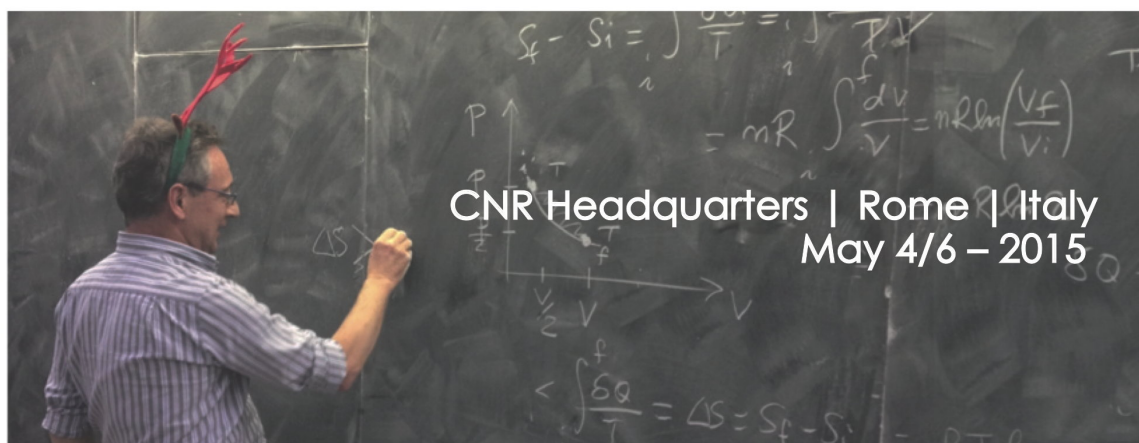




COMPUTER SIMULATIONS FOR CONDENSED PHASE SYSTEMS

From Correlated Electrons to Novel materials



CNR Headquarters | Rome | Italy
May 4/6 – 2015

Invited speakers

Massimo Altarelli, European XFEL, Hamburg - Germany
Ole Krogh Andersen, Max-Planck-Institut, Stuttgart - Germany
Wanda Andreoni, Ecole Polytechnique Fédérale, Lausanne - Switzerland
Stefano Baroni, International School for Advanced Studies, Trieste - Italy
Federico Capasso, Harvard University - USA
Roberto Car, Princeton University - USA
Stephen Fahy, University College of Cork - Ireland
Annalisa Fasolino, Radboud University Nijmegen - The Netherlands
Alessio Filippetti, CNR Istituto Officina dei Materiali, Cagliari - Italy
Donald R. Hamann, Rutgers University - USA
Gianni Jacucci, Università di Trento - Italy
Steven Louie, University of California, Berkeley - USA
Franco Meloni, Università di Cagliari - Italy
Elisa Molinari, CNR Istituto di Nanoscienze, Modena - Italy
Saverio Moroni, CNR Istituto Officina dei Materiali, Trieste - Italy
Michele Parrinello, Eidgenössische Technische Hochschule Zürich, Switzerland
Luciano Pietronero, Università La Sapienza, Roma - Italy
Raffaele Resta, Università di Trieste - Italy
Matthias Scheffler, Fritz-Haber-Institut, Berlin - Germany
Ari P. Seitsonen, École Normale Supérieure, Paris - France
Annabella Selloni, Princeton University - USA
Sandro Sorella, International School for Advanced Studies, Trieste, Italy
Erio Tosatti, International School for Advanced Studies, Trieste, Italy
Cyrus J. Umrigar, Cornell University - USA
Angelo Vulpiani, Università La Sapienza, Roma - Italy

Organisers

Fabio Affinito
CINECA, Bologna - IT

Paola Alippi
CNR-ISM, Roma - IT

Claudio Attaccalite
CNRS, Grenoble - FR

Lilia Boeri
Graz University of Technology - AT

Michele Cascella
University of Oslo - NO

Paola Gori-Giorgi
VU University, Amsterdam - NL

Leonardo Guidoni
Università dell'Aquila - IT

Daniele Varsano
CNR-NANO, Modena - IT

PROGRAM AND ABSTRACT BOOKLET



SAPIENZA
UNIVERSITÀ DI ROMA



lenovo



EUROPEAN
SCIENCE
FOUNDATION



ACKNOWLEDGEMENTS

The Organizers are very grateful to

CLAUDIA MARGAROLI (<http://www.claudiamargaroli.com>) for designing the conference logo and poster, and to the following scientific networks, institutions and companies for partial financial support:

PSI-K

Psi-k is a wide network of European researchers working closely with many friends and colleagues around the world that is intended to help build cooperation in the field of computational electronic structure calculations, in particular for crystalline quantum systems whose wave function Ψ has an associated wave vector \mathbf{k} defining its periodicity, hence the name. The network is funded by the European Science Foundation.

SAPIENZA AWARDS 2013

Proprietà statistiche di sistemi complessi classici e quantistici, a project lead by professor Angelo Vulpiani.

CNR - DSFTM

The Department of Physical Sciences and Technologies of Matter (DSFTM) of National Research Council (CNR) coordinates 11 Institutes spread all over the national territory in 56 branches that host 750 researchers. A comparable number of associated scientists from Universities participates in the activities. DSFTM Institutes carry out research spanning from fundamental issues, at the frontier of knowledge, to applicative topics, in responses to societal challenges and in agreement with the goals of Horizon 2020 at European level, namely Environment, Aerospace, Agri-food, Life Sciences, Communications, Information processing and storage, preservation of Cultural Heritage, Energy, Health and Wellness.

CNR - ISM (Istituto di Struttura della Materia)

The Institute performs cutting-edge research in an interdisciplinary field between physics, chemistry and materials science. Its activities find applications in areas such as energy, environment, biological systems, electronic and magnetic devices, and cultural heritage. The institutes activities range from theoretical modeling to development of prototypal devices. This is achieved via the study of processes, the preparation and functionalization of materials, and the characterization of their structural and electronic properties with novel instrumentation and methodologies.

CRISIS LAB

Crisis Lab is a strategic research project financed by Italian Government and coordinated by CNR - ISC (Istituto dei Sistemi Complessi) with the aim of creating an Observatory of risks in domains ranging from finance, energy, markets, transport and urban systems, with interdisciplinary methodology based on the new science of Complex Networks. The focus of the Crisis lab is to develop models using empirical data to describe the vulnerabilities of diverse socio-technical systems which have a complex underlying dependency structure. (<http://www.crisislab.it>)

ERC

The European Research Council within the VII Framework Program of the European Union is contributing through the project ERC-IDEAS MultiscaleChemBio. It is a 6-year research project lead by Leonardo Guidoni aimed to overcome current limitations in the study of electronically correlated systems by developing and applying multiscale, innovative and unconventional computer simulation techniques. The project involves research teams at the Department of Physics of La Sapienza University of Rome and at the Department of Physics and Chemistry, at the University of L'Aquila.

LENOVO

Lenovo is a 39-billion-dollar global company leader in providing innovative technology to different market segments consumers, professionals, large companies. Our portfolio of reliable, high-quality products and services includes PC's (for example, the historical Think line or the YOGA brand of multimodal products), workstations, servers, storage, smart TV and a family of mobile products such as smartphones (including the Motorola brand), tablets and apps. Last news (for Italy) at www.lenovo.com/it, [Twitterlenovoitalia](https://twitter.com/lenovoitalia) - www.facebook.com/lenovoitalia Facebook, [LinkedIN https://www.linkedin.com/company/lenovo-italia](https://www.linkedin.com/company/lenovo-italia)

PROGRAM

Monday, May 4th

8:30 registration

Paola Alippi
introduction

Chair: Fabio Affinito

**Luigi Nicolais,
Egidio Longo**
opening address

Angelo Vulpiani
A (random) tour around
quantum mechanics,
condensed matter and
reductionism

Federico Capasso
Structured light with
metasurfaces

10:30 coffee break

Tuesday, May 5th

Elisa Molinari
Exciting graphene
nanosystems

Chair: Daniele Varsano

Annalisa Fasolino
Subbands of new oxide
heterostructures: the
LaAlO₃/SrTiO₃ interface

Matthias Scheffler
Big data of materials
science – critical role
of the descriptor

Stefano Baroni
What I cannot compute, I do
not understand: fathoming
atomic heat transport from
the struggle to simulate it!

11:00 coffee break

Wednesday, May 6th

Gianni Jacucci
Autopoiesis & Cognition,
an outstanding outcome
of Phenomenology

Chair: Claudio Attaccalite

Massimo Altarelli
Theory challenges from X-ray
free-electron lasers

Luciano Pietronero
New metrics for economic
complexity: the intangible
fitness of countries and
complexity of products

Michele Cascella
closing remarks

11:00 coffee break

Monday, May 4th

11:30

Wanda Andreoni

CO₂ Capture in Amine solutions: an update on modeling and simulations

12:00

Erio Tosatti

Modeling versus realistic first-principles calculations / simulations in condensed matter theory

12:30

Annabella Selloni

Water adsorption and oxidation on metal oxides

13:00

Michele Parrinello

Atomistic modeling of crystal nucleation and growth

Chair: Leonardo Guidoni

13:30

lunch

Tuesday, May 5th

Cyrus J. Umrigar

Zero-temperature quantum Monte Carlo methods and the sign problem

Stephen Fahy

Ultrafast photoexcitation and decay of coherent phonons

Sandro Sorella

What about phase separation in the Hubbard model?

Saverio Moroni

Coexistence, interfacial energy and microemulsions of 2D dipolar bosons.

Chair: Paola Gori-Giorgi

lunch

Monday, May 4th

15:00

Ole K. Andersen

Band structure of the purple bronze $\text{LiMo}_6\text{O}_{17}$

15:30

Donald R. Hamann

Ab-initio pseudopotentials: from BHS to ONCVSP

16:00

Steven G. Louie

Electrons and excitons in quasi 2D materials

16:30

Roberto Car

Van der Waals bonded crystals: a challenge for density functional theory

Chair: Lilia Boeri

Tuesday, May 5th

Who cares about cores?

In this panel discussion, different generations of students and coauthors will briefly illustrate major achievements and anecdotes of their academic/professional activity related to the scientific and/or human interaction with Giovanni Bachelet.

