we are planning to estimate the purely electronic and ionic contributions to electric polarization and thereby to find the main source of electric polarization in $TbMnO_3$.

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P 20

Molecular study of electrical doping in pentacene: F6-TCNNQ films

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Molecular doping of organic semiconductors has become a very common approach in the organic electronics field [1]. In this context, doping brings several technological advantages. First, this increases the conductivity of organic layers by several orders of magnitude and ensures Ohmic contacts to the corresponding electrodes. Moreover, doped transport layers also allows for the optical adjustment of the structure of organic light emitting diodes (OLED) and solar cell (OSC) with substantial improvements in their efficiency [2]. In spite of this, no common consensus has been achieved yet on how molecular doping occurs at the molecular scale. Only in recent years, research has been devoted to this topic with some literature works addressing it with experimental and theoretical techniques [3-5].

In this contribution, we will present a study on an archetypal p-doped molecular system composed of the hole transporting matrix pentacene and the strong electron-acceptor 2,2-(perfluoronaphthalene-2,6-diylidene) dimalononitrile (F6-TCNNQ). The aim of this study is to bring together computational results and experimental evidence. Calculations at the DFT-D3 level will be shown both for the single molecules and molecular complexes. Computational results will be compared to measured spectroscopic data, such IR and Raman spectra, and UV-VIS absorption. By combining theoretical and experimental techniques, we will draw conclusions on the interaction mechanism in the system under study.

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P 21

CALCULATIONS OF GROUND STATE COHESIVE PROPERTIES OF BINARY COMPOUND SEMICONDUCTORS CRYSTALLINE STRUCTURE USING FHI-AIMS CODE

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A density functional theory is going to be used to investigate the material properties of binary compound semiconductors bulk crystalline structures. Specifically DFT based code FHI-aims is going to be used to study different phases the bulk structures and calculate the ground state cohesive properties of the most-stable structure of each semiconductor under study. The computations is planned to carried out within generalized gradient approximations GGA and the local-density approximation LDA of the density-functional theory using FHI-aims code. It is expected that the most stable phase of each semiconductor crystalline structure will be found and the ground state properties such as lattice constant, cohesive energy, bulk modulus and energy bands will be computed and compared with the results obtained using other method and experimental values. We expect our results to be in agreement with experimentally found values within reasonable percentage errors.

P 22

First Principles Theory of Low-Energy Electron Reflectivity

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Based on density functional theory, we develop a self-consistent description of low-energy electron reflectivity spectra of both free-standing thin films and thin films on substrates. Our approach utilizes wavefunctions for a thin multilayer slab together with wavefunctions of bulk substrate, if any. For free-standing films, by combining wavefunctions for positive and negative wavevectors, we forms states with only outgoing character on one side of the slab, and hence deduce the electron reflectivity [1]. For thin films on a substrate, we match the states on one side of the slab to bulk states of the substrate [2]. Our results compare well with experimental data for graphene on SiC and on various metallic substrates. From our modelling, we find that the minima of reflectivity arise from states with wavefunctions localized between the graphene layers rather than on the layers, as previously suggested [3]. The energies of the reflectivity minima are sensitive to the layer spacing between graphene and substrate, thus our method also provide a way to determine the layer spacing by comparing with the experimental reflectivity curve.

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P 23

Wave function imaging of transition metal impurities near the H/Si(111) surface

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Despite the difficulties encountered in fabricating magnetic semiconductors, we think that it is still worthwhile to investigate doping of silicon by 3*d* transition metals since it may have a strong impact on the field of spintronics. Imaging of electronic states on the atomic scale is possible with state-of-the-art scanning tunneling microscopy (e.g., for Mn:GaAs [1]) and can be used to improve the fundamental understanding of impurity-host and impurity-impurity interactions.

Here we present an *ab initio* viewpoint on Cr, Mn and Fe impurities near the H/Si(111) surface, which has the specialty of providing a similar chemical environment as bulk Si does, while keeping the impurities accessible to surface analysis techniques. Our discussion focuses on magnetic and energetic characteristics of isolated and interacting impurities and their detection with (magnetic) scanning tunneling microscopy, which is able to discriminate between interstitial and substitutional defects of different depth. According to our calculations, single impurity wave functions are less extended than those of Mn in GaAs, which makes it harder to get ferromagnetic coupling between dilute impurities in Si. We devise a strategy how magnetic scanning tunneling microscopy can be used to understand the impurity-impurity interaction on an atomic scale. Furthermore, the influence of correlation effects is discussed by comparing hybrid functional results to GGA+U calculations. We show how experiments can clarify whether or not such approaches beyond conventional density functional theory are useful in this field.[2,3]

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P 24

First-principles Hybrid functional Study of the Band structures of Lanthanide Sesquioxides

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Lanthanide sesquioxides are a group of compounds of particular interest for a variety of technical applications such as catalysis, lasers and magnetooptics. The theoretical investigation of these materials with common density functional theory (DFT) methods is hampered by t he considerable influence of f-electrons on the physical properties, *e.g.* by f-levels entering the forbidden gap and superimposing a periodic behavior on the optical bandgaps along the lanthanide series Ln=La,...,Lu [1]. A suitable method for the simulation of the electronic and optical properties, e.g. from defects, should thus catch the experimental features arising from the correlated f-electrons, yield good estimates for the electronic bandgaps and allow for total energy calculations, favourably in an economic way. Standard local DFT methods, while being economic, fail miserably at this task. It was recently shown [2] that $G_{(0)}W_0$ many-body corrections on common LDA+U calculations restore the correct behavior, but this method is computationally expensive and does not yield total energies. We show that hybrid fucntionals, which preserve the capability of total energy calculations, while amending for the shortcomings of local DFT at the cost of increased computational effort, are capable of reproducing the experimental band gap trends both qualitatively and quantitatively on the level of quasiparticle $G_{(0)}W_0$ methods.

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P 25

Transition metal catalysis on gold surfaces

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Transition metal catalysis as well as catalysis on metal surfaces belong to the most important aspects of modern organic chemistry. An interesting question in this context is whether the two approaches can be combined to yield new catalysis schemes. Experimental research in this direction has been carried out by developing a special bisoxazoline ligand, which can bind to a metal surface via thioether side groups, while coordinating metal ions to the ring nitrogen atoms. So far, the metal complex could only be synthesized by treating the already surface-bound bare ligand with metal ions, which might indicate that it is only stable in such an arrangement and the catalytic activity could therefore only be utilized on metal surfaces.

This project aims at elucidating the atomistic details by theoretically modelling the metal complex on a Au(111) surface slab. To this end, the structure of the ligand was first optimized *in vacuo* with and without different metal ions. Further procedure will include determining the structure of the complex on the surface as well as the corresponding surface reconstruction, and calculating the binding energy in different orientations to identify the ideal binding geometry. Furthermore, different metal ions will be placed in the resulting cavity to calculate complexation energies. Finally, the determination of catalytic reaction mechanisms and optimum pathways is planned in order to evaluate the potential of this kind of systems for organic synthesis.

P 26

Sequential quadratic programming algorithm for *ab initio* structure-activity relationships of catalysts on amorphous supports

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Methods for modeling catalytic sites on amorphous supports lag far behind methods for modeling catalytic sites on metal surfaces, zeolites, and other crystalline materials. Typical strategies use cluster models with arbitrarily chosen constraints to model the rigid amorphous support, and these constraints influence catalyst site activity. Alternatively no constraints are used, which results in catalytic sites with unrealistic flexibility. We present a systematic *ab initio* method to model isolated metal active sites on insulating amorphous supports using small cluster models. A sequential quadratic programming framework helps us relate chemical properties, such as the activation energy, to active site structure. The algorithm is first illustrated on an Empirical Valence Bond model energy landscape. We then use the algorithm to model an off-pathway kinetic trap in olefin metathesis by isolated Mo sites on amorphous SiO_2. The cluster models were terminated with basis set deficient fluorine atoms to mimic the size and electronegativity of oxygen in an extended SiO_4 framework. We also discuss limitations of the current algorithm formulation.