**Chair: Alessio Filippetti
Ari P. Seitsonen**

17:00

coffee break

17:30

poster session

coffee break

poster session

20:30

social dinner

Franco Meloni with photo archive by **Raffaele Resta**

Contents

Invited talks: abstracts	7
Massimo Altarelli (Hamburg, Germany, EU) <i>Theory challenges from X-ray Free-Electron Lasers</i>	7
Ole K. Andersen (Stuttgart, Germany, EU) <i>Band structure of the purple bronze $\text{LiMo}_6\text{O}_{17}$</i>	7
Wanda Andreoni (Lausanne, Switzerland) <i>CO_2 Capture in Amine solutions: an update on modeling and simulations</i>	8
Stefano Baroni (Trieste, Italy, EU) <i>What I cannot compute, I do not understand: fathoming atomic heat transport from the struggle to simulate it!</i>	8
Federico Capasso (Cambridge, Massachusetts, USA) <i>Structured light with metasurfaces</i>	9
Roberto Car (Princeton, New Jersey, USA) <i>Van der Waals bonded crystals: a challenge for density functional theory</i>	9
Stephen Fahy (Cork, Ireland, EU) <i>Ultrafast photoexcitation and decay of coherent phonons</i>	9
Annalisa Fasolino (Nijmegen, The Netherlands, EU) <i>Subbands of new oxide heterostructures: the $\text{LaAlO}_3/\text{SrTiO}_3$ interface</i>	10

Alessio Filippetti and Ari P. Seitsonen (Cagliari, Italy and Paris, France, EU) <i>Who cares about cores: a panel discussion of all-time GBB veterans</i>	10
Donald R. Hamann (Newark, New Jersey, USA) <i>Ab-initio pseudopotentials: from BHS to ONCVSP</i>	10
Gianni Jacucci (Trento, Italy, EU) <i>Autopoiesis and Cognition, an outstanding outcome of Phenomenology – What’s in it for a Physicist?</i>	11
Steven G. Louie (Berkeley, California, USA) <i>Electrons and excitons in quasi 2D materials</i>	12
Franco Meloni and Raffaele Resta (Cagliari and Trieste, Italy, EU) <i>Friendships that work: from 1980 up to now (dinner talk)</i>	12
Elisa Molinari (Modena, Italy, EU) <i>Exciting graphene nanosystems</i>	12
Saverio Moroni (Trieste, Italy, EU) <i>Coexistence, interfacial energy and microemulsions of 2D dipolar bosons</i>	12
Michele Parrinello (Zurich, Switzerland) <i>Atomistic Modeling of Crystal Nucleation and Growth</i>	13
Luciano Pietronero (Rome, Italy, EU) <i>New Metrics for Economic Complexity: Measuring the Intangible Fitness of Countries and Complexity of Products</i>	13
Matthias Scheffler (Berlin, Germany, EU) <i>Big Data of Materials Science – Critical Role of the Descriptor</i>	14
Annabella Selloni (Princeton, New Jersey, USA) <i>Water adsorption and oxidation on metal oxides</i>	14
Sandro Sorella (Trieste, Italy, EU) <i>What about phase separation in the Hubbard model?</i>	14

Erio Tosatti (Trieste, Italy, EU) <i>Modeling versus realistic first principle calculations/simulations in condensed matter theory</i>	15
Cyrus J. Umrigar (Ithaca, New York, USA) <i>Zero-temperature quantum Monte Carlo methods in real space and occupation number space and the sign problem</i>	16
Angelo Vulpiani (Rome, Italy, EU) <i>A (random) tour around quantum mechanics, condensed matter and reductionism</i>	16
Poster abstracts	17
Claudio Attaccalite (Grenoble, France, EU) <i>FIESTA: French Initiative for Electronic Simulations with Thousands of Atoms</i>	17
Matteo Barborini (Modena, Italy, EU) <i>Scanning tunnelling spectroscopy imaging from quantum Monte Carlo</i>	17
Paolo Barone (L'Aquila, Italia, EU) <i>Coupling ferroelectricity with spin-valley physics in oxide-based heterostructures</i>	18
Valentina Brosco (Rome, Italy, EU) <i>Optimum Wannier orbitals for the Hubbard model and Gutzwiller functionals</i>	18
Elena Cannuccia (Grenoble, France, EU) <i>Combined first principle calculations and experimental study of the phonon modes in the GeV_4S_8 compound</i>	19
Matteo Capone (Rome, Italy, EU) <i>Water oxidation mechanisms in photosynthesis by Quantum Mechanics / Molecular Mechanics simulations</i>	19
Giancarlo Cappellini (Cagliari, Italy, EU) <i>Computational investigation on the electronic, optical and transport properties of hexathiapentacene in the molecular and solid phases</i>	20
Arianna Carbone (TU Darmstadt, Germany, EU) <i>Ab-initio study of strongly correlated nucleons: from nuclei to nuclear matter</i>	20

Fafa Chiker (Sidi Bel Abbes, Algeria) <i>First principles studies of structural, thermal and electronic properties of ZrSiO₄, ZrGeO₄ and HfSiO₄ dielectric materials</i>	21
Sergio Ciuchi (L'Aquila, Italy, EU) <i>Non-perturbative effects of electron-phonon interaction in strongly disordered system</i>	21
Andrea Di Luca (Rome, Italy, EU) <i>Efficient inclusion of polarization effects in classical molecular dynamics by fluctuating RESP (F-RESP) charge model</i>	22
Laura Fanfarillo (Madrid, Spain, EU) <i>Electronic correlations in multiorbital systems and iron superconductors: Hund vs Mott</i>	22
Barbara Gregori (Roma, Italy, EU) <i>Conformational analysis of a modified peptide: Infrared spectroscopy and Density Functional Theory</i>	23
Jerzy Goraus (Katowice, Poland, EU) <i>Band structure calculations have been performed within Virtual Crystal Approximation for the (Fe_{1-x}Mn_x)₂P series using FP-LAPW/APW+lo method</i>	23
Conor Hogan (Rome, Italy, EU) <i>Ab initio simulations of atomic gold wires on silicon surfaces</i>	24
Jun Kang (Antwerp, Belgium, EU) <i>Electronic Properties, Carrier Mobility and Strain Response of TiS₃ Nanoribbons</i>	24
Stefano Lariccia (Roma, Italy, EU) <i>Requirements and conceptual modeling of information infrastructure and home automation of a retirement house for active and long-lived seniors</i>	25
Antonio Lasanta Becerra (Rome, Italy, EU) <i>Fluctuating hydrodynamics of a lattice model with inelastic collisions and conserved momentum</i>	25
Adriano Mosca Conte (Rome, Italy, EU) <i>Oxidation of ancient paper: a non-destructive spectroscopic methodology for cultural heritage preservation</i>	26

Henry Odhiambo (Maseno University, Kenya) <i>Electronic and optical properties of hexagonal and cubic $Ge_2Sb_2Te_5$</i>	26
Giovanni Onida (Milano, Italy, EU) <i>Circular dichroism (CD) spectra of amino–acid molecules</i>	27
Daniele Ottaviani (L’Aquila, Italy, EU) <i>Competing factors on the frequency separation between the OH stretching modes in water</i>	27
Raphael Peltzer (Oslo, Norway, EU) <i>Solvent dynamics controls the stability and reactivity of Grignard reagents</i>	28
Marco Polimeni (Rome, Italy, EU) <i>Dynamics at the peptideanatase $TiO_2(101)$ interface</i>	29
Carlo Presilla (Rome, Italy, EU) <i>Probabilistic representation of quantum systems.</i>	29
Maria Stella Prete (Rome, Italy, EU) <i>Graphene-like two dimensional Nitrides: an ab-initio study</i>	30
Seyda Horzum Sahin (Antwerp, Belgium, EU) <i>Dimensional-Crossover-Driven Bandgap Transition in h-AlN</i>	30
Hasan Sahin (Antwerp, Belgium, EU) <i>Theoretical and Experimental Investigation of Monolayer Portlandite</i>	31
Alessandra Satta (Cagliari, Italy, EU) <i>Degradation of Cd-yellow Paints: an ab initio study of the adsorption of water and oxygen on $CdS \{10.0\}$ surface</i>	31
Niccolò Scopigno (Rome, Italy, EU) <i>Metal-to-superconductor transition, mesoscopic disorder and intrinsic charge instability in oxide heterostructures</i>	32
Mohamed Tadout (Rabat, Algeria, EU) <i>First principles calculations of GaN and AlN nanosheets</i>	32

Invited talks: abstracts

Theory challenges from X-ray Free-Electron Lasers

Massimo Altarelli

European X-ray Free-Electron Laser Facility, 22761 Hamburg, Germany, EU

Free-electron Lasers (FELs) have started operating since a few years. The salient features of these x-ray sources are the very short pulses, down to a few fs duration, and the extremely high peak power, exceeding that from the best synchrotron sources by many orders of magnitude. Experiments using these revolutionary sources have started to open up new frontiers for x-ray physics. The scientific case and the first results include time-resolved studies of dynamics on sub-ps scales, applications to structural biology by nano-crystallography and studies by imaging of non-periodic systems, and investigation of high-energy density phenomena such as the production of warm dense matter. At the same time, the very short duration of the pulses opens up the possibility to explore the dynamics of electronic and structural properties on an unprecedented time scale, well below the ps region. The challenges, but also the potential scientific pay-off, for theoretical investigations of time-dependent properties are briefly described.

Band structure of the purple bronze $\text{LiMo}_6\text{O}_{17}$

Ole K. Andersen*

Max Planck Institute for Solid State Research, Stuttgart, Germany, EU

$\text{LiMo}_6\text{O}_{17}$ displays metallic quasi-1D behavior that is unusually robust against 3D crossover before superconductivity at $\approx 0.9\text{K}$, and a large anomalous Luttinger liquid density-of-states exponent $\alpha \approx 0.6$. The crystal structure is 3D and complicated with 12 molybdenums per primitive cell, 6 of which are inequivalent. Nonetheless, in all existing calculations the band-structure around the Fermi energy is surprisingly simple, showing two nearly degenerate 1D bands. For all occupied bands, which in fact form 3 sets of quasi-1D bands running in different directions, there is nearly perfect agreement between recent high-resolution, low-temperature ARPES measurements and the LDA. This band structure, in particular the small perpendicular dispersion of the conduction band, we explain by deriving an effective t_{2g} TB Hamiltonian from an FP-NMTO downfolding calculation. Since each t_{2g} Wannier function covers 4 Mo sites, we expect a small value of the Hubbard U , consistent with the good LDA description of ARPES. The conduction-band Bloch functions look like strings of pancakes. This implies strong long-ranged Coulomb interactions (V) which might explain the large value of α .

*In collaboration with: M. Haverkort, Y. Nohara, L. Dudy, J.W. Allen, J.D. Denlinger, J. He, and M. Greenblatt

CO₂ Capture in Amine solutions: an update on modeling and simulations

Wanda Andreoni

EPF-Lausanne, Switzerland

Wet capture of CO₂ mainly employs amine aqueous solutions, and primarily aqueous monoethanolamine (MEA) at a given concentration. In spite of the extensive experimental research aimed at improving process performance also with alternative solvents, only a few attempts have been made to characterize the relevant chemical reactions with computational methods. I will briefly report on our recent “ab initio”^{1,2,3} molecular dynamics simulations of CO₂ uptake and release in MEA aqueous solutions. The focus will be on the new insights thus obtained and on the comparison of our results with previous calculations and experimental data.

¹Ma, C.; Pietrucci, F.; Andreoni, W. under review

²Ma, C.; Pietrucci, F.; Andreoni, W. JPCL 2014, 5, 16721677.

³Guido, C. A.; Pietrucci, F.; Gallet, G. A.; Andreoni, W. JCTC 2013, 9, 2832.

What I cannot compute, I do not understand: fathoming atomic heat transport from the struggle to simulate it!

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy, EU

Modern simulation methods based on electronic-structure theory have long been thought to be unfit to compute heat transport coefficients within the Green-Kubo formalism. This is so because the quantum-mechanical energy density from which the heat flux is derived is inherently ill defined, thus allegedly hampering the use of the Green-Kubo formula. I believe that every property that can be measured can also be computed, at least in principle. If it cannot, it's that the underlying theory is still incomplete. Steered by this conviction, we¹ have derived an expression for the adiabatic energy flux from density-functional theory that permits the ab initio simulation of atomic thermal transport using equilibrium molecular dynamics. The resulting thermal conductivity is shown to be unaffected by the above-mentioned ill-definedness of quantum mechanical energy densities and currents. Our new methodology is demonstrated by comparing results from ab-initio and classical molecular-dynamics simulations of a model liquid-Argon system, for which accurate inter-atomic potentials are derived by the force-matching method, and finally applied to compute the thermal conductivity of heavy water at ambient conditions.

¹“We” refers to Aris Marcolongo, Paolo Umari, to whom goes my gratitude for the fruitful and pleasant collaboration, and myself.

Structured light with metasurfaces

Federico Capasso

Harvard University, Cambridge, , Massachusetts, USA

Metasurfaces are optically structured surfaces using subwavelength spaced optical elements such as resonators that allow one to design the wavefront of scattered light in practically arbitrary ways. Generalized laws of reflection and refraction, vortex beams, radially polarized vector beams and other states of structured light will be discussed. A new approach to design optical components has emerged from this work (Flat Optics) which has led to the demonstration of flat lenses with no spherical and chromatic aberrations.

Van der Waals bonded crystals: a challenge for density functional theory

Roberto Car

Princeton University, Department of Chemistry, Princeton, New Jersey, USA

Van der Waals (vdW) dispersion interactions are ubiquitous in nature and constitute the main binding force in organic molecular crystals. These systems have long been a challenge for density functional theory (DFT) because standard semilocal approximations for the correlation energy miss the nonlocal vdW contribution. This situation changed in the last decade with the emergence of vdW inclusive functionals, in which dispersion forces are not a simple post-DFT correction but are derived self-consistently from a density functional. This approach improves significantly the agreement of the calculated geometries with experiment but a close match of theory and experiment is only obtained when the large anharmonic effects characteristic of soft condensed matter are properly taken into account. I will use the example of pyridine-like molecular crystals to illustrate these concepts. Finally, I will comment on hydrogen bonded (HB) systems like water and ice that require a subtle balance between directional HB interactions and dispersion forces.

Ultrafast photoexcitation and decay of coherent phonons

Stephen Fahy

Department of Physics, University College Cork, Ireland, EU

The recent development of x-ray free electron laser (XFEL) facilities with femtosecond time resolution has opened up exciting new possibilities for the study of coherent phonon dynamics. In conjunction with ultrafast pump-probe experiments, simulations based on first-principles electronic structure theory offer considerable insight into these processes. In this presentation, I will discuss two aspects of the dynamics of the A_{1g} and E_g zone-centre phonons in photo-excited bismuth: (1) electronic forces that drive atomic motion following ultrafast photoexcitation and (2) the subsequent decay of coherent motion. I will show that incoherent scattering processes cause the electronic forces that drive low-symmetry E_g coherent phonon motion to decay much more rapidly than the forces driving the high-symmetry A_{1g} mode. I will discuss anharmonic phonon decay in classical terms and show that the decay of coherent phonons gives rise to resonant squeezing of phonon branches near points of the Brillouin zone, where energy conservation is satisfied in the usual three-phonon picture of anharmonic decay. For the typical amplitude of coherent A_{1g} phonon motion that is feasible in ultrafast pump-probe experiments, this squeezing causes temporal oscillations of the diffuse x-ray scattering signal, which should be observable with time- and momentum-resolved x-ray probe techniques available at current XFEL facilities.

Subbands of new oxide heterostructures: the LaAlO₃/SrTiO₃ interface

Annalisa Fasolino

Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands, EU

Heterostructures of oxide materials have been recently realized. Much interest in these structures has been triggered by the observation of a high-mobility electron gas at the LaAlO₃/SrTiO₃ interface, an unexpected, and as yet unexplained, feature in view of the fact that the constituent materials are both insulators. We have studied the subband formation at this interface in the low density regime, in good agreement with the experimental observation of multiple bands Shubnikov-de Haas oscillations.¹ We also discuss the effect of different domains, anisotropy and Rashba spin splitting.

¹L. W. van Heeringen¹, G. de Wijs, A. McCollam, J. C. Maan and A. Fasolino Phys. Rev. B 88, 205140 (2013) and in preparation.

Who cares about cores: a panel discussion of all-time GBB veterans

Alessio Filippetti (a) and Ari P. Seitsonen (b)

(a) CNR Istituto Officina dei Materiali, Cagliari, Italy, EU;

(b) École Normale Supérieure, Paris, France, EU

In this panel discussion, different generations of students and coauthors will briefly illustrate major achievements and anecdotes of their academic/professional activity related to the scientific and/or human interaction with Giovanni Bachelet. The range of activities presented here will give a chance to appreciate in full display the breadth and depth of Giovanni's interests and teachings.

Ab-initio pseudopotentials: from BHS to ONCVSP

Donald R. Hamann

Department of Physics and Astronomy Rutgers University, USA

The routine use of ab-initio pseudopotentials to perform accurate density-functional calculations of many properties of solids dates from the publication of the BHS periodic table.¹ I will discuss this landmark and the subsequent development of new pseudopotential formulations. The recent introduction of the ONCVSP formalism and code² returns norm-conserving potentials to a position competitive with the more complex forms that have been introduced in the intervening years. I will outline this method and its capabilities. I will review a resurgence of activity benchmarking sets of pseudopotentials against all-electron calculations and show representative ONCVSP results. New ONCVSP-based periodic tables are appearing, closing the circle back to BHS.

¹G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B 26, 4199 (1982).

²D. R. Hamann, Phys. Rev. B 88, 085117 (2013).

Autopoiesis and Cognition, an outstanding outcome of Phenomenology – What’s in it for a Physicist?

Gianni Jacucci

Università di Trento, Italy, EU

Perception experiments on vision in frogs and in humans brought Maturana and Varela - two phenomenology poised biologists - to introduce the notion of autopoiesis and cognition, as the realisation of the living: constituent processes are auto produced by living organisms; this ability being the peculiar defining characteristic of the living. The processes affecting perception described by Maturana and Varela consist of *reflexive feedback mechanisms* in living systems, influencing cognition and behaviour. A case of *second order cybernetics*. “*Living systems are cognitive systems, and living as a process is a process of cognition. This statement is valid for all organisms, with or without a nervous system.*”¹ The auto-production of constituent processes characterises groups as well as social processes - e.g., in the cooperative behaviour of directionally coordinated flight, in a flock of birds.² In contrast to the cooperative phenomena in the inanimate world, this is not just the result of interaction potential or vision - between units at a distance, but of autopoiesis of the living group: a complex, peculiar, sensorial perception, cognition, and group behaviour regulatory process: “*...correlation(s) scale with the system’s size and swarms exhibit a near-maximal degree of correlation at all sizes...*”³ Beyond perception and behaviour in the physical world, *autopoiesis-and-cognition* also governs the human mental life, and the welfare of communities and societies. Personal knowledge as described by the phenomenology thinker and chemist Polanyi –the tacit ability of humans to read meaning from details around a focus⁴– is dependent on past experience, personal interests, and mood, of individuals and groups: room for the appearance of *reflexive feedback mechanisms* in the social. What about the physicist, and the physics community? Phenomenological “*apparitions*”, as are central in biology (e.g., the astonishing directional coordination in the flight of distant birds), can be identified also in physics research: phenomenology as a position, and an investigation approach. Apparitions are seen in social aspects of the scientists’ work.⁵ Latour turns back time in the case of the discovery of the “double helix”.⁶ Deconstructing statements, machines and articles, it is possible to arrive at a point where scientific discovery could have chosen to take other directions, demonstrating how social context and technical content are both essential to understanding scientific activity: is this *autopoiesis*? Heidegger’s phenomenology is best exhibited⁷ in his analysis of the situation of early Christian communities, through the Letters of St. Paul (Heidegger 2004), commented by Claudio Ciborra.⁸ “*The phenomenological understanding is nothing else than an intuitive going along the meaning. It must stay close and present to the total situation of the phenomenon... Capacity to accompany - being intimate, love. Love as motivating ground of the phenomenological understanding - given necessarily in its sense of enactment.*” Sounds familiar to a physicist.

¹Humberto Maturana and Francisco Varela, 1979. *Autopoiesis and Cognition: The Realization of the Living*. Boston Studies in the Philosophy of Science. Paperback, 1991.

²Information transfer and behavioural inertia in starling flocks, by A. Attanasi, A. Cavagna, L. Del Castello, I. Giardina, T. S. Grigera, A. Jelić, S. Melillo, L. Parisi, O. Pohl, E. Shen, M. Viale, *Nature Physics* **10**, 691696 (2014).

³Finite-Size Scaling as a Way to Probe Near-Criticality in Natural Swarms, A. Attanasi, A. Cavagna, L. Del Castello, I. Giardina, S. Melillo, L. Parisi, O. Pohl, B. Rossaro, E. Shen, E. Silvestri, and M. Viale, *Phys. Rev. Lett.* **113**, 238102 (2014).

⁴M. Polanyi, *The Tacit Dimension*, Anchor Books, New York 1966.

⁵See Bruno Latour, *Science in Action: How to Follow Scientists and Engineers through Society*, Harvard 1987, his study on the discovery of the structure of DNA by Watson and Crick.

⁶Watson J., *The Double Helix*, 1968.

⁷M. Heidegger, *The Phenomenology of Religious Life*, Indiana University Press (2004).

⁸Getting to the Heart of the Situation: The Phenomenological Roots of Situatedness, Claudio Ciborra, London School of Economics, IULM University, Milan University of Oslo - Draft (edited by MP) May 2004.

Electrons and excitons in quasi 2D materials

Steven G. Louie*

*Physics Department, University of California at Berkeley, and
Lawrence Berkeley National Lab, Berkeley, California, USA*

Experimental and theoretical studies of atomically thin quasi two-dimensional (2D) materials and their nanostructures have revealed that these systems can exhibit highly unusual behaviors. Owing to their reduced dimensionality, these systems present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry, many-body interaction, and substrate screening effects often play a critical role in shaping qualitatively and quantitatively their properties. In this talk, we present theoretical studies on quasi-2D systems such as monolayer and few-layer transition metal dichalcogenides (e.g., MoS₂, MoSe₂, WS₂, and WSe₂) and metal monochalcogenides (such as GaSe and FeSe) as well as graphene. Several quantum phenomena are discussed, including novel and dominant exciton effects, tunable magnetism, and electron supercollimation by disorder in these materials. We investigate their physical origins and compare theoretical predictions with available experimental data.

*This work was supported in part by the National Science Foundation and Department of Energy.

Friendships that work: from 1980 up to now (dinner talk)

Franco Meloni (a) and Raffaele Resta (b)

(a) Università di Cagliari, Italy, EU; (b) Università di Trieste, Italy, EU

Exciting graphene nanosystems

Elisa Molinari

Universit di Modena e Reggio Emilia, and CNR - Istituto Nanoscienze, Modena, Italy, EU

Excitations in graphene nanostructures are discussed as a laboratory to understand unusual electronic interactions from huge exciton binding to few-particle states and nanoplasmonics, and as a key to design frontier spectroscopies and functionalities. Ab initio theoretical results will be compared with different sets of experimental data recently obtained on atomically controlled systems.

Coexistence, interfacial energy and microemulsions of 2D dipolar bosons

Saverio Moroni

CNR-IOM, Trieste, Italy, EU

The superfluid-crystal quantum phase transition of a system of purely repulsive dipolar bosons in two dimensions is studied by quantum Monte Carlo simulations at zero temperature. We determine freezing and melting densities and estimate the energy per unit length of a macroscopic interface separating the two phases. The results rule out the microemulsion scenario for any physical realization of this system, given the exceedingly large predicted size of the bubbles.

Atomistic Modeling of Crystal Nucleation and Growth

Michele Parrinello

*ETH Zurich, Department of Chemistry and Applied Sciences and
Università della Svizzera italiana, Informatica, ICS, Via G.Buffi 13, 6904 Lugano, Switzerland*

Understanding crystal growth on nucleation is crucial for controlling crystal properties. Nucleation however takes place on a time scale that exceeds our ability to simulate this phenomena by straightforward atomistic molecular dynamics simulation. To this effect, we have developed metadynamics as very successful enhanced sampling method. We apply this approach to the study of nucleation from solution. We unveil the complex nature of this process and its deviation from standard theories. Finally, by taking advantage of recent development we are able to compute nucleation rates.