P 27

The magnetoelectric effect and phonon properties in double-perovskite structure

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Multiferroics, defined as materials with coexistence of at least two of the electric, elastic and magnetic orders, have attracted enormous research activities recently [1]. As a new development, double-perovskite multiferroic compounds of the form $A_2BB'O_6$ have been theoretically and experimentally designed. To this group of material belongs for instance Bi_2NiMnO_6 (BNMO). Experimental studies of BNMO thin films have confirmed the strong coupling between magnetic and ferroelectric phases [2,3]. In spite of sufficient experimental findings and DFT calculations [4], a well motivated microscopic model describing the situation is still missing. Based on a microscopic model with a biquadratic magnetoelectric coupling we investigated the properties of Bi_2NiMnO_6 thin films. We focused on the spin- phonon coupling. We demonstrate that such a coupling is quite relevant in the double perovskite structure. Using Green's functions the phonon spectrum is calculated which is determined by the polarization and the magnetization. In particular, the influence of the magnetoelectric coupling on phonon excitation and its damping is analyzed. The phonon energy and its damping offer a kink at the magnetic phase transition temperature. The phonon energy is enhanced if an external magnetic field is increased, whereas, the damping of the phonons decreases. The observed behavior is a strong evidence for a magnetoelectric coupling.[5]

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P 28

Liquid alkaline-earth metals. An orbital-free *ab initio* study with force matching pseudopotentials.

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Molecular dynamics (MD) is a powerful simulation technique for the study of the properties of liquid systems, and the last two decades have witnessed a large spread in the application of ab initio molecular dynamics methods (AIMD) based on the density functional theory (DFT)[1]. Most AIMD methods are based on the Kohn-Sham (KS) orbital representation of the DFT (KS-AIMD methods), which requires powerful computational resources imposing severe restrictions on the size of the systems and the simulation times. However, some of these constraints can be alleviated by the so-called orbital-free ab initio molecular dynamics (OF-AIMD) method which, by disposing of the electronic orbitals of the KS formulation, provides a simulation method where the number of variables describing the electronic state is greatly reduced, enabling the study of larger samples (thousands of particles) and for longer simulation times (tens of ps).

Experimental measurements of the properties of liquid alkaline-earth metals are not very abundant, probably because of its high chemical reactivity and gas adsorption ability. For Be, only the sound velocity has been measured experimentally, and it is extremely high [2]. Liquid Mg has been recently studied by x-ray techniques and results for the static and dynamic structure are available, showing a peculiar behavior in the second peak of the structure factor, S(q), similar to that found for several transition metals [3,4], that has been linked with the presence of icosahedral arrangements present in the liquid that increase upon supercooling. For liquid Ca, Sr and Ba, the experimental information is somewhat old [5].

We have studied globally the properties of these systems through orbital-free ab initio molecular dynamics simulations where the local pseudopotentials were adjusted via force matching to those obtained through KS calculations with non local-pseudopotentials. The results obtained show some common trends in their properties, such as the distorted second peak in the structure factor present in the recent measurements for Mg.

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P 29

Hybrid α-γ Cyclic Peptide Nanotubes - A Theoretical Study

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The quantum mechanics/molecular mechanics ONIOM calculations have been performed to study the structure and metal-ion binding properties of all-trans cyclo[1R-3S-γ-Acc-Gly]$_3$ hexapeptide nanotube ((TAG)$_3$ PNT) [1]. The intersubunit distances and tube angle of (TAG)$_3$ PNT exhibited the sturdy nature of (TAG)$_3$ stacks upon Li^+, K^+, Mg^{2+}, and Zn^{2+} enclosure. The calculated dimer binding energies of (TAG)$_3$ PNT and its ionic complexes confirm that the building blocks are bound by C=O...H-N hydrogen bond interactions. The binding energy of (TAG)$_3$ PNT with ions interacting at the surface cavity exhibit the affinity of ions at the entrance of the channel and the many-body analysis for the ion interacting at the central region substantiates the major contribution of two-body interactions to the total binding energy. In general, the binding energies of (TAG)$_3$ PNT metal ion interacting complexes with well-maintained channel shows α-γ hybrid cyclic peptides [2] as the promising peptidic nanochannels of biological interests.

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P 30

Untangling the Mechanisms of Energy Transfer in Photosynthesis

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As part of a project to qualify and quantify the mechanisms of energy transfer in photosynthesis, I am using time-dependent density functional theory to calculate the transition dipoles and spectral properties (e.g. absorption, emission, and excited state lifetimes) of a family of experimentally and theoretically interesting chromophores. Specifically, I am producing data for xanthene and a series of rhodamines and fluorasceins. In the context of this work, I will also look at the efficacy of different functionals within the TDDFT framework, including but not limited to PBE, B3LYP, long range corrected functionals like omega-B97, and meta-GGAs. Eventually I will use DFT/GW/BSE to examine how separation and orientation of chromophores in arrays affect energy transfer dynamics.

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First Principles Prediction of a New Low Temperature Phase in Boron Carbide

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Published phase diagrams for boron carbide, a material used in nuclear reactor shielding and tank armor, consist of a single ”B4C” phase with no composition range change from 1000K to 2350K. Extending this behavior to 0K is thermodynamically implausible due to third law of thermodynamics violations and suspect phase labeling from symmetry considerations. In this work, we use first principles calculations to model the phase diagram, and we predict a new low temperature phase in three different ways. First, we directly construct the partition function in the semi-grand ensemble by enumerating all states of interest at given temperatures for different cell sizes. Next, we propose a free energy model with fitted parameters to obtain the phase diagram, which gives quantitatively similar results to published phase diagrams in the high carbon limit. Finally, we derive an effective potential from total energy calculations and perform Monte Carlo simulations. All three methods yield a low temperature ordered phase that transitions to the observed phase near 600K. Work is currently underway to describe the phase transition using Landau formalism.

P 32

Time-Resolved Photoelectron Imaging Spectra from Non-Adiabatic Molecular Dynamics Simulations [1]

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We present an efficient method for the simulation of time-resolved photoelectron imaging (TRPEI) spectra in polyatomic molecules. Our approach combines trajectory-based molecular dynamics, that account for non-adiabatic effects using surface hopping, with an approximate treatment of the photoionization process using Dyson orbitals as initial and Coulomb waves as final electron states. The method has been implemented in the frame of linear response TDDFT. As an illustration, we simulate time- and energy-resolved anisotropy maps for the furan molecule and compare them with recent experimental data [2]. Our method can be generally used for the interpretation of TRPEI experiments allowing to shed light into the fundamental photochemical processes in complex molecules.

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P 33

Electronic and magnetic properties of zigzag edged triangular graphene flakes

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The graphene flakes we consider have equilateral triangular shapes with zigzag edges (n-TGF), wheren denotes the number of edge hexagonal cells in one side of the triangle. Termination of these n-TGF structures with several elements (of the first two rows of the periodic table) and application of electric field to these flakes alter their electronic and magnetic properties.

In accordance with previous studies [1,2], we find that bare flakes have large spin magnetic moment values of 4(n-1) μB, whereas they reduce to (n-1) μB for full saturation of edges with Hydrogen, Lithium, Beryllium or Flour atoms. Moreover we have studied possible termination of other elements like Boron, Carbon and Nitrogen. Hydrogen and Flour atoms prefer to bind at the top of an edge Carbon atom. Unlike Hydrogen and Flour termination, the other atoms prefer to bind at the bridge sites.

Recent studies [3,4] show that the magnetic moments of triangular graphene flakes can be controlled by applied electric field. We show that the value of total spin polarization of triangular graphene flakes can be changed by tuning an applied in-plane external field. We demonstrate that, in these flakes total spin polarization can be reduced stepwise with the applied field. The electric field control of ferromagnetism in TGFs promises a new route for spintronic applications.

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P 34

Chemical thermodynamics for abundant solar energy

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Photovoltaics are a highly promising source of low-carbon energy. Currently, global photovoltaic energy production is on the Gigawatt scale – in order to have a meaningful impact on the global energy crisis it is necessary to move to Terawatt-scale production.[1] The chalcogenide Cu_2ZnSnS_4 (CZTS), with related selenides, offers a viable thin-film absorber material composed entirely of relatively abundant elements. While there is a considerable body of experimental literature, exploring a range of synthesis routes, theoretical work has focused on electronic structure and defect stability.[2,3] For high-throughput production of photovoltaic panels, modest pressures and temperatures are preferred – it is difficult to vacuum seal part of a roll-to-roll glass or steel production line. Encouragingly, a record module efficiency has been set by a liquid-based method which could be plausibly scaled to printing and annealing stages.[4] In general, a substrate is coated by evaporation or electrodeposition of metal-containing precursors. In the annealing stage, gaseous sulfur and/or selenium enter the deposited material and a number of precursors react to form the final product.