New Metrics for Economic Complexity: Measuring the Intangible Fitness of Countries and Complexity of Products

Luciano Pietronero

University of Rome Sapienza and Institute of Complex Systems, ISC-CNR, Rome, Italy, EU

Economic Complexity refers to a new line of research which portrays economic growth as a process of evolution of ecosystems of technologies and industrial capabilities. Complex systems analysis, simulation, systems science methods, and big data capabilities offer new opportunities to empirically map technology and capability ecosystems of countries, industrial sectors and companies, analyse their structure, understand their dynamics and measure economic complexity. This approach provides a new vision of a data driven fundamental economics in a strongly connected, globalised world. In particular here we discuss the COMTRADE dataset which provides the matrix of countries and their exported products.^{1,2,3} According to the standard economic theory the specialization of countries towards certain specific products should be optimal. The observed data show that this is not the case and that diversification is actually more important. The situation is different for companies or sectors which seem instead to specialize only on few products. The crucial challenge is then how to turn these qualitative observations into quantitative variables. We have introduced a new metrics for the Fitness of countries and the Complexity of products which is a sort of economic version of the Google Page rank approach. The direct comparison of the Fitness with the country GDP gives an assessment of the non-expressed potential of the country. This can be used as a predictor of GDP evolution or stock index and sectors performances. These results are also useful for risk analysis, planning of industrial development and strategies to exit from the poverty trap. Analogously the Complexity of products can be compared with its added value leading also to new information. The dynamics in the GDP-Fitness plane reveals a heterogeneous structure and certain areas behave in a laminar way (high predictability) while others appear turbulent (low predictability). This situation requires an analysis inspired to the theory of Dynamical Systems and it is not appropriate to study with the usual regressions. Recently we are considering the extension of these ideas also to the Fitness of Companies which are instead mostly specialized in terms of products. This requires different datasets and a new algorithm. The implication of the present study for the general problem of Big Data Science will be discussed.

¹A. Tacchella, M. Cristelli, G. Caldarelli, A. Gabrielli and L. Pietronero: A New Metrics for Countries Fitness and Products Complexity, *Nature: Scientific Reports*, 2-723 (2012)

²M. Cristelli, A. Gabrielli, A. Tacchella, G. Caldarelli and L. Pietronero: Measuring the Intangibles: A Metrics for the Economic Complexity of Countries and Products, *PLOS One* Vol. 8, e70726 (2013).

³M. Cristelli, A. Tacchella, L. Pietronero: Heterogeneous Dynamics of Economic Complexity, *PLOS One* 10(2): e0117174 (2015) and *Nature* editorial 2015: <http://www.nature.com/news/physicists-make-weather-forecasts-for-economies-1.16963>

Big Data of Materials Science – Critical Role of the Descriptor

Matthias Scheffler*

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, EU

Statistical learning of materials properties or functions so far starts with a largely silent, non-challenged step: the choice of the set of descriptive parameters (termed descriptor). However, when the scientific connection between the descriptor and the actuating mechanisms is unclear, causality of the learned descriptor-property relation is uncertain. Thus, trustful prediction of new promising materials, identification of anomalies, and scientific advancement are doubtful. We analyze this issue and define requirements for a suited descriptor.¹ For a classical example, the energy difference of zincblende/wurtzite and rocksalt semiconductors, we demonstrate how a meaningful descriptor can be found systematically.

*in collaboration with: L. M. Ghiringhelli, J. Vybiral, S. V. Levchenko, C. Draxl

¹L. M. Ghiringhelli, J. Vybiral, S. V. Levchenko, C. Draxl, and M. Scheffler, Phys. Rev. Lett. 114, 105503 (2015)

Water adsorption and oxidation on metal oxides

Annabella Selloni

Princeton University, Department of Chemistry, Princeton, New Jersey, USA

Water splitting on metal oxide surfaces has attracted enormous interest for decades. In this talk I shall discuss water adsorption and oxidation on metal oxides, focusing on the structure of adsorbed water layers and the mechanism of proton-coupled-electron transfer at the titania-water interface.

What about phase separation in the Hubbard model?

Sandro Sorella

SISSA, Trieste, Italy, EU

A new scheme is introduced for a fast and smooth convergence to the thermodynamic limit with finite size cluster calculations. This is obtained by modifying the energy levels of the non interacting Hamiltonian in a way consistent with the corresponding one particle density of states in the thermodynamic limit. After this modification exact free electron energies are obtained with finite size calculations and for particular fillings that satisfy the so called "closed shell condition". In this case the "sign problem" is particularly mild in the auxiliary field quantum Monte Carlo technique and therefore, with this technique, it is possible to obtain exact converged energies for the Hubbard model for $0 < U < 4t$ by numerical simulations of reasonably small clusters. We establish in this way whether phase separation occurs or does not occur in the low doping region and moderate correlation regime of this model.

**Modeling versus realistic first principle calculations/simulations
in condensed matter theory**

Erio Tosatti*

International School for Advanced Studies (SISSA), and CNR-IOM Democritos, Trieste, Italy, EU

A split between different approaches and philosophies historically divides the condensed matter theory and materials simulation community, roughly speaking, into two.

One approach is based on models – idealized simple hamiltonians that can be solved to describe the essence of phenomena, many of which of strong current interest. A small subset might include Hubbard models describing Mott transitions and certain strongly correlated superconducting states, Anderson models describing transport and Kondo effects across magnetic nanocontacts, Tomlinson and Frenkel-Kontorova models describing superlubric sliding friction. These famous models describe the essence of deep physical phenomena, but are plagued by arbitrariness and based on parameters that are generally unknown and must be determined empirically.

The alternative approach is based on realistic, either classical or first principles electronic structure calculations and quantitative simulations. In principle free of arbitrary parameters, these calculations attempt at addressing the real systems in their much greater complexity. To achieve that goal however, they must generally resort to mean-field approximations such as local density functional theory, whose nature is often incompatible with the many-body physics that must be described.

While both approaches are essential– and Giovanni Bachelet contributed to both – either of them alone is incomplete, and efforts to join them are under way on many fronts. I will mention some examples developed within our group, that illustrate modest but revealing attempts at joining together realistic calculations and model approaches. Depending on available time, my examples will include the Mott and superconducting states of Cs_3C_{60} ,¹ the zero-bias STS Kondo conductance anomaly of $\text{NO}/\text{Au}(111)$ ² and sliding friction.³

*Sponsored by contracts: ERC No. 320796 MODPHYSFRICT; SNSF No. CRSII_136287/1 Sinergia; EU/Japan No. 283214 LEMSUPER.

¹M. Capone, M. Fabrizio, C. Castellani, E. Tosatti, "Colloquium: Modeling the unconventional superconducting properties of expanded A_3C_{60} fullerenes", *Rev. Mod. Phys.* **81**, 943 (2009); S. Naghavi, M. Fabrizio, E. Tosatti, to be published.

²P. Lucignano, R. Mazzarello, A. Smogunov, M. Fabrizio, E. Tosatti, "Kondo conductance in an atomic nanocontact from first principles" *Nature Materials* **8**, 563 (2009); R. Requist, S. Modesti, P. P. Baruselli, A. Smogunov, M. Fabrizio and E. Tosatti, "Kondo conductance anomaly across the smallest spin 1/2 radical molecule: ab initio theory vs. experiment", *PNAS* **111**, 69 (2014).

³A. Vanossi, N. Manini, M. Urbakh, S. Zapperi, and E. Tosatti, "Colloquium: Modeling friction: From nanoscale to mesoscale *Rev. Mod. Phys.* **85**, 529 (2013).

**Zero-temperature quantum Monte Carlo methods in real space
and occupation number space and the sign problem**

Cyrus J. Umrigar

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853, USA

This talk will provide an overview of various zero-temperature QMC methods, discuss their advantages and disadvantages, and the nature of the infamous Sign Problem. Then the recently developed Semistochastic Quantum Monte Carlo method,¹ which combines some of the advantages of Exact Diagonalization with those of the FCIQMC^{2,3} method will be discussed.

¹F.R. Petruzielo, A.A. Holmes, Hitesh J. Changlani, M.P. Nightingale, C.J. Umrigar, Phys. Rev. Lett. **109**, 230201, (2012).

²George H. Booth, Alex Thom and Ali Alavi, J. Chem. Phys. **131**, 054106 (2009).

³Deidre Cleland, George H. Booth, and Ali Alavi, J. Chem. Phys. **132**, 041103 (2010).

A (random) tour around quantum mechanics, condensed matter and reductionism

Angelo Vulpiani

University of Rome "La Sapienza", Department Physics, Rome, Italy, EU

Classical mechanics is not just the $\hbar \rightarrow 0$ limiting case of quantum mechanics: for a chaotic classical system, the proper classical limit can be obtained from quantum mechanics only taking into account the influence of the outer environment. Despite Dirac's claim even with the help of powerful computers and efficient numerical methods, quantum chemistry is not merely applied quantum mechanics. It is correct to say that quantum mechanics + (semi)classical physics is able to describe the observable features of molecules. The study of pyramidal molecules shows that the (semi)classical limit does not follow in a straightforward way from quantum mechanics but is a consequence of the interaction of single molecules with an external environment.

Poster abstracts

FIESTA: French Initiative for Electronic Simulations with Thousands of Atoms

Claudio Attaccalite

Institut Neel, CNRS, BP 166, 38042 Grenoble Cedex 9, France, EU

The Fiesta code¹ implements the GW and Bethe-Salpeter formalisms using Gaussian bases and resolution-of-the-identity techniques (RI-SVS density and RI-V Coulomb metric).² Dynamical screening contribution to the self-energy is explicitly accounted for through a contour deformation approach. Self-consistency on the wavefunctions is implemented at the static COHSEX level. Tamm-Dancoff approximation (TDA) or full Bethe-Salpeter calculations can be performed. The code presently reads input Kohn-Sham eigenstates from the open-source Siesta and NWChem packages so that all-electron or pseudo-potential calculations can be performed with standard quantum chemistry bases or with the numerical orbitals generated by the Siesta package. Any DFT code dumping all Kohn-Sham eigenstates (occupied/unoccupied) expressed on a Gaussian basis, plus the exchange-correlation contribution to the Kohn-Sham eigenvalues, can be branched very straightforwardly onto the Fiesta code.

¹<http://perso.neel.cnrs.fr/xavier.blase/fiesta/>

²"Excited states properties of organic molecules: from density functional theory to the GW and Bethe-Salpeter Green's function formalisms", C. Faber, P. Boulanger, C. Attaccalite, I. Duchemin, and X. Blase, *Phil. Trans. R. Soc. A.* **372** 20130271 (2014).