Ab initio thermodynamics offers a way to systematically screen the viability of this annealing reaction under realistic processing conditions, examining the effect of temperature and partial pressures on the equilibrium. Density functional theory calculations are carried out with FHI-aims, and thermal properties calculated using the harmonic approximation with Phonopy. By combining literature data with *ab initio* calculations for a range of precursors and products, the final step of the calculation is very rapid and can be carried out interactively for arbitrary reaction systems. This tool is intended for use in selecting candidate CZTS-forming systems for further investigation, whether theoretical or practical.

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P 35

Solution of the *GW*-based quasiparticle-equation beyond the diagonal approximation: improvements in energies and wavefunctions

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One of the most used approaches for the computational study of solids, nanoscale systems and molecules is the density functional theory (DFT). However, as is well known, DFT calculations of single particle excitation spectra, e.g. ionization potentials, often suffer from approximations in exchange correlations potentials. To systematically improve the estimation of quasi-particle energies for molecular system, we have implemented the so called GW method into a standard quantum chemistry package (G_0W_0-level). The approach represents a perturbative expansion of the many-body Green's function with respect to the screened interaction, W.

A central mathematical step in GW is the solution of the quasiparticle (qp-) equation. It finds the poles of the (approximate) many-body Greens function, that define the qp-energies. A common simplification in this procedure is to neglect all off-diagonal elements of the self-energy matrix, that enters the qp-equation. We investigate the quantitative error associated with this approximation for a typical set of molecules and find significant effects. Including the off-diagonal terms the ionization potential experiences shifts (usually towards less binding) reaching 100mV or more.

Off-diagonal elements of the self energy not only shift qp-energies; they also induce deviations of the qp-wavefunctions from their DFT-based Kohn-Sham parents. We investigate the resulting impact on screening within a novel self-consistency cycle. It takes into account the deformation of the qp-states already when calculating the qp-polarization and W.

P 36

Electron transport through chemically linked armchair carbon nanotubes

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Carbon nanotube (CNT) thin films are flexible materials where randomly oriented nanotubes form a very thin network. The advantages of CNT networks are good electrical conductivity and high mechanical strength, which is important from the point of view of applications. These CNT thin films could be used as transparent electrodes in new kinds of displays or in sensor applications. Basic conductivity properties have been presented in a recent study, where the effect of the tube length and diameter on the electrical conductivity of a CNT network has been investigated both experimentally and computationally [1]. In addition, the distributions of chirality and orientation of nanotubes have turned out to be important.

The transport properties of CNT networks can be understood by considering first a single carbon nanotube junction (CNJ) and its conductivity. The geometry of the CNJ affects the electron transport through the junction significantly. Moreover, charge brought to the junction and pressure applied to the film may change the conductance [2].

Here we present an outline of our project the goal of which is to model the electron transport through CNJs using first-principles methods. We will use the FHI-aims all-electron code that includes an implementation of the Landauer-Büttiker formalism. This makes it possible to calculate the transport through various CNJs. An example we are going to study is a junction in which two armchair carbon nanotubes are connected with a covalent linker molecule. An important question is if the conductance of such a CNJ can be increased with a linker molecule. Other cases could be armchair nanotubes connected with some transition metal atoms.

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P 37

Non-collinear Magnetic Structure of RB$_4$(R=Rare-earth)

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Although Rare-earth tetraborides share the same tetragonal ThB_4 crystal structure(Spcae group P4/mbm), they have many interesting physical properties. Some of them such as DyB_4 and TbB_4 have quadrupolar moment, and this quadruploar moment ordered in a manner ferro-like or antiferro-like[1]. In TbB_4, it has multistep plateaus in magnetization[2]. DyB_4, GdB_4, TbB_4, HoB_4 are experimentally believed to have noncollinear antiferromagnetism in the ab-plane. There are some experiments which try to clarify the magnetic ground state, Resonant X-ray scattering, Spherical Neutron Polarimetry, Neutron diffraction, X-ray diffraction[3-6]. However, the experimental results are indicating different magnetic ground states, that is, the interpretations of the magnetic structure differ a little bit experiment by experiment.

Our first research plan is to elucidate the magnetic structure of these materials based on the DFT calculation. The magnetic structure of TbB_4, DyB_4, HoB_4 is thought to be strongly influenced by orbital ordering through Spin-Orbit coupling. So, we're going to analyze the orbital ordering by DFT calculation too. The 2nd research plan is to investigate the physical origin of noncollinear antiferromagnetism in ab-plane. To do this, I'll use a model Hamiltonian based on Monte Carlo simulation with Shastry-Sutherland lattice, topologically equivalent to a lattice formed by rare-earth ions in RB$_4$.

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P 38

GW calculations of rare-earth hexaborides $R\mathrm{B}_6$

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Our project is in its early stage, therefore this abstract seems somewhat "non-specific" and more or less like a proposal.

Boron rich compounds such as $R\mathrm{B}_4$, $R\mathrm{B}_6$, $R\mathrm{B}_{12}$ are characterized by boron clusters. Many of them draw attention by their thermoelectric applicability.

The origin of weak ferromagnetism in $R\mathrm{B}_6$ with (R= Ca,Eu) has been of great interest. Also whether they are semimetallic or insulating has been a controversial issue. In CaB_6, it is found that the inclusion of dynamic screening effect is crucial, which comes from many body interaction in solid.

Therefore, advanced tools such as GW approximation or modified Becke Jones potential (MBJ) method beyond density functional theory (DFT) will be necessary to investigate the physical properties of $R\mathrm{B}_6$, especially about the metalicity or the size of a gap.

It is also worthwhile to employ the dynamic mean field theory (DFT+DMFT) method for the description of this kind of systems.

In this project, we will adopt the GWA (MBJ) and/or the DFT+DMFT method to investigate the electronic structures of $R\mathrm{B}_6$ compounds.

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Molecular Dynamics Study of Cement-Aqueous Solution Interfacial System

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Cement is one of the most successful material with the long history because of its cost and mechanical performance. Moreover, it is recently considered as a candidate for the solid fixation of Cs^+ ion, which is a problematic radioactive ion from nuclear power plant, because it adsorbs ions on the surface. The importance on the surface chemistry of cement thus becomes significant. The structures of the cement is complicated, and considered as nano-crystalline aggregation phase with two distinct local structures, tobermorite and jennite, by the difference of Ca/Si ratio and the silica-chain length. The goal of this research is to detect which structural or compositional feature is essential to ionic adsorption into cement matrix.

By using molecular dynamics simulations, we have studied the aqueous solution-mineral (cement) interfacial systems for two different cement local structures (tobermorite and jennite) and two different solutions (NaCl and CsCl). It was found that Na^+ ion could form both inner-sphere complex and outer-sphere complex, without full hydration shell and with full hydration shell at the time of adsorption, respectively. In contrast, Cs^+ ion could only form inner-sphere complex for both mineral cases. This finding is in good correspondence with previous NMR studies. Executing DFT calculation for such systems, more exact information about the adsorption structures and essential mechanism will be revealed. Compatible NMR chemical shift with the previous study will be also calculated. It will enhance our understanding on cement materials especially in the case of the solid fixation.

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P 40

A systematic DFT study on the phase stability and effective charge of 60 chalcogenide (ZnX, CdX, PbX) phases for MD potential development

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Lead, cadmium and zinc chalcogenides are widely considered to be promising nanocrystal materials, due to their opto- or thermoelectronic properties. To understand the formation of nanocrystals it is important to know the properties of the various crystal structures that can appear. The relative stability of phases is determined by Density Functional Theory[1] calculations, using the VASP[2] code. PAW-GGA-PBE[3] functionals were used for these calculations. The rock salt, zinc blende, wurtzite, honeycomb en CsCl structures of CdX, PbX and ZnX (where X = O, S, Se, Te) have been considered, 60 phases in total. Lattice parameters are obtained, as well as the Bader charge, rose curves and values of the bulk modulus. Bader charges were always found to be lower than the effective charges used in semi-empirical potentials. The results will be used to develop transferrable potentials for MD simulations. Special attention will be devoted to the simulation of the honeycomb (HC) crystal phase, which is regularly found as a result of MD simulations, although the occurence of this phase has not been observed. Finally, it will be assessed whether the Hubbard-U (GGA+U) potential will affect the relative stability of phases.

Figure skipped:(a) Energy vs. volume plots for different crystal structures of CdTe. (b) Band structure plot for CdSe.