Scanning tunnelling spectroscopy imaging from quantum Monte Carlo

Matteo Barborini (a), Sandro Sorella (b), Stefano Corni (a), Massimo Rontani (a)

(a) Centro S3, CNR-Istituto di Nanoscienze, Via Campi 213/a, 41125 Modena, Italy, EU

(b) SISSA, International School for Advanced Studies and DEMOCRITOS National Simulation Center, Via Bonomea 265, 34151 Trieste, Italy, EU

Scanning tunnelling spectroscopy (STS) is an experimental technique able to visualize electronic states in nano-objects, such as quantum dots or molecules. Ideally, through Scanning Tunneling Spectroscopy (STS), the many-body observable that is accessible at low temperatures is the spectral density resolved in space and frequency.¹ After integrating over the energy in a neighborhood of the electrochemical potential, one obtains a positively defined quantity that can be regarded as the square modulus of the Quasi-particle Wave Function (QPWF) of the electron that is subtracted (hole QPWF, h-QPWF) or added (e-QPWF) to the N electron molecule during the STS experiment.^{2 3}

In this work we present a recently defined quantum Monte Carlo (QMC) algorithm to calculate the h-QPWF and the e-QPWF with a procedure that is similar to the correlated sampling technique already used to calculate energy differences in QMC. We present first results on atoms and molecules at the Variational Monte Carlo (VMC) level, using an Antisymmetrized Geminal Power (AGP) wave function. This work is supported by MIUR- PRIN 2012 MEMO.⁴

¹G. Maruccio et al., *Nano Lett.* **7**, 2701 (2007); M. Rontani et al. *J. Appl. Phys.* **101**, 081714 (2007).

²M. Rontani and E. Molinari, *Phys. Rev. B* **71**, 233106 (2005); D. Toroz, M. Rontani and S. Corni, *J. Chem. Phys.* **134**, 024104 (2011); D. Toroz, M. Rontani and S. Corni, *Phys. Rev. Lett.* **110**, 018305 (2013).

³C. J. Umrigar, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **23**, 17 (1989)

⁴Casula M. and Sorella S., *J. Chem. Phys.* **119**, 6500 (2003) Casula M. et al., *J. Chem. Phys.* **121**, 7110 (2004).

Coupling ferroelectricity with spin-valley physics in oxide-based heterostructures

P. Barone (a), K. Yamauchi (b), T. Shishidou (c), T. Oguchi (b), S. Picozzi (a)

(a) CNR-SPIN 67100 L'Aquila IT

(b) ISIR-SANKEN, Osaka University, 567-0047 Japan

(c) ADSM, Hiroshima University, 739-8530 Japan

Due to their potentiality in next-generation electronics, the exploration of novel electronic degrees of freedom represents an active field of research in condensed matter physics. The valley index, labeling degenerate energy extrema in momentum space, has been recently suggested as a promising candidate for information encoding in graphene and 2D crystals with honeycomb structure.¹ The pseudospin character of valley degrees of freedom in these materials implies that bulk inversion symmetry must be broken in order to allow for the emergence of valley-contrasting physics.² We therefore explore the possibility to permanently control the valley phenomenology via a ferroelectric polarization, which could open the path to novel device paradigms. Most of the well-known ferroelectric materials are transition-metal oxides with perovskite structure, where the hexagonal geometry can be realized in (111) heterostructures comprising a bilayer oxide sandwiched by an isostructural insulator.³ We focus on the ferroelectric BiAlO₃/BiIrO₃ heterostructure, where the complex interplay among trigonal crystal field, layer degrees of freedom and spin-orbit coupling mediates a strong spin-valley coupling and complex Rashba- and Dresselhaus-like spin textures. Density-Functional Theory calculations are supplemented by effective Hamiltonian analysis, clarifying the microscopic origin of the spin-valley coupling as well as its interplay with the ferroelectric polarization.

¹A. Rycerz et al., Nature Phys. 3, 172 (2007)

²X. Xu et al., Nature Phys. 10, 343 (2014)

³D. Xiao et al. Nat. Commun. 2, 596 (2011)

Optimum Wannier orbitals for the Hubbard model and Gutzwiller functionals

Valentina BroSCO

CNR and Dipartimento di Fisica, Università “La Sapienza”, Rome, Italy, EU

Density Functional Theory (DFT) has long been the ubiquitous starting point for electronic structure computations in solid-state physics and quantum chemistry. Most numerical methods based on DFT, however, fail in systems at or close to the Mott insulating regime, when the energy associated to the tunneling of electrons becomes small compared with the typical electron-electron repulsion energies. Even in the simple case of the H₂ molecule, the commonest DFT approaches perform reasonably well at the equilibrium distance, when electrons have substantial tunneling among the atoms, but they fail in the molecular analog of the Mott regime, when each electron is localized on one H atom. Starting from simple examples, in this work we illustrate the key features a density functional should have to describe the Mott transition. We then turn our attention to study the mapping between continuum and lattice models and we provide a method to find the “best” Wannier orbitals to write the lattice Hamiltonian whose ground state properties are eventually addressed within a generalized variational Gutzwiller approach. In certain simple cases, the whole procedure yields a reduced density matrix functional which can be readily used. Retaining the simplicity of minimal-basis models but using the “best” Wannier orbitals, the approach described in this talk may provide a natural extension of Gutzwiller theory and other lattice methods to the continuum.¹

¹Work done in collaboration with: P. Gori-Giorgi, G. Lopez, J. Lorenzana, D. Varsano, Z.-J. Ying.

**Combined first principle calculations and experimental study
of the phonon modes in the GeV₄S₈ compound**

Elena Cannuccia

Institut Laue Langevin BP 156 38042 Grenoble France

Combined first principle calculations and experimental study of the phonon modes in the GeV₄S₈ compound. The lattice dynamics of the GeV₄S₈ compound has been investigated using both density functional calculations, and Raman/Infrared (IR) measurements. While the coherence between the computed and the experimental data is very good in the low temperature phase (25K, Imm2), the agreement for the high temperature one (300K, F43m) is such that it raised the question about the validity of the F43m space group. Using group theory and first principles calculations we show that the IR/Raman phonon modes are only compatible with the I4m2 space group. This issue has a consequence on the possible interpretation of the Mott transition induced by an electric pulse.

**Water oxidation mechanisms in photosynthesis by
Quantum Mechanics / Molecular Mechanics simulations**

Daniele Bovi (a), Daniele Narzi (a), Matteo Capone (b), and Leonardo Guidoni (a,b)

(a) Dept. of Chemical and Physical Science, Univeristy of L'Aquila, Italy, EU

(b) Dept. of Chemistry, La Sapienza - University of Rome, Italy, EU

Water oxidation in photosynthetic organisms occurs through the five intermediate steps S₀-S₄ of the Kok cycle in the oxygen evolving complex of Photosystem II (PSII). Along the catalytic cycle, four electrons are subsequently removed from the Mn₄CaO₅ core by the nearby tyrosine Tyr-Z, which is in turn oxidized by the chlorophyll special pair P680, the photo-induced primary donor in PSII. Recently, two Mn₄CaO₅ conformations, consistent with the S₂ state (namely, S₂^A and S₂^B models) were suggested to exist, maybe playing a different role within the S₂ to S₃ transition [Bovi *et al.*, *Angew. Chem. Int. Ed.* 2013 vol. 52, pp. 11744]. Here we report multiscale *ab initio* DFT+U simulations revealing that upon such oxidation the relative thermodynamic stability of the two previously proposed geometries is reversed, the S₂^B state becoming the leading conformation. In this latter state a proton coupled electron transfer (PCET) is spontaneously observed at 100 fs at room temperature dynamics [Narzi *et al.*, *PNAS* 2014 vol. 111, pp. 8723]. The Mn-cluster, which is tightly electronically coupled along dynamics to the Tyr-Z tyrosyl group, releases a proton from the nearby W1 water molecule to the close Asp61 on the femtosecond timescale, thus undergoing a conformational transition increasing the available space for the subsequent coordination of an additional water molecule. The results can help to rationalize previous spectroscopic experiments and confirm, for the first time to our knowledge, that the water-splitting reaction has to proceed through the S₂^B conformation, providing the basis for a structural model of the S₃ state.

**Computational investigation on the electronic, optical and transport properties
of hexathiapentacene in the molecular and solid phases**

G. Cappellini, R. Cardia and G. Malloci

Physics Department-UniCa and IOM-CNR/UOS-Cagliari, Cittadella di Monserrato (CA), Italy

The hexathiapentacene molecule (HTP), a derivative of pentacene (PNT) obtained by symmetric substitution of the six central hydrogens with sulfur atoms, has recently received increasing attention for its potential applications in organic electronic devices. We present a Density Functional Theory (DFT) investigation of the electronic, optical and transport properties of HTP molecule, in its molecular and solid phases. For the first part of the work we performed all-electron calculations using the hybrid exchange-correlation functional B3LYP in conjunction with a Gaussian localized orbital basis set to expand the molecular orbitals. Electron affinities, ionization energies, fundamental energy-gaps, optical absorption spectra, exciton binding energies, and reorganization energies for holes and electrons have been calculated and compared with the corresponding observables of PNT and with the available experimental data. Following sulfur functionalization we found an increase of both ionization energies and electron affinities, a sensible reduction of the fundamental electronic gap, and a redshift of the optical absorption onset. Notably, the intensity of the first absorption peak of HTP falling in the visible region is found to be nearly tripled with respect to the pure pentacene molecule. As to the corresponding HTP molecular solid, we performed our simulations within a plane-wave+pseudopotential framework using the PBE exchange-correlation functional, with the inclusion of an empirical correction taking into account dispersive interactions. The comparative analysis between the ground-state and excited-state properties of solid-state HTP and PNT confirmed the general findings obtained for the isolated molecules.

Ab-initio study of strongly correlated nucleons: from nuclei to nuclear matter

Arianna Carbone (a), Carlo Barbieri (b), Arnau Rios (b), Andrea Cipollone (c), Artur Polls (d)

(a) TU Darmstadt, Germany, EU

(b) University of Surrey, UK, EU

(c) CMCC Bologna, Italy, EU

(d) Universitat de Barcelona, Spain, EU

Ab-initio approaches to nuclear systems represent the path to understand the complicated behavior of such systems from first microscopic principles. The strong correlation which characterizes the nucleon-nucleon interaction is analyzed within the ab-initio nonperturbative Self-Consistent Green's Function theory. To deal with the unavoidable presence of many-nucleon interaction, we have recently extended this approach to include the effect of three-body forces. This improved theoretical formalism used in conjunction with chiral nuclear interactions, derived from the low-energy effective theory of quantum chromodynamics, provides a realistic description of finite nuclei as also infinite nuclear matter. We show how the advent of these highly sophisticated computational techniques is pushing towards the investigation of the most exotic regions of the nuclear chart and the comprehension of neutron-rich matter found in neutron stars.

**First principles studies of structural, thermal and electronic properties
of ZrSiO₄, ZrGeO₄ and HfSiO₄ dielectric materials**

F. Chiker, F. Boukabrine, H. Khachai, A. Yakoubi

*Laboratory of Study of Materials and Optical Instruments, Physics Department,
University of Djilali Liabes, Sidi Bel Abbes, Algeria.*

The study of orthosilicates, zircon (ZrSiO₄), hafnon (HfSiO₄) and thorite (ThSiO₄) are of particularly importance, since these compounds are effective radiation resistant materials suitable for fission reactor applications and for storage of nuclear waste. In the present study, we have examined theoretically the structural, thermal, and electronic properties, for some representative orthosilicates dielectrics such as ZrSiO₄, ZrGeO₄, and HfSiO₄. From our calculated structural properties (lattice constants a and c , as well as the internal parameters u and v) we found an excellent agreement with their corresponding experimental values. This is largely sufficient to allow the further study of thermal and electronic properties. The thermodynamic properties of the above mentioned orthosilicates compounds are not very well studied yet. Therefore, the study of macroscopic thermodynamic properties through the study of electronic structure in the bulk of the compound will help in understanding the behavior of these compounds under temperature and pressure conditions. Since, our calculated thermal expansion coefficient as functions of pressure and temperature increases with temperature, and then converges to a nearly constant value at high temperature. In contrast, the thermal expansion coefficient decreases strongly with increasing pressure. Whereas, in a harmonic crystal, the calculated specific heat capacity at constant volume CV increases at low temperature and approaches the constant $3R$ at high, initially CV rises rapidly between $T=0K$ and about $500K$ before it starts to saturate. The value of CV of ZrSiO₄ at $300K$ is $98 J/mol.K$ which is smaller than $110 J/mol.K$ of both ZrGeO₄ and HfSiO₄. Further, while the entropy and enthalpy increase monotonously with increasing temperature, the free energy decreases monotonically with increasing temperature. The enhancement of entropy induced the disorder; moreover, the increasing in enthalpy decreases the stability in these compounds. At room temperature, the values of enthalpy, entropy and free energy are too close in both ZrGeO₄ and HfSiO₄ but are different from the values of ZrSiO₄. Finally, our calculated band gaps are found to be: $E_g = 5.96 eV$ (Indirect gap at N) for ZrSiO₄, $E_g = 5.79 eV$ for ZrGeO₄, and $E_g = 7.33 eV$ (Indirect Gap N) for HfSiO₄, these values agree well with the available experimental data for all compounds, this is because of the MBJ method correction.