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P 41

The nature of topological phases in graphene with transition metal (TM) adatoms: a first-principles study

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Kane and Mele's prediction of a spin-orbit coupling (SOC) induced quantum spin Hall effect in graphene [1] has inspired numerous studies on graphene as a prototype for a two-dimensional topological insulator (TI). The weak SOC of carbon atoms in realistic graphene, however, renders the conjectured TI gap essentially unobservable. As a means to enhance the intrinsic SOC and to realize the TI states, hybridization of graphene with heavy adatoms has been proposed, and recent theoretical studies, in fact, have predicted the quantum spin Hall effect [2] as well as the quantum anomalous Hall effect [3] in graphene with 5d metal adatoms such as osmium and tungsten. These intriguing results consequently suggest that there still remains much to be studied about the aforementioned systems. In our work, with a thorough study using theoretical models and first-principles-based calculations, we seek to gain further insight into understanding the exact nature and physics of TI phases in graphene decorated with TM adatoms. More specifically, some of what we plan to focus our investigation on include i) precise hybridization characteristics of TMs' d orbitals with graphene states and the transport behavior between the two by studying a wider range of adatoms species (i.e., 3d, 4d, 5d atoms), ii) effects and roles of the magnitude and the direction of adatoms' magnetic moments in modifying graphene's electronic structure, and iii) exact TI gap opening mechanisms by exploring the changes in local as well as graphene-only band structures at very low to higher adatom densities.

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P 42

Electromagnetic modelling for insulating nanocomposites

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Low loss electric energy transportation research with focus on insulating materials with high dielectric breakdown strength, low dielectric losses and robustness over time under high voltage field at low frequencies is the main issue here. Insulating nanocomposites have experimentally been shown to have improved electrical properties as compared with pure polymer materials. [1, 2]

The cause of these improvements is not yet fully understood. Existing electro-chemical models [3] don't capture electro-dynamical behavior. These models introduce an interaction zone between nanoparticle and polymer, and such zones have been observed in experiments [4]. Electromagnetic simulations for a material with embedded nanoparticle result in significantly higher fields as compared with fields in a pure bulk material under the same conditions [5]. Taking an interaction zone into account can decrease the maximum field intensity. However simple constitutional relationships do not account for the experiments.

Considering the interfacial region of nanocomposites, chemical and quantum mechanical effects become important. Of high interest are the electron band gap structure of insulating polymers and its changes (defect states) due to interaction with nanoparticles. We want to use DFT as an instrument to examine the process of space charge transport in the interaction zone under an external field, e.g. by using nonequilibrium Green's function. We are interested in insulating nanocomposites such as organic polymers (epoxy, polyethylene) with inorganic nanofiller (silica SiO_2, alumina Al_2O_3). We believe that DFT-based results will help us to explain how embedding nanoparticles can improve the electric properties of insulating materials.

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Atomic and electronic structure of F-doped TiO_2

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TiO_2 also known as Titania, has been shown to be a material with a huge range of possible technological applications, such as solar cells, sensors and, in special, photocatalyst. It is also well known that the band gap of this material is closer to 3 eV, this value makes the material only sensitive to the ultra-violet radiation. To take advantage of the visible spectra of the light a narrower band gap is needed. An important challenge is to modify the material to achieve a variation on its electronic structure in a way that closes the band gap in order to make this material more effective under visible radiation. In this work we present a theoretical work focused in the understanding and rationalization of the electronic structure of the F-doped titania in its different polymorphs. For doing this we have performed a series of ab-initio calculations in order to find the best way to properly describe, as accurate as possible, the electronic structure of this material to further elucidate the role of the Fluor atoms in the electronic structure. Here we shown and discuss the performance of different functionals and methods (GGA, GGA+U, Hybrid functionals and GW) for the 3 different TiO_2 polymorphs.

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P 44

Relative Stability of Wurtzite and Zinc-Blende CdSe Nanocrystals as a Function of Vacancy Concentration

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Semiconductor nanocrystals are often synthesized by wet chemistry, resulting in off-stoichiometric compositions. Therefore, vacancies exist in nanocrystals and can play an important role in determining the nanocrystalline structure and physical properties. For example, it was previously found that the presence of vacancy defects stabilize the haxonite mineral.[1] However, the effect of vacancy defects on semiconductor nanomaterials still remains to be explored.

In this project, we investigate cadmium selenide (CdSe), a nanocrystal model system, and we focus on its relative stability in the wurtzite (WZ) and zinc blende (ZB) forms, as a function of defect concentration. The *ab-initio* density functional theory (DFT) is employed, and all the calculations will be carried out using the *ab-initio* VASP[2-5] code using the GGA-PBE[6,7]/PAW[8,9] potentials and approaches.

We will use WZ and ZB CdSe supercells to study how the type of vacancy sites (Cd or Se), the location of vacancy sites, and the vacancy concentration affect the total energy. Subsequently, we will study the energy-vacancy concentration relationship by changing the number of vacancies from zero to ten in hexagonal-close-packed (HCP) and cubic-close-packed (CCP) $Cd_{54}Se_{54}$ supercells, respectively. We expect to find a trend in the energy difference of WZ CdSe and ZB CdSe with respect to the vacancy concentration.

The results of this theoretical study will be compared with experimental results from TEM studies. The WZ phase is dominantly present in general, but in certain cases the CdSe NCs were observed to ba all in the ZB crystal structure, and were found to fuse into larger crystals by oriented attachment during *in-situ* heating. We expect that the DFT calculations will shed light on whether a particular off-stoichiometry can stabilize the ZB phase over the WZ phase.

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P 45

Self-assembled monolayers of gluthatione on Au(111)

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Self-assembled monolayers (SAMs) of thiols on Au(111) are a model system in surface science and, in addition, have numerous applications from the nanotechnological point of view (1). In particular, alkanethiol SAMs on Au(111) present vacancy islands("pits") whose nature has been a matter of discussion for a long time. Nowadays their origin can be explained by considering the formation of thiolate-gold adatom, which causes a considerable reconstruction of the Au(111) surface. Aromatic thiols, in contrast, do not seem to induce the formation of gold-thiol complexes. Glutathione (GSH) is a ramified thiol with bears hydrophilic groups which has been very little studied on Au(111). It is a tripeptide of great relevance in biological processes, due to the fact that it is the main antioxidant produced by cells and a species of considerable importance for different metabolic routes. The goal of this project was to study glutathione SAMs on Au(111) under the frame of the recent surface models which involve the formation of some kind of gold adatom-adsorbate species.

To this end, glutathione SAMs were prepared by incubating Au(111) substrates in aqueous GSH solutions. Characterization was performed with the following surface techniques: cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS) and in-air scanning tunneling microscopy (STM). Our results show that GSH adsorbs on Au(111) through a thiol ate bond. The thiol coverage is considerably lower than that of alkanethiols, which can be attributed to steric reasons. Unlike alkanethiols, and even if glutathione is not an aromatic thiol, its adsorption does not induce the formation of gold adatom-thiolate species, as revealed by the absence of vacancy islands.

To better analyze the S-Au interface, our next step will be to propose a model for the GSH SAM based on high resolution STM images and taking into account the coverage obtained by CV and XPS. Calculations based on the Density Funtional Theory (DFT) will be performed using the VASP (The Vienna Ab initio Simulation Package) program version VASP.5.2.12, which allows the inclusion of van der Waals terms to account for adsorbate-adsorbate interactions. Calculations will be done via the Atlante supercomputer, which is part of the Spanish Supercomputing Web (RES) at the Scientific-Technological Park of Las Palmas de Gran Canaria University (ULPGC), Spain. These studies will be done with the scientific advisory and supervision of Dra. Pilar Carro (University of La Laguna (ULL), Spain). Electronic structure calculations will center in the description of the geometrical parameters of GSH, as well as in the energetic analysis. In the case of GSH-capped nanoclusters, different sizes will be considered (up to approximately 200 atoms).

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P 46

The mechanism of sulfur poisoning on the Ni/YSZ anode of solid oxide fuel cells: Model for Calculations The role of the oxygen vacancy

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The Ni/YSZ (yttrium-stabilized zirconia) is the most popular anode material of SOFCs. However, a major issue in the long-term stability and activity of the anode catalyst is its poor resistance toward poisonous compounds presented in the feed stream. Trace amounts of H_2S presented in biomass generated syngas streams are enough to deactivate the catalyst .Therefore, it is desirable to understand the mechanism of sulfur poisoning on the Ni/YSZ anode since such information is applicable to mitigating the deactivation and to developing sulfur tolerant anode material.

It is found that the adsorbed S does not favor to be adsorbed at the stoichiometric Ni/YSZ interface. Instead, it diffuses much easily away from the stoichiometric Ni/YSZ interface due to the repulsion between adsorbed S^- and the interface O^2. However, when an O vacancy is introduced at the Ni/YSZ interface, the diffusion direction is reversed. The adsorbed S diffuses back to the Ni/YSZO_v interface and is trapped at the oxygen vacancy, and therefore blocks the pathway of the oxygen ion transfer. As a result, the oxygen ion transfer resistance would be increased and the SOFC performance would drop.

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MULTIFERROICITY IN LAYERED PEROVSKITES

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We have explored via first-principles calculations two possible ways to achieve multiferroicity in a layered-perovskite "topological" [1] ferroelectric $La_2Ti_2O_7$ (LTO). We find that (i) low-concentration substitution of Ti by V produces robust unidirectional ferromagnetic (FM) order, resulting in a small-gap proper multiferroic material; (ii) the isovalent substitution of Mn for Ti produces multiferroicity with weak FM order due to canting of AF Mn spins, and large magnetoelectric coupling. First-principles calculations are performed in the generalized gradient approximation to density functional theory (DFT), as implemented in VASP [2], and electron-ion interaction is described within the PAW scheme in both cases. For V-doping of LTO in the experimental monoclinic $P2_1$ structure, we find a proper multiferroic, with V dopants aligning in FM-ordered chains or chain fragments, and always preserving both the insulating nature and FM unidirectional order. The origin of the robust FM order lies in the structural anisotropy of the layered host, favoring directional orbital overlap; V-based magnetic chains indeed exhibit both FM spin order and antiferro-orbital order. Preliminary non-collinear spin-orbit calculations show that polarization switching by the coercive field causes a full magnetization switching.

Then we considered the full isovalent substitution of Mn for Ti, i.e. the compound $La_2Mn_2O_7$ (LMO). For this compound we assumed the simpler orthorhombic Cmcm and $Cmc2_1$. The polarization is still parallel to **c** and is about 0.17 C/m^2, comparable to displacive ferroelectrics. The estimated T_C is about 1500 K. The stable magnetic structure is an approximate G-type AF, as expected from superexchange between Mn^{4+} with majority t_{2g} orbitals. The estimated average J is 5 meV which corresponds to a Neél temperature T_N=270 K in the Ising 3D AF model. Magnetic noncollinear spin-orbit calculations reveal that spins nearly point along the **c** direction, but are slightly canted in the **bc** plane making LMO a a weak ferromagnet. Interestingly, LMO has a lattice-mediated magnetoelectric tensor α over 70 times that of the paradigmatic Cr_2O_3 magnetoelectric [3], with only non-diagonal elements resulting in a cross-field response of the type $M_y=\alpha E_z$.

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Vertex Approximations in Many-Body Theory

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We develop approximations to the vertex function in Hedin's equations. The vertex function is neglected in established approaches to Hedin's equations, principally the GWA, in contrast to Green's function and screened interaction, polarizability and self-energy, so as to obtain a simplified but tractable system of equations. Density functional theory then permits to make inroads into the resulting system of equations by providing an orbital basis, the Kohn-Sham propagator and polarization as a starting point for evaluating the remaining, approximate relations. In this context we plan to give a more prominent role to the vertex, and in the process, also to DFT. As an illustrative equation between a many-body quantity and a DFT quantity we may allege the Sham-Schlüter equation involving the self-energy, and we might look at corresponding equations involving the vertex. Information on general characteristics of the vertex function is scant, but we hope to get enough bearings (e.g. [1], [2], [3], [4], [5]) from symmetry, model systems, DMFT, to obtain workable expressions. At the same time we may profit from the open nature of the problem to circumvent costly calculations that have led to the neglect of the vertex so far. We plan to test our work in FHI-aims, whose post-DFT potential has ultimately been demonstrated along related lines, with F. Caruso *et al*. implementing a scGW framework [6].

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Comparison of Some Dispersion-Corrected and Traditional Functional as Applied to Small Induction -Dispersion Complexes, para-Benzoquinone - Pyrimidine Dimer and Peptides.

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Dispersion Corrected Density Functional Theory has received much attention in recent literature as a method capable of improving the poor performance of older functionals for weakly bounded dispersion complexes [1]. The scope of this study is to evaluate the performance of few popular representatives of this new class of dispersion corrected functionals (namely M06, M06-2X, M06L, B97D, wB97-xD) and traditional DFT (B3LYP, X3LYP, PBE1PBE) against high-level ab initio methods (MP2 and CCSD(T)) and experimental data. Presented research involves: 1. the study of induction enhanced dispersion complexes of HF and LiF with Ne, Methane and 2-Butyne [2]; 2. a reinvestigation of the relative stability of π-stacking and hydrogen bonded complexes of para-benzoquinone and pyrimidine (BQ-Pyr) [3]; 3. a comparison of energetics and structural properties of model polyalanine secondary structures calculated using DFT methods [4]. In each case the dispersion corrected functional do not show significant improvement over traditional DFT, but they predict results contradicting experiments. We observe that functionals parametrized to treat dispersion overestimate, sometimes by quite a lot, dispersion when mixed with induction., incorrectly predict the most stable conformer of the BQ-Pyr dimer, significantly overestimate the enthalpies of folding of the α-helix, and predict unreasonable structures that contain Ramachandran phi and psi and C=O...N H-bonding angles that are out of the bounds of the databases compiled β-sheets.

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P 50

Comparative Study of the Thermoelectric Properties of PbTe and Bi

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Thermoelectric materials provide a way to generate electricity from waste heat [1,2]. Understanding of transport processes in the state-of-art thermoelectric materials may provide guidelines for design of materials with reduced thermal conductivity and/or improved electrical conductivity and Seebeck coefficient, and thus improved thermoelectric figure of merit and efficiency.

Lead telluride (PbTe) has been shown to be an effective thermoelectric material at temperatures around 500 K [2]. PbTe is a narrow gap semiconductor, which crystallises in the rock-salt structure [3]. In addition, it shows a tendency towards Peierls distortion, and possesses an exceptionally low thermal conductivity.

Bismuth (Bi) is expected to be chemically similar to PbTe and, in a broad sense, it can be thought of as a covalent counterpart of PbTe. It relaxes to a rhombohedral structure, which represents a Peierls distorted rock-salt structure [4]. Bi is a semi-metal with a higher thermal conductivity and a lower thermoelectric figure of merit than PbTe [5].

Due to the similarities of the two materials, it warrants study to understand how the ionic character of bonding in PbTe gives rise to a larger figure of merit with respect to Bi. Here we study how the interplay of covalency and ionicity (or the lack thereof) affects the electronic and phonon band structures of PbTe and Bi. We carried out Density Functional Theory calculations using ABINIT code [6]. We also calculate the thermal conductivity of these materials using the Boltzmann transport theory [7], and we analyse the role of ionicity in establishing a lower thermal conductivity in PbTe than in Bi.

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Evaluating thermodynamical properties of nanoclusters with Parallel Tempering Monte Carlo

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The study of the stability of transition-metal (TM) nanoclusters is an important problem in the context of nanoscience as TM systems and their alloys are used in a wide range of technological applications. To understand the stability of TM nanoclusters as a function of temperature, we calculated the thermodynamical properties (internal energy, heat capacity, and etc) of TM nanoclusters. The calculations were performed using our implementation of the Parallel Tempering Monte Carlo (PTMC) [1], which provide better results when compared with standard Monte Carlo simulations. In particular, we obtain a better description of the thermodynamic properties near the phase transition. We studied the thermodynamical properties of Lennard-Jones nanoclusters as a benchmark for our implementation of the PTMC. With this method, we were able to reproduce all results published in the literature for the Lennard-Jones nanoclusters [2,3], in particular, the phase transition temperature for various nanoclusters sizes. Then, we applied our method to the study of binary nanoclusters composed by Au and Pd using empirical pair potentials, in order to understand the stability and the phase transition of these systems. Furthermore, we combine our implementation with first-principles potentials based on density functional theory as implemented in the Fritz-Haber Institute-Ab-initio molecular simulation (FHI-AIMS) package to study the thermodynamical properties of small nanoclusters.