Non-perturbative effects of electron-phonon interaction in strongly disordered system

Sergio Ciuchi (a,b) and Domenico di Sante (a,c)

(a) Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, Italy, EU

(b) CNR-ISC, Italy, EU

(c) CNR-SPIN, Italy, EU

Using a combinations of DMFT, Typical Medium Theory, and Self-Consistent Non Crossing Approximation we study the half-filled disordered Holstein model. We found that near the Anderson localized phase the electron-phonon interaction is able to drive the states near the Fermi energy toward localization. In the metallic phase polaronic signatures could be found up to very small values of e-ph coupling. Phonon quantum fluctuations instead favor metallic phase. These results which are relevant for high electron density can be of direct relevance to disordered electron-phonon materials such as covalent semiconductors or A15 compounds.

**Efficient inclusion of polarization effects in classical molecular dynamics
by fluctuating RESP (F-RESP) charge model**

Andrea Di Luca (a), Daniele Ottaviani (b), Daniele Bovi (b), and Leonardo Guidoni (b)

(a) Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, Rome, Italy, EU
(b) Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio, 67100 L'Aquila, Italy, EU

Classical molecular dynamics simulations based on fixed point charge models severely fail in describing the dynamics of molecular condensed systems in which the electronic polarization effects play an important role, such as ionic liquids and molecular liquids of conjugated molecules. Several approaches has been introduced so far to overcome this drawbacks and to describe molecular polarizabilities, as for instance the Drude oscillator models and the AMOEBA force field. These schemes anyway are not always adequate to describe intra-molecular polarization effects, and they are also more computationally expensive than traditional force-fields since they need a self consistent solution for the polarizable part. In this work we present a new model for a force-field which include polarizabilities on atoms through a fluctuating charge model based on RESP (restrained electrostatic potential) fitting of Quantum Mechanics / Molecular Mechanics simulations. Such model does not provide computational overloads with respect to traditional RESP fixed point charges. Preliminary results on liquid water show that few parameters are enough to reproduce with reasonable accuracy the polarization of QM/MM water molecules.

Electronic correlations in multiorbital systems and iron superconductors: Hund vs Mott

Laura Fanfarillo

ICMM-CSIC, Madrid, Spain, EU

The Mott transition, at which a material expected to be metallic by band theory becomes insulator, is probably the most dramatic manifestation of electronic correlations. Mott phenomena have been widely studied in single-orbital systems and play a crucial role in the physics of high temperature cuprate superconductors, which are doped Mott insulators. Contrary to cuprates which can be described with single orbital models, iron superconductors are multiorbital materials. The nature and strength of correlations in iron superconductors, key to understand the superconductivity, have been debated since their discovery. During these years new concepts such as Hund metals have been introduced to emphasize the role played by Hund's coupling in setting a bad metallic state. On spite of a wide effort a coherent description of this state, including its relation with Mott physics was lacking.

In this work, we use a slave-spin approach to analyze the electronic correlations in multiorbital systems. We study how the intraorbital interaction U , the Hund's coupling J_H and the electronic filling n affect the electronic correlations of the system and clarify the relationship between Hund's coupling and Mott physics. We identify the origin of the bad metallic behavior induced by Hund's coupling in the suppression of the double occupancy of a given orbital, i.e. the same process responsible for the Mott insulating state at half-filling. At the same time, we uncover an unexpected behavior of charge fluctuations which differentiate Hund metals from Mott systems.

**Conformational analysis of a modified peptide:
Infrared spectroscopy and Density Functional Theory**

Barbara Gregori (a), Maria Elisa Crestoni (b), Simonetta Fornarini (b), Leonardo Guidoni (a,c)

(a) Dipartimento di Fisica, Università La Sapienza, Rome, Italy, EU

(b) Dipartimento di Chimica e Tecnologie del Farmaco, Università La Sapienza, Rome, Italy, EU

(c) Dipartimento di Scienze Fisiche e Chimiche, University dell'Aquila, Italy, EU

S-nitrosoglutathione is an important reservoir for nitric oxide, a key signaling molecule in vivo. An approach to shed light on the conformational preferences of protonated S-nitrosoglutathione [GSNO+H] is presented, based on Infrared multiple photon dissociation IRMPD spectroscopy, backed by density functional theory calculations. The structural/conformational features of the sample [GSNO+H]⁺, obtained under mild electrospray ionization conditions, have been assayed both in the 1000-1900 cm⁻¹ fingerprint region at the Centre Laser Infrarouge d'Orsay (CLIO) and in the X-H (X=N, O) stretching range (3300-3700 cm⁻¹) using a tabletop parametric oscillator/amplifier (OPO/OPA) laser source. The conformational landscape has been explored through a systematic search of different possible peptide structures by using force-field calculations followed by extensive quantum chemical calculations performed at both B3LYP and MP2 levels of theory using 6-311+G(sdf,2p) basic set. The experimental IRMPD spectrum is in very good agreement with the calculated IR spectra of the lowest energy conformers protonated at the amino group, the thermodynamically most basic site. Sampled ions comprise a thermally averaged population of at least three conformers, all characterized by a folded arrangement stabilized by intramolecular hydrogen bonds linking the ammonium hydrogens with the backbone carbonyl groups and so closing seven- and five-membered rings. The highly diagnostic N-O stretching mode, unambiguously identified in a comparative examination with the native protonated glutathione [GSH+H]⁺ and the ¹⁵NO-labelled ion [GS¹⁵NO+H]⁺, may be regarded as a characteristic signature of the S-nitroso motif.

**Band structure calculations have been performed within Virtual Crystal Approximation
for the (Fe_{1-x}Mn_x)₂P series using FP-LAPW/APW+lo method**

Jerzy Goraus

University of Silesia, Katowice, Poland, EU

Both pristine compounds, Fe₂P and Mn₂P crystallize in hexagonal structure, however, the alloy series within some Mn concentration range crystallizes in orthorhombic structure. We performed structural optimization using paraboloid fit for the doped series within hexagonal unit cell and we observed anomalous behaviour of the lattice parameters in the concentration range where the orthorhombic phase was reported in experiment. Transition metals in Fe₂P unit cell occupy two inequivalent Wyckoff positions. It was postulated from Mossbauer measurements that with increased iron concentration the 3f position is occupied first. Our calculations also confirm this observation.

Ab initio simulations of atomic gold wires on silicon surfaces

Conor Hogan

CNR-ISM, via del Fosso del Cavaliere 100, 00133 Rome, Italy, EU

Gold adsorption on flat and stepped Si(111) surfaces is known to induce regular and spatially-dense quasi-1D nanostructure arrays.¹ Single or multiple atomic Au chains form within the terraces, while rows of Si dangling bonds and graphitic structures form at the step edge. Besides the obvious potential for nanoelectronics, these systems constitute an excellent test bed for investigating quasi-1D physics, including metal-insulator phase transitions, Peierls distortions, CDWs, and well as more recently discovered magnetic atomic chains of silicon.² However, controversy persists as to the exact geometry and electronic structure of many of these systems.³ One technique that offers precise microscopic insight is reflectance anisotropy spectroscopy (RAS), which is particularly sensitive to the intrinsic 1D nature of the Au-stabilized systems.⁴ Here we demonstrate how careful simulations of RAS experiments using Density Functional Theory provides direct insight into the surface reconstruction geometry (step morphology and buckling, Si/Au stoichiometry) and electronic structure (chain metallicity, adatom doping) across a range of similar systems.⁵ In particular we will demonstrate the ability of RAS to probe the delicate interplay between charge distribution at the step edge, adatoms, and gold chains, and when carried out in tandem with hydrogen doping, how it offers a novel route for tuning the unique properties of these systems.⁶

¹F. Himpsel et al, J. Phys.: Cond. Mat 13, 11097 (2001).

²S.C. Erwin and F. J. Himpsel, Nature Commun. 1:58 (2010).

³T. Abukawa and Y. Nishigaya, Phys. Rev. Lett. 110, 036102 (2013); S. Kwon and M. Kang, Phys. Rev. Lett. 113 086101 (2014); J. Kautz, M.W. Copel, M. S. Gordon, R. M. Tromp, and S. J. van der Molen, Phys. Rev. B 89, 035416 (2014).

⁴N. McAlinden and J. F. McGilp, Euro. Phys. Letters 92, 67008 (2010)

⁵C. Hogan, E. Ferraro, N. McAlinden, J. F. McGilp, Phys. Rev. Lett. 111, 087401 (2013); C. Hogan, N. McAlinden, J. McGilp, Phys Stat Sol B 249, 1095-1104 (2012)

⁶C. Hogan, E. Speiser, S. Chandola, N. Esser, J. Aulbach, J. Schafer, in preparation.

Electronic Properties, Carrier Mobility and Strain Response of TiS₃ Nanoribbons

Jun Kang, Hasan Sahin, and Francois M. Peeters

Department of Physics, University of Antwerp, Belgium, EU

The electronic properties, mobility and strain response of TiS₃ nanoribbons are investigated from first-principles calculations. Two types of ribbons with different orientations are studied, labeled as aTiS₃NRs and bTiS₃NRs. The aTiS₃NRs have large edge energy ranging from 450 to 480 meV/Å. On the other hand, the bTiS₃NRs are found to have small edge energy around 60 meV/Å, suggesting that their isolation from 2D monolayer is not difficult. All the aTiS₃NRs are metallic, and exhibit non-zero magnetic moment. The spin density is contributed mostly by edge atoms. On the contrast, all the bTiS₃NRs have direct band gaps at the Γ point. Interestingly, the gap value and the band edge position are almost independent of the ribbon width, indicating strong edge effects. This feature promises a constant band gap in a bTiS₃NR with rough edge, where the ribbon width differs in different regions. The mobility of bTiS₃NRs is calculated by using the deformation potential theory in combine with the effect mass approximation. The bTiS₃NRs exhibit high electron mobility in the order of 10³ cm²/(Vs). The hole mobility of the bTiS₃NRs is one order lower, but it is enhanced compared with the monolayer case, due to a reduction in hole effective mass. The band gap of bTiS₃NRs is strain tunable. It increases with increasing tensile strain, and a direct-to-indirect band gap transition can be triggered by strain. Moreover, local strain in a bTiS₃NR creates a type-I band offset, which can induce carrier localization and charge transport barrier. The direct, width-independent and strain tunable band gap, as well as the high carrier mobility, promise bTiS₃NRs great application potentials in many fields of nanoelectronics, such as field-effect devices, opto-electronic applications and strain sensor.