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The Thermal transport properties in graphene and its derived nanostructures

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Graphene and its derived nanostructures have recently become the hot spot of scientific community due to the unique electronic properties and their potential to become the mainstream materials in future device fabrications [1]. In addition to the fascinating electronic properties, actually, impressive thermal transport properties have also been revealed in this novel carbon nanometrials [2-5], for instance, superb thermal conductivity ($\sim$ 5000 W/mK) [2], obvious anisotropic thermal transport [3], unique negative differential thermal conductance [4], and exceptional thermal rectification efficiency [5]. These novel thermal properties imply that graphene and its nanostructures are promising candidates for future nanoscale thermal management and phononic engineering. In recent years, using the Nonequilibrium Green's function method our group gives a systematic study of the thermal transport properties in graphene and its derived nanostructures [6-10]. (a) It is found that the thermal conductivity of graphene nanoribbon can be reduced significantly by isotopic superlattice modulation [6]. The thermal transport property strongly depends on the superlattice period length and the isotopic mass. (b) The results show that the heat flux runs preferentially along the direction from narrow to wide terminals, presenting an evident ballistic thermal rectification effect in the asymmetric three-terminal graphene nanojunctions [7]. (c) Based on folded graphene nanoribbons we report a new thermal conductance modulator which performs analogous operations as the rheostat in electronic circuits [8]. (d) The thermal transport properties of hexagonal boron nitride nanoribbons are investigated as well. An obviously anisotropic thermal transport phenomenon is observed in this nanoribbon [9]. (e) Graphyne, a new allotrope of carbon, is a hot spot in present nanomaterial research community. Interesting thermal transport property is also observed in this novel nanoribbon [10].

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Optical properties and charge-transfer process studies for efficient organic photovoltaic cells: ab-initio simulations

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At the interfaces formed by two contacted materials (donor and acceptor) interesting phenomena with a big number of applications for designing optoelectronic devices take place. This is the operating principle of organic photovoltaic cells (OPCs) which have attracted much attention due to its low-cost of fabrication and clean conversion of light. The efficiency and viability of OPCs depend strongly on tailoring and control of the interfaces at the molecular scales. Despite this current understanding and for designing more efficient devices, the role played by the charge-separation processes and the optical properties at the interfaces need to be addressed carefully. Thus, this project will use ab- initio simulations based on many-body theory approximation (GW approximation) to model one of the most important processes taking place at the interfaces of OPCs, the charge-transfer process. This process is critical to device performance and depends sensitively on the electronic and atomic structure of the interfaces such as the energy alignment of the charge transferred states. In such a sense, the project will be devoted to suggest and study improved heterojunctions based on: graphene nanoribbons, organic semiconductors and dyes. Special attention will be given to nanoribbons as an acceptor due to its transparency and unique optoelectronic properties which allow tuning their band gap through a proper design of their length, width, and edge structure. Thus, we will tailor the nanoribbons by edge functionalization, doping and tuning of the band gap, in order to explore its role over the charge transfer states and obtain improved heterojunctions.

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Multiscale simulations to guide development and applications of the next generation of Ultrasfast Electron Microscopes

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The ability to image material transformations at the ps to fs timescale with atomic scale resolution opens the door to the investigation of a variety of interesting physical phenomena, including the numerous electron-phonon cooperative effects in strongly correlated systems[1,2]. The focus of this work is to present our progress in developing an ultrafast electron microscope and in the study of correlated electron systems that reflect measurements taken with this instrument.

The proposed electron microscope is a complex system, in which a high brightness electron beam (between $10^5 - 10^9$ particles) is generated in order to take snapshots at fs timescales. The theoretical treatment of the system, therefore, necessitates exploration on multiple levels. To do this, we start by showing how a continuum model can be used to simulate the whole microscope column with all the optical elements, to optimize the position and strength of each one and make qualitative predictions.

We then proceed to examine in more detail how the electron pulse traveling through the column is created and how the characteristic of the emitting surface influences the achievable experimental resolution. This is a challenging problem as it requires simulating the creation, interaction and trajectories of between $10^4 - 10^6$ charged particles, each representing between 10 and 100 electrons. We show how the onset of the so-called virtual cathode regime hinders the emission of electrons from the photocathode surface and how this can be overcome by increasing the extracting electric field[3]. The simulation data presented shows good agreement with the experimental measurements[4].

We have recently started investigating strongly correlated electron materials, which exhibit a variety of complex and coupled atomic, spin and electronic structures and can be imaged with this Ultrasfast Electron Microscope. We will show some preliminary data on our efforts in developing an efficient multiscale method of simulating the exciting laser pulse, the imaging electron beam and their interaction with the sample, to shed light on mechanisms underlying the response of these complex materials.

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P 55

Computation and Interpretation of Mössbauer Parameters of $Li_{7-3x}Fe_x^{3+}La_3Zr_2O_{12}$ garnets.

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Li-oxide garnets are excellent Li-ion conductors with high mechanical, thermal, chemical, and electrochemical stability above approximately 100 C. Since Geiger et al. [1] have shown that Al^{3+} stabilizes the cubic Li-oxide garnets at ambient conditions, a high interest occurs respectively for a possible use in Li-ion batteries. Though much research on $Li_7La_3Zr_2O_{12}$ garnet has made in the past several years, a number of questions remains open. This is especially true with regard to the role of substitutional cations (e.g. Al, Ga, Fe, etc.) and their effect on phase stability, ionic conductivity and crystal-chemical properties. In order to understand these issues, we investigated a series of Fe^{3+}-containing $Li_7La_3Zr_2O_{12}$ garnets by using Mössbauer spectroscopy. According to the crystal chemistry Fel^{3+} has the possibility to incorporate instead of Li in the sites 24d, 48g or 96h. Especially 24d with 4 neighbored Li (96h) allows 3 possible arrangements with different probabilities. These considerations are confirmed by the Mössbauer spectrum exhibiting broad quadrupole splitting distribution. Further contributions from Fe^{2+} impurities lead to a spectrum which cannot be interpreted in detail without first-principles calculations. For all first-principle computation the Li^+ environment of Fe^{3+} or Fe^{2+} were arranged on the basis of crystal chemical considerations proposed in literature. [2,3] A body centered (I-type) Bravais lattice, namely $Li_{56-x}Fe^{x+}La_{24}Zr_{16}O_{96}$, was used as a structural input. All calculations are based on spin-polarized DFT methods. Geometry optimizations were performed using the Vienna ab initio simulation package (VASP) [4,5] with the generalized gradient approximation (GGA-PBE) [6], a projector-augmented wave (PAW) [7] method and pseudopotentials. Mössbauer parameters were derived from the corresponding wave function by using the adaptive numerical all-electron linearized augmented plane wave (LAPW) [8] method of the Wien2k code [9].

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Controlling the Accuracy-Simplicity Tradeoff in Building Physical Models

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When constructing physical models from infinite sets of orthogonal bases, we often encounter two problems: 1) choosing the best bases in the infinite set to use; and 2) knowing which terms in the expansion to remove when a there are restrictions on the number of basis functions that can be included (enhancing the sparsity). A recent application of compressive sensing to alloy cluster expansions [1] provides the methodology to overcome the first problem: minimization of the l_1 norm selects the optimal basis functions from a large set, if the solution is known to be sparse in that basis. Reweighted l_1 minimization [2] allows the sparsity of the solution to be improved, which helps solve the second problem.

I present methods for selecting penalty functions for reweighted l_1 minimization to control sparsity. The selection of appropriate penalty functions for use in reweighted l1 minimization allows the sparsity of physical models to be controlled optimally for very large sets of basis functions.The main body text of your abstract goes here. The abstract length should not exceed one page.

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Effect of aromatic hydrocarbons on the vibronic structure of emission and absorption spectra of (dibenzoylmethanato)boron difluoride (DBMBF2) derivatives

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Recently, interest in the synthesis and study of (dibenzoylmethanato)boron difluoride (DBMBF2) derivatives has increased because of useful photophysical and photochemical properties of these compounds. DBMBF2 is characterized by large extinction coefficients, large two-photon absorption cross section, intense fluorescence with a high quantum yield, and high photostability DBMBF2 and its derivatives in the first excited singlet state form exciplexes with aromatic hydrocarbons, which exhibit strong fluorescence. Its maximum shifts to longer wavelengths with increasing electron-donating properties of the hydrocarbon. This feature can be used to create optical chemical sensors for aromatic hydrocarbons based on DBMBF2. It was also found that the absorption and fluorescence spectra of DBMBF2 derivatives essentially depend on the position of the O-allyl substituent. Theoretical calculations of gas-phase absorption and emission spectra at the TDDFT-PBE0/SVP level provide a good agreement with the obtained experimental data. However, a more detailed analysis of the vibronic structure of absorption and fluorescence bands of different DBMBF2 derivatives would provide a better understanding of its origin. Our work is directed toward finding the most appropriate way of describing vibronic structure in the emission and absorption spectra of O-allyl derivatives of DBMBF2 using DFT and TDDFT. We will also estimate solvent effects using PCM. Calculations of vibronic structure in the emission and absorption spectra are based on Lax's model[1-18].

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Carbon Under Extreme Conditions

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Carbon and carbon compounds play an important role in the chemistry and physics of planets. In Neptune and Uranus for example the abundance of carbon in the form of methane amounts to 10-15% of the total mass. It was shown that methane can dissociate under the extreme conditions in the interior of these planets and may precipitate in the form of diamond [1]. Another example is the extrasolar super-Earth 55 Cancri e which has recently been discussed to contain 10-70% of carbon [2] leading to a planet that consists perhaps of a huge amount of diamond. The modeling of the interior structure of such planets requires precise knowledge of the phase diagram and equation of state (EOS) of carbon in a wide range of pressures and temperatures. A variety of high pressure phases have been proposed including the BC8 phase at pressures above 1 TPa followed by a simple cubic (SC) phase above 2.9 TPa [3], which have yet to be experimentally confirmed.
In our work we investigate the diamond-BC8 coexistence line for temperatures up to 7000 K using the Vienna Ab Initio Simulation Package (VASP [4]). The transition pressure is obtained from the free enthalpies of the respective phases. We take into account the vibrational entropies by calculating phonon dispersions with Phonopy [5]. Results are compared with other theoretical calculations.

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Direct Spin injection in GaN AlN ZnO

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GaN,AlN and ZnO form the backbone of today's display industry. Selective spin-injection into these materials would allow the development of opto-electronic spintronic devices. These materials are traditionally classed as semiconductors due to high defect concentration, however developments in growth technology has allowed the growth of high quality insulating films, opening the opportunity for spin filtering and spin injection through the TMR affect.

In this work we investigate the possibility of spin-filtering in the Fe[111]/X/Fe[111] and BCC Co[111]/X/Co[111] junctions, where $X \in$(GaN, AlN and ZnO). We have applied density functional theory and non-equilibrium Green's function formalism to investigate the ground state properties and tunneling properties of the proposed junctions. We show that at the Γ-point GaN, AlN and ZnO the Δ_1 is the slowest decaying state along the [0001] direction. Coupling this state to the available states in Fe/Co, we demonstrate the potential of these devices for spin-injection.

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Probing the interaction of DNA nucleobases with diamondoids through atomistic simulations

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Understanding the interaction of biomolecules with materials is essential in view of the variety of potential applications in the integration of these two systems can lead to. To this end, we investigate the interaction of DNA with diamondoids. The latter are a wide family of tiny hydrogen- terminated diamond clusters which have shown high technological potential ([1],[2]). We probe this interaction through quantum-mechanical computer simulations. We focus on the hydrogen bonding possibilities of the different DNA nucleobases with the lower diamondoids with respect to their relative distance and orientation ([3],[4]). Our aim is also to investigate ways to promote the binding between these two units. Accordingly, we functionalize the diamondoid by replacing one of it's hydrogens with atomic groups, such as amine groups, and study the respective binding probabilities of these two molecules. We probe this binding through the binding energy and the electronic structure of the nucleobase-diamondoid system and reveal the specific role of their frontier orbitals. In the end, we discuss the importance of our results in view of realizing a diamondoid functionalized nanopore for electrically reading out the DNA sequences ([5]).

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Modelling the MOVPE Growth of GaP on Si(001) by DFT: from Precursor Decompositions to thin Layer Properties

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Decomposition mechanism classes of triethylgallane and tert-butyl phosphine, which are used as precursors for the MOVPE coating of Si-integrated, functionalized III/V-semiconductor materials [1,2], were examined with quantum chemical methods. MP2 and dispersion-corrected PBE [3] were used to calculate thermodynamic and kinetic properties at realistic reactor conditions. Our results provide chemical understanding of class-specific elementary reactions - thermodynamically motivated decomposition networks show pathways to resulting species like atomic Ga and P, respectively. However, due to large thermal barriers, the most likely candidates for adsorption were identified as the two original precursor molecules next to GaH_3 (gallane) and GaH.

This study will consistently be expanded to related surface processes in periodic PAW models [4] investigating adsorption, heterogeneous decomposition, migration and growth towards GaP thin layers. Multiscale modelling approaches [5] like kinetic MC or AIMD will complement this project.

The atomic structure of the GaP/Si(001) interface is known from HR-TEM images [6], however, its electronic configuration urges investigation by high-accuracy simulation methods. As the band structure is determined by the distribution of both ions and electrons (and resulting polarization or stress forces), the ability to calculate and potentially manipulate the former is of highest importance for optoelectronic and electron transport applications based on this material.

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SIMULATIONS OF PHOTOABSORPTION AND PHOTOIONIZATION SPECTRA COMBINING REFLECTION PRINCIPLE WITH DFT METHODS

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Quantitative modeling of molecular electronic absorption is of vital importance in various scientific fields from atmospheric chemistry to technology. Reflection principle was shown to yield accurate estimates of electronic spectra even for larger systems or solvated molecules. To model correctly the position, shape and intensity of the photoabsorption or photoionization spectrum, we need to pay a particular attention to the selection of electronic structure method. Due to often prohibitive computational cost of the multi-reference methods, DFT and its time-dependent variant become the obvious choice for the extended molecular systems. However, not every functional can be used for excited states. We present two case studies: (a) small water clusters and (b) solvated nitrate anion.

In the case of water clusters, we model the valence photoelectron spectrum of water comprising of three peaks which correspond to the ionization from $1b_1$, $3a_1$ and $1b_2$ molecular orbitals. We concentrate on the influence of the correct sampling procedure (based on classical molecular dynamics, harmonic wave function or path integrals) and on the choice of the DFT functional. The modeled spectra are compared with experiment when available and with highly accurate EOM-CCSD method otherwise [1,2].

The spectroscopy of nitrate anion and its solvation represents another interesting case, principally because the absorption band centered at $\sim$300 nm is symmetrically forbidden. However, there is experimental evidence for this process. We discuss the correct description of the symmetrically forbidden band and the role of solvation using selected DFT functionals.

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Investigating the role of electrodes on the thermal stability of HfO_x based RRAM devices

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For the purpose of assessing the effects of electrodes on the thermal stability of HfO_x based RRAM devices, two types of samples namely:TiN (25nm)/HfO_x/Ti (10nm) and Pt (25nm)/HfO_x/Pt (25nm), with a HfO_x thickness of 10nm, were processed and characterized. For simplicity, we refer to Pt/HfO_x/Pt as Pt/Pt and TiN/HfO_x/Ti as TiN/Ti. We show that the forming voltage (V_F)decreases with increasing temperature (T) for both TiN/Ti and Pt/Pt samples [1]. TiN/Ti devices exhibit a lower VF due to the sub-stoichiometric region created in the HfOx film by the oxygen-gettering action of the Ti metal during the device fabrication [2].Kinetic Monte Carlo (KMC) model was used to reproduce the forming process[3]and good agreement was observed between the model and experimental results. DC sweeps were performed at different temperatures in order to investigate the thermal stability of the devices states. Set (V_{set}) and reset (V_{reset}) voltages measured on TiN/Ti devices are shown to decrease with increasing T [1]. The same tests performed with Pt/Pt show that only the reset voltage decreases with rising T while the set voltage increases with it. Also Ron and R_{off} show different trends: R_{off} increases with rising T, while R_{on} remains constant.Furthermore, R_{off} values for Pt/Pt and TiN/Ti samples were measured at different temperatures and we found that R_{off} for Pt/Pt increases with rising T and never restores its initial state while for TiN/Ti, R_{off} does decrease with it and restores its initial state. Hence, increasing the temperature induces a permanent change of state in Pt/Pt samples.

In order to understand the effect of O_i interstitials on the poor thermal stability of the CF observed in Pt/Pt samples, DFT simulations with GGA-PBE functional were performed using VASP [4]. The formation energy of O_i with Ti (0.76 eV) is much lower than that of O_i with Oxygen vacancy (V_o) (8.07 eV). On the other hand, the formation energy of a V_o in HfO_2 plus an Oi in Pt leading to PtO (7.91 eV) indicates that there is hardly any energy gain in the Pt-O bond formation. For this reason, we consider that most of the O_i generated during set remain dispersed within the HfO_2 film in Pt/Pt samples. This results in the inferior performances of Pt/Pt cells due to the large availability of (O_i) in the HfO_x matrix, which accelerates the T-induced re-oxidation of the conductive region thus resulting in higher Roff thermal instability.