**Requirements and conceptual modeling of information infrastructure
and home automation of a retirement house for active and long-lived seniors**

Stefano Lariccia

Università La Sapienza, Roma, Italy, EU

Research on new models of care organisation demonstrates that advanced ICT systems and services may have the potential to respond to, amongst others, the increasing burden of chronic disease and the complexity of co-morbidities and in doing so contribute to the sustainability of health and care systems. One challenge in re-designing health and care systems is to develop integrated care models that are more closely oriented to the needs of patients and older persons: multidisciplinary, well-coordinated, anchored in community and home care settings, and shifting from a reactive approach to proactive and patient-centred care. Our proposals goes beyond the current state of art in tele-health and tele-care systems by developing new approaches for integrated care and nursery supported by ICT systems and services. Requirements and conceptual modeling of information infrastructures and home automation of a retirements house designed for active and long-lived seniors. The “House of the thinkers who never retire” is conceived as a place where the outside and inside are not delimited by walls, or other physical obstacles, but rather are semantic based delimiters: the subjects which the thinker is interested can get in, while it remains to ‘any person outside animate or inanimate which the thinker is not interested. Supervision, monitoring and help for physical movements are designed using the principle of least possible invasiveness.

**Fluctuating hydrodynamics of a lattice model
with inelastic collisions and conserved momentum**

Antonio Lasanta Becerra

Istituto dei Sistemi Complessi, Consiglio Nazionale delle Ricerche, Rome, Italy

Dipartimento di Fisica, Università “La Sapienza”, Rome, Italy, EU

We introduce a model described in terms of a scalar velocity field on a 1d lattice, evolving through collisions that conserve momentum but do not conserve energy. Such a model naturally addresses fluidized granular media, but may also describe active fluids, such as motile microorganisms or biofilaments. We deduce non-linear fluctuating hydrodynamics equations for the macroscopic velocity and temperature fields: The equations replicate the hydrodynamics of shear modes in a granular fluid, and predict the instability of homogeneous cooling state (HCS) at large size or inelasticity, which appears as a close relative to flocking phenomenon in active fluids. We compute also the exact shape of long range spatial correlations which even far from the instability have the physical consequence of modifying the cooling rate.

**Oxidation of ancient paper: a non-destructive spectroscopic methodology
for cultural heritage preservation**

**Adriano Mosca Conte (a,b), Olivia Pulci (a,b), J. Lojewska (c), J. Bagniuik (c), Ihor Kupchak (d),
Claudia Violante (a), Lorenzo Teodonio (a,b), Mauro Missori (b)**

(a) ETSF, MIFP, Dipartimento di Fisica, University of Rome Tor Vergata, I-00133 Rome, Italy, EU

(b) Istituto dei Sistemi Complessi, CNR, 00015 Monterotondo Scalo RM, Italy, EU

(c) Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland, EU

(d) MIFP, V. Lashkarev Inst. of Semicond. Phys. of Nat. Acad. of Sciences, 03680 Kiev, Ukraine

Some of the most important masterpieces of our culture, knowledge and art are stored on paper. The conservation of this fragile material is a challenge involving both communities of cultural heritage and material sciences. To this goal an innovative diagnostic method^{1,2} based on non-destructive optical spectroscopic techniques combined with computational simulations based on TDDFT ab-initio theoretical condensed matter methods has been set up and applied to unvaluable peaces of art, such as the famous Leonardo Da Vinci's self-portrait.³ In this poster presentation, I will show how this method has been used in order to deepen our knowledge on oxidation processes occurring in aged paper and causing visual and structural damage to historical documents.

¹A. Mosca Conte, O. Pulci, A. Knapik, J. Bagniuik, R. Del Sole, J. Lojewska, and M. Missori, Phys. Rev. Lett., **108**, 158301 (2012)

²M. Missori, O. Pulci, L. Teodonio, C. Violante, I. Kupchak, J. Bagniuik, J. Lojewska, and A. Mosca Conte, Phys. Rev. B, **89**, 054201 (2014)

³A. Mosca Conte, O. Pulci, M. C. Misiti, J. Lojewska, L. Teodonio, C. Violante, and M. Missori, Appl. Phys. Lett., **104**, 224101 (2014)

Electronic and optical properties of hexagonal and cubic Ge₂Sb₂Te₅

Henry Odhiambo

Maseno University, Kenya

The electronic and optical properties of hexagonal and cubic Ge₂Sb₂Te₅ have been calculated using the QUANTUM ESPRESSO and Yambo codes. The study has considered the variation of electronic band gaps with lattice constants using the LDA with non-linear correction, where it was established that both phases are apparently metallic at equilibrium. Upon increasing *a*, it was found that the hexagonal phase had a maximum gap of 0.22 eV at a *c/a* value of 3.49 whereas the cubic phase had a maximum gap of 0.23 eV at a much higher *c/a* value of 10.62. Findings of the optical absorption spectra of both hexagonal and cubic Ge₂Sb₂Te₅ obtained using time dependent density functional theory (TDDFT) and the partially self-consistent GW (GW₀) are also reported. The absorption edge has been observed at 0.48 eV using TDDFT and at 0.21 eV using GW₀ for the hexagonal phase.

Circular dichroism (CD) spectra of amino–acid molecules

Elena Molteni, Guido Tiana and Giovanni Onida

Dipartimento di Fisica and ETSF, Via Celoria 16 20133 Milano

We study the conformational dependence of circular dichroism (CD) spectra of amino–acid molecules by means of an efficient ab–initio DFT approach which is free from the typical gauge invariance issues arising with the use of localized basis sets and/or real–space grids. We analyze the dependence of the chiroptical spectra on the backbone dihedrals in the specific case of alanine, and consider the role of side chain degrees of freedom at the examples of leucine, phenylalanine and serine, whose sidechains have different physico–chemical properties. The results allow one to identify the most diagnostic regions of the CD spectra, and to critically compare the conformations which match the experimental CD data with conformations extracted from the rotamer library. The inclusion of a solvation shell of explicit water molecules and its effect on the CD spectrum are analyzed at the example of alanine.

Competing factors on the frequency separation between the OH stretching modes in water

Chao Zhang (a), Daniele Ottaviani (b), Thomas D. Kühne (c),

Andrea Zen (d), and Leonardo Guidoni (b)

(a) Department of Chemistry, University of Cambridge, United Kingdom, EU

(a) Dept. of Physical and Chemical Sciences, University of L'Aquila, 67100 L'Aquila, Italy, EU

(b) Institute of Physical Chemistry and Center for Computational Sciences, Johannes Gutenberg University Mainz, Staudinger Weg 7, D-55128 Mainz, Germany, EU

(c) Physics Department, Sapienza - University of Rome, P.le A. Moro 5, 00185 Rome, Italy, EU

Recent simulations demonstrated that the inhomogeneous broadening as observed in the vibrational spectra of liquid water at ambient conditions can be viewed as a large vibrational splitting of symmetric and asymmetric OH stretching modes, due to the asymmetry of the local hydrogen-bonding network [C. Zhang, R. Khaliullin, D. Bovi, L. Guidoni, T. Kuhne, *J. Phys. Chem. Lett.*, 2013, 4(19), pp 3245-3250]. In this work it's shown that the finite temperature and the liquid phase do not only modulate the local hydrogen-bonding asymmetry of water molecules, but also the intramolecular coupling strength (called k_{intra}). These two factors compete together in the determination of the overall magnitude of the frequency separation between the two OH stretching modes in water at ambient conditions. Following a fourth-order fitting procedure for the water Potential energy surface [A. Zen, D. Zelyazov, and L. Guidoni *J. Chem. Theory Comput.*, 8, 42044215 (2012)] we can extract the k_{intra} values directly from the fitted hessian matrix and we can compare it to the others values of interest (like the frequency splitting of the vibrational modes $\delta_{omega_{13}}$), in order to prove the relationship between k_{intra} and the asymmetries of the local environment around each water molecule.

Solvent dynamics controls the stability and reactivity of Grignard reagents

Raphael Peltzer(a,b), Odile Eisenstein (b,c), Michele Cascella (a,b)

(a) Department of Chemistry, University of Oslo, Norway (b) Centre for Theoretical and Computational Chemistry (CTCC), Norway, EU (c) CNRS, Université de Montpellier, France, EU

The Grignard reaction is widely applied in organic chemistry for synthesis of a carbon-carbon bond between a nucleophilic organometallic halide of nominal formula R-Mg-X, and an electrophilic carbon.¹ Despite the well established experimental practice, the molecular details of such reactions are not well understood yet. The several issues related to Grignard reagents comprise the aggregation states of the R-Mg-X molecules, the possible co-existence of multiple structures for such aggregates, as well as the coordination chemistry of the involved Mg²⁺ ions. In our work, we are investigating what are the possible chemical species at thermal equilibrium when two molecules of a model Grignard reagent (CH₃MgCl) interact in tetrahydrofuran solvent (THF). Our study involves ab-initio molecular dynamics, where the electronic problem is solved by Density-Functional-Theory² using the Perdew-Burke-Ernzerhof exchange-correlation functional.³ Enhanced sampling of the conformational space is achieved by metadynamics simulations.⁴ Our preliminary results indicate that the various thermally accessible compounds are characterised by different solvation structures. In particular, all steps leading to the (CH₃MgCl)₂ = Mg(CH₃)₂ + MgCl₂ reaction (Schlenk equilibrium) are directly controlled by the dynamics of THF molecules, which act both as both nucleophile and leaving groups at the Mg²⁺ centre. Therefore, understanding reactivity of Grignard reagents implies taking into consideration solvent molecules as direct components of the reaction pathways.

¹D. A. Shirley, "The Synthesis of Ketones from Acid Halides and Organometallic Compounds of Magnesium, Zinc, and Cadmium", *Org. React.* 8, 2858 (1954)

²G. Lippert, J. Hutter, M. Parrinello, "The Gaussian and augmented-plane-wave density functional method for ab initio molecular dynamics simulations. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*" (*Theoretica Chimica Acta*) 103 (2): 124,140. (1999).

³J.P. Perdew, B. Kieron, M. Ernzerhof, "Generalized Gradient Approximation Made Simple", *Physical Review Letters* 77 (18): 3865 (1996).

⁴A. Laio, M. Parrinello, "Escaping free-energy minima", *Proceedings of the National Academy of Sciences of the United States of America* 99 (20): 12562 (2002)

Dynamics at the peptideanatase TiO₂(101) interface**Marco Polimeni (a), Loukas Petridis (b), Caterina Arcangeli (c),
Francesco Buonocore (c), Olivia Pulci (a), Jeremy C. Smith (b))***(a) NAST Centre c/o University of Rome Tor Vergata, Rome, Italy, EU**(b) Center for Molecular Biophysics Oak Ridge National Laboratory, TN, USA**(c) ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic
Development, Casaccia, Rome, Italy, EU*

The specific recognition of inorganic materials surface by small peptide sequences is a widely investigated research topic with fields of application ranging from nanoelectronics to medicine and pharmacology¹. In this framework, the aim of our work is to investigate from a computational viewpoint, the interaction between a particular identified hexapeptide (RKLPDA sequence), and the TiO₂(101) anatase surface². Our MD simulations showed a preferential adsorption of the RKLPDA peptide via its aspartate terminal amino acid, in partial contrast with the quantum calculation predictions³. In order to understand this lack of agreement, probably due to an inappropriate choice of the force field, it is necessary to study and build specific force fields employing ab-initio techniques based on density functional theory (DFT) that can be used in MD simulations.