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Effects of the anisotropy on the phonon optical modes of Silicon nanowires: An *ab-initio* study

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Silicon nanowires (SiNWs) are 1-D semiconductor nanostructures that have been extensively studied theoretical and experimentally [1] in the recent years due to their potential applications. An important tool for characterization of nanowires are the phonon vibrational modes, since a variety of properties such as thermal transport, the Raman and infrared response of the material are understood by using the phonon theory. The effect of orientation on the frequency of the radial breathing mode (RBM), and other phonon optical modes of silicon nanowires (SiNWs) is investigated by means of first principles Density Functional Theory approach through the generalized gradient approximation and the finite displacement supercell scheme. We compare the RBM frequency of SiNWs orientated in three different directions [001], [111], and [110] where the nanowires are modeled by removing atoms outside a circumference in the desired growth direction according to the supercell scheme [2]. Results show, that the SiNWs are stable in the three chosen directions since there is no negative frequencies in their phonon band structure and density of states. A clear dependence of the RBM frequency with respect of the growth direction of the nanowires and the phonon confinement was observed as the RBM frequency decreased with an inverse power law in each nanowire direction, with the fitting parameters dependent of the growth direction. We also observe a broadening in the frequency of H vibration modes as the nanowire diameter increases. These results could be useful for characterization of the nanowires through Raman spectroscopy techniques.

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Native Defects and Hydrogen Impurities in $SrZrO_3$

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Point defects are known to play a key role in affecting the properties of complex oxides and their heterostructures [1, 2]. Using first-principles hybrid functional calculations [3], the electronic and optical properties of native vacancies and hydrogen dopants in cubic $SrZrO_3$ have been investigated. Oxygen vacancies form deep-donor levels in the bandgap, and are most likely to form in the 2+ charge state for realistic Fermi-level positions. Cation vacancies form deep acceptor states; holes localize on neighboring oxygen atoms, which are displaced towards the vacancy center by up to 0.9 Å in the case of strontium vacancies (V_{Sr}). The hole localization makes the center paramagnetic. We examine the luminescence properties of V_{Sr} by inspecting the calculated configuration coordinate diagram, finding that electron-hole recombination at V_{Sr} can account for the blue photoluminescence observed in Sr-deficient $SrZrO_3$ [4]. As was reported previously for $SrTiO_3$ [5], in the positive charge state, hydrogen prefers to incorporate interstitially (H_i) at an off-axis site, where it forms an O-H bond of 0.99 Å. For Fermi levels near the conduction band H_i becomes negatively charged and prefers to be located halfway between adjacent Sr atoms. The transition between charge states, $\varepsilon(+/-)$, is found 0.44 eV below the conduction-band minimum. Hydrogen impurities can also incorporate substitutionally on an oxygen site (H_O), forming a shallow donor state. However, the formation energy is high when compared to H_i. Calculations are also performed using the more traditional GGA functional [6], and compared with the hybrid calculations. In general, although increasing computational demand, the hybrid functional results are found to be superior to the GGA for the electronic structure of $SrZrO_3$.

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Kondo-effect in binuclear metal-organic molecules

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Unpublished STM-measurements on a binuclear metal-organic molecule, (Ni(hexafluoroacetylacetonate)$_2$)$_2$bipyrimidine ((Ni(hfacac)$_2$)$_2$(bpym)), of the Wulfhekel group show that the system undergoes a Kondo-effect with a spin that is located near the Ni-atom. The system is very interesting from a theoretical point of view because here the Kondo-effect occurs in the presence of two spins that compete for screening by conduction electrons.
The poster will report about ongoing theoretical work. We investigate the local (Kohn-Sham) spectral function on both Nickel-atoms via an embedded DFT-calculation. As it turns out the relative peak-broadenings are sensitive to the binding of the molecule to the substrate. Since this broadening also enters the Kondo-temperature, T_K, DFT predicts a trend for the dependency of T_K on the substrate coupling that can be tested experimentally.

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Structure and Electronic Properties of Au Intercalated Hexagonal-Boron-Nitride/Graphene Bilayer

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Based on density functional calculations, we study the structural and electronic properties of Au-intercalated hybrid bilayer composed by a single layer hexagonal-boron-nitride (h-BN) and a single layer of graphene. Focusing on Au substituted doping in the h-BN layer, we find that the C-C bond length in the lower graphene layer has only minor changes, which implies that the lower graphene layer in h-BN/graphene bilayer keeps well the original C lattice. Our results show that the Au-doped h-BN/graphene bilayer structure is stable with Au atom tightly confined in a small region between the upper and lower layers, with an estimated energy barrier about 1.94 eV for the Au dopant to diffuse to the lower graphene layer. Semiconductor to metallic change is found due to the generation of localized mid-states near the Fermi level arising from the hybridization between the occupied states of the Au atom and the B, C, N atom in h-BN/graphene hybrid bilayer. Charge transfer occurs from Au dopant to both h-BN layer and graphene layer, increasing the carrier density in the ultra-thin atomic hybrid bilayer. Detailed of this work can be found: Physica E 49 (2013) 111.

Key words: first-principles, doping, hexagonal-boron-nitride, graphene, hybrid bilayer

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DFT calculations of electronic and magnetic structure of CuMnAs and other I-Mn-V compounds

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Semiconductor spintronics traditionally utilizes ferromagnetic semiconductors. Such semiconductors are, however, rare and have low Curie temperatures. Recent observation of a large magnetoresistance in an antiferromagnet (AFM) based tunnel junction[1] opens the prospect for utilizing AFM semiconductors instead. Promising candidates are antiferromagnetic I-Mn-V compounds. Two such compounds, LiMnAs[2] and CuMnAs[3], were recently synthetized by MBE. LiMnAs is a room-temperature antiferromagnetic semiconductor, but it is problematic due to the reactive nature of Li. CuMnAs does not suffer from such issues and it is also a room-temperature antifferomagnet, but it is a semimetal. Little is know experimentally about most of the other I-Mn-V compounds. We performed a series of DFT calculations, concentrating mostly on various CuMn-V compounds, to understand their electronic and magnetic properties.

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Electronic and optical properties of Cu-based semiconductors

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Cu-based materials have been intensively studied owing to their desired optical properties for photovoltaic application [1]. Currently, ternary (e.g., $CuInSe_2$) and quaternary semiconductors (e.g., $Cu_2ZnSnSe_4$) are among the most efficient materials. However, it is still very difficult to prepare high quality materials in experiments. On the theory side, despite much earlier effort [2], our understanding of their basic crystal structures, electronic, and optical properties is still far from satisfactory. As a result, there are substantial uncertainties in the fundamental properties.

Our previous research found that the difficulties for theoretical research come from the dual nature of Cu d states and that the PBE+U+G_0W_0 (U = 4 eV) method can give reasonable electronic band structures and gaps [4]. While this method dealing with the Cu d^{10} states satisfactorily, it fails for systems that containing partially filled d states. For example, it, as well as other currently widely used methods in the first principles materials modeling community, strongly overestimates the band gap of $CuFeS_2$. The main difficulty arises from an effective treatment of the partially filled Fe d states. In this regard, we turn our attention to the more accurate methods used in computational chemistry, such as the MP2. In addition, a comparison between different approaches could provide meaningful guidance for the research.

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Simulation of the Absorption Spectra of Organic Chromophores in Condensed Phase

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We use multi-level simulation methods which are based on frozen-density dmbedding theory (FDET) [1-3] combined [4] with linear-response time-dependent density-functional theory (LR-TDDFT) [5] to investigate the condensed phase environment effect on the absorption spectra of organic chromophores. We treat the environment either explicitly or statistically which can be solvents, porous solids (like zeolites), biochemical systems (like proteins), etc.

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Ab-initio Study of H-Doping and Oxygen vacancy at anatase TiO_2(001) surface

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Titanium dioxide (TiO_2) is a widely used material with many industrial applications [1]. Because of the photo-catalytic activity and environmental compatibility, it has tremendous potential applications in solar cells, dying industries, electronic devices, sensors and transformers [2-5]. Density functional-pseudopotential computations were performed to study the effects of hydrogen doping and oxygen vacancy on electronic structure and stability of (001) surface of TiO_2 in the anatase phase. In the framework of *ab-initio* atomistic thermodynamic, we argue that the anatase TiO_2 prefers a defected oxygen layer termination in the (001) direction. The obtained electronic structures indicate that deep hydrogen doping in this stable termination creates a mid-gap state about 0.52 eV below the conduction band and hence decreases the band gap of the system. This phenomenon may explain the enhanced photocatalytic activity of the anatase TiO_2(001) surface after hydrogenation.

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