¹M. Sarikaya, C. Tamerler, A. Jen, K. Schulten, F. Baneyx, *Nat. Mater.* 2003, 2, 577-585; Shiba, K. *Curr. Opin. Biotechnol.* 2010, 21, 241-425

²K.I. Sano and K. Shiba, *J. Am. Chem. Soc.* 125, 14234 (2003).

³J. Schneider and L. C. Ciacchi, *J. Chem. Theory Comput.*, 7, 473 (2011)

Probabilistic representation of quantum systems.**Carlo Presilla***Sapienza Universita di Roma*

The evolution of systems as varied as bosons or fermions in a lattice, classical dynamical systems, biological populations, networks, etc., are described by a linear differential equation with respect to time. It is a result established only few years ago¹ that the solution of this equation, for real or imaginary time, admits an exact probabilistic representation in terms of a proper set of Poisson processes. On the basis of this Feynman-Kac-type formula, we have developed a Monte Carlo algorithm to perform unbiased numerical simulations and a method yielding semi-analytic results for the evolution in the limit of an infinitely long time. In this limit, in fact, the use of probabilistic techniques of cumulant expansion and large deviations has allowed to write down exact expressions for the ground state energy of closed systems.

¹*Europhys. Lett.* 243, 48 (1999)

Graphene-like two dimensional Nitrides: an ab-initio study

Maria Stella Prete (a), Adriano Mosca Conte (b),

Friedhelm Bechstedt (c), Paola Gori (d), Olivia Pulci (b)

(a) *University of Rome Tor Vergata, via della Ricerca Scientifica, 1, Rome, Italy*

(b) *ETSF, MIFP, ISC, University of Rome Tor Vergata, via della Ricerca Scientifica, 1, Rome, Italy*

(c) *ETSF, IFTO, Friedrich-Schiller-Universitaet, Max-Wien-Platz 1, 07743 Jena, Germany*

(d) *ETSF, University of Rome Roma Tre, via della Vasca Navale 79, Rome, Italy*

Nitride- based materials possess unique optical properties which make them essential in light emitting devices.¹ Here, we investigate by ab-initio (DFT, GW and BSE approaches) and model methods² the electronic and optical properties of III-N two-dimensional compounds (BN, GaN, InN, AlN). Stable honeycomb structures graphene-like are found, with no buckling. Due to the different electronegativity of III and V atoms, a charge transfer occurs and a gap opens, so no Dirac cone is found in these 2D materials.³ Confinement effect and reduced 2D screening strongly enhance excitonic effects, creating electron-hole pairs with large (\sim eV) binding energy and tunable optical gap, making these materials good candidates for novel optoelectronic devices.

¹Yun Ji et al. Appl. Phys. Lett 104, 143506 (2014)

²O. Pulci, M. Marsili, V. Garbuio, I. Kupchak and F. Bechstedt Phys. Stat.Sol.(b) 1-6 (2014) [3] P. Cudazzo, I.V. Tokatly, A Rubio, Phys. Rev. B 84, 085406 (2011)

³H. Sahin, S.Cahangirov, M. Topsakal, E. Akturk, R.T. Senger, and S.Ciraci Phys. Rev. B 80, 155453 (2009)

Dimensional-Crossover-Driven Bandgap Transition in h-AlN

Seyda Horzum Sahin

University of Antwerp, Belgium, EU

We investigate structural, electronic and vibrational properties of bulk, bilayer and monolayer structures of h-AlN by using first-principles calculations. We show that the hexagonal phase of the bulk h-AlN is a stable direct-bandgap semiconductor. Differing from some other two-dimensional crystal structures such as graphite, h-BN and TMDs, here the ionic interlayer interaction is dominant between the h-AlN layers. Calculated phonon spectrum displays a rigid-layer shear mode at 274 cm^{-1} and an Eg mode at 703 cm^{-1} which are observable by Raman measurements. In addition, single layer h-AlN is an indirect bandgap semiconductor with a nonmagnetic ground state. For the bilayer structure, AA-type stacking is found to be the most favorable one and interlayer interaction is strong. While N-layered h-AlN is an indirect bandgap semiconductor for $N= 1 - 10$, we predict that thicker structures ($N>10$) have a direct-bandgap at the Γ -point. The number of layer dependent bandgap transitions in h-AlN is interesting in that it is significantly different from the indirect-to-direct crossover obtained in the transition metal dichalcogenides.

Theoretical and Experimental Investigation of Monolayer Portlandite

Hasan Sahin

University of Antwerp, Belgium, EU

Ca(OH)₂ crystals, well-known as Portlandite, are grown in layered form and we found that they can be exfoliated on different substrates. We performed first principle calculations to investigate the structural, electronic, vibrational and mechanical properties of bulk, bilayer and monolayer structures of this material. Different from other lamellar structures such as graphite and transition metal dichalcogenides, intralayer bonding in Ca(OH)₂ is mainly ionic, while the interlayer interaction remains a weak dispersion-type force. Unlike well-known transition metal dichalcogenides that exhibit an indirect-to-direct band gap crossover when going from bulk to a single layer, Ca(OH)₂ is a direct band gap semiconductor independent of the number layers. The in-plane Young's modulus and the in-plane shear modulus of monolayer Ca(OH)₂ are predicted to be quite low while the in-plane Poisson's ratio is larger in comparison to those in the monolayer of ionic crystal BN. We measured the Raman spectrum of bulk Ca(OH)₂ and identified a low-frequency mode E_u(T) at 280 cm⁻¹ and high-frequency -OH stretching mode A_{1g} at 3620 cm⁻¹. In this study bilayer and single layer Portlandite (Ca(OH)₂) are predicted to be stable and their characteristics analyzed. Our results can guide further research on ultra-thin hydroxides.

Degradation of Cd-yellow Paints: an ab initio study of the adsorption of water and oxygen on CdS {10.0} surface

Laura Giacopetti and Alessandra Satta

CNR-IOM UOS Cagliari and Dipartimento di Fisica, Università di Cagliari, Monserrato (CA), Italy.

The cadmium yellow paints (CdS) used in impressionist and modernist paintings in early 1900s are undergoing several deterioration processes including whitening and discoloration. A relevant effect produced at the surface of the paintings is the growth of discolored crusts formed mainly by white globular hydrated cadmium sulfate (CdSO₄*nH₂O) and cadmium carbonate (CdCO₃). Recent studies ascribe to an initial photo-oxidation process of CdS the input for the formation of such whitish compounds. Despite the large number of experimental studies on altered yellow paints, the origins and roles of these compounds remain unclear. In fact, in the syntheses of CdS, reagents such as CdCO₃ and CdSO₄ are employed both in the dry and wet process and their identification alone does not constitute conclusive proof of photo-oxidation.^{1 2} Also, structural defects in CdS may play a role in the pigment alteration process.³ In order to understand the oxidation and hydration mechanisms of the whitish globules, at atomic level, we present a theoretical study of points defects, namely Cd- and S-vacancies, both in the bulk and in the hexagonal non-polar {10.0} surface. The interaction between the {10.0} defective surface of CdS and O₂ and H₂O molecules is then studied to simulate the combined effects of exposure to air and humidity. To this end the surface of CdS containing Cd- and S- vacancies was simulated according to the slab geometry and was next covered by oxygen, a water molecule and a combination of O₂ + H₂O. More specifically, we determined the favorite adsorption sites and calculated the adsorption energies of the different molecules on top of the surface. The details of the electronic structure of the interactions are given via the bonding charge analysis along with a thorough description of the geometry. Also, For this purpose, we adopted a first principles method within the framework of the Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA-PBE) with the use of ultrasoft pseudopotentials as implemented in the quantum-ESPRESSO package.⁴

¹J. L. Mass, R. Opila, B. Buckley, M. Cotte, J. Church, A. Mehta, Appl Phys A (111), 59 (2013)

²G. Van der Snickt, J. Dik, M.Cotte, K. Janssens, J. Jaroszewicz, W. De Nolf, J. Groenewegen, L. Van der Loeff, Anal. Chem (81), 2600 (2009),

³Cesaratto A. ,C. D'Andrea, et al., Anal. Methods (6), 130 (2014).

⁴P. Giannozzi . et al., Journal of Physics: Condensed Matter (21), 395502 (2009), www.quantum-espresso.org

**Metal-to-superconductor transition, mesoscopic disorder
and intrinsic charge instability in oxide heterostructures**

Niccolò Scopigno, Sergio Caprara, Marco Grilli

Physics Department, University La Sapienza, Rome, Italy, EU

The observation of a two-dimensional (2D) metallic state at the interface of two insulating oxides have attracted much attention in the last decade. Among its many intriguing properties are a large Rashba spin-orbit coupling (RSOC) and a metal-to-superconductor transition, both tunable by an external gate voltage. Numerous experiments indicate that the 2D electron gas (EG) is inhomogeneous: transport measurements reveal a peculiar metal-to-superconductor (SC) transition suggestive of charge inhomogeneity at the mesoscopic scale.¹ Motivated by the fact that these inhomogeneities persist in ever cleaner samples we propose they might result from an intrinsic electronic phase separation (EPS). We point out two generic mechanisms which can drive the interfacial EG towards such an EPS, based on (i) a density-dependent RSOC² and (ii) the electrostatic electron confinement at the interface.³ Investigating how the two densities of the phase-separated EG change upon varying the gate voltage we obtain the phase diagram at zero temperature. The resulting diagram has a dome-like shape and closes at negative gate voltage, signaling the existence of a quantum critical point (QCP). We argue that this QCP is related to the recently observed quantum critical behaviour of LaTiO₃/SrTiO₃.⁴

¹S. Caprara, et al., Phys. Rev. B (Rapid Communications) 88, 020504(R); S. Caprara, D. Bucheli, N. Scopigno, N. Bergeal, J. Biscaras, S. Hurand, J. Lesueur, and M. Grilli, Supercond. Sci. Technol. 28 (2015) 014002.

²S. Caprara, F. Peronaci, and M. Grilli, Phys. Rev. Lett. 109, 196401 (2012); D. Bucheli, M. Grilli, F. Peronaci, G. Seibold, and S. Caprara, Phys. Rev. B 89, 195448 (2014).

³N. Scopigno, D. Bucheli, S. Caprara, J. Biscaras, N. Bergeal, J. Lesueur, and M. Grilli, in preparation.

⁴J. Biscaras, N. Bergeal, S. Hurand, C. Feuillet-Palma, A. Rastogi, R. C. Budhani, M. Grilli, S. Caprara, J. Lesueur, Nature Materials 12, 542 (2013).

First principles calculations of GaN and AlN nanosheets

M. Tadout, H. Zaari, O. Mounkachi, A. Benyoussef and M. Benaissa

Laboratoire de Magnetisme et Physique des Hautes Energies L.M.P.H.E. (URAC 12),

Faculte des Sciences, Universite Mohammed V, B.P.1014 Rabat , Morocco

First principles calculations were performed to study the electronic structures of gallium nitride (GaN) and aluminum nitride (AlN) nanosheets in order to understand the influence of sheet stacking (in terms of thickness) on structural and electronic properties, as well as the relative stabilities of fully and partially hydrogenated nitride nanosheets. Unlike bare GaN and AlN nanosheets terminating with polar 0001 surfaces, their hydrogenated counterparts preserve the initial wurtzite configuration. Specifically, the dielectric function, absorption coefficient, optical conductivity, extinction index, reflectivity and their fraction index of both type of nanosheets are calculated for both parallel and perpendicular electric field polarizations. The results show that the optical spectra are isotropic along these two polarizations. Optical conductivity in both the parallel and the perpendicular electric field starts with an indirect gap (instead of indirect gap for bulk counterparts) which confirms that nitride nanosheets have a semiconductor property.