PISACMS 2019 August 26 – 30 Paris Campus Pierre et Marie Curie





Carried by Sorbonne Universities, LabEx MATISSE (MATERIALS, Interfaces, Surfaces, Environment) is a multidisciplinary project on the borders of the chemistry, physics and Earth sciences and mobilizes a critical mass of research laboratories around the study of materials, so natural as synthetic, in the service of big socioeconomic stakes. It federates 18 prestigious actors around interdisciplinary projects.

MATISSE gathers exceptional skills regarding elaboration of materials by chemical or physical ways, characterization of the properties since the nanometric scale up to the kilometer, even under extreme conditions, and finally, of modelling in terms of composition, dimension and function.

Research

MATISSE has for objective to understand the fundamental principles governing the organization of the material to be able to develop original materials by playing on their dimensionality and feature. For the first time, the parallel between natural materials and synthetic materials is exploited in a forward-looking way by involving jointly the chemistry, the physics and the Earth sciences. This original approach will drive to a better understanding and to a control of materials in the environment (e.g. change, biodegradation, contamination), and materials for the environment (e.g. cleanup, green catalysis, management of natural resources).

Innovation

MATISSE received an exceptional support on behalf of industrial partners, what testifies from them, of a real trust in the skills of this consortium, and in its capacity to be answered the main stakes which settle in materials science today. We can quote the management of mining resources, the storage of waste, the protection against the corrosion, the soil remediation, the elaboration of materials environment-friendly

Formation

MATISSE will participate in the development of interdisciplinary and international training program at the level Master's degree and doctorate. These students and PhD students constitute a reservoir of highly considered staffs so in the academic as industrial environment.

Matisse funds full PhD and postdoc fellowships including salary and functioning. One call is open every year. More here: www.matisse.upmc.fr









Welcome PISACMS, Aug. 26 – Aug. 30 2019, PARIS, FRANCE

The aim of this school is to form new generations of young researchers to atomic, molecular and condensed phase computational methods, from theory to the most advanced approaches, going from the very microscopic to the macroscopic: Density Functional Theory, classical Monte-Carlo and molecular dynamics, ab initio molecular dynamics, metadynamics, linear response, lattice-Boltzmann methods, Quantum Monte-Carlo.

Our ambition is to make students aware of the fundamental principles of each methods, and then able to choose the most adapted one(s) for a given scientific problem. The broad panel of approaches we propose, both via theory lessons and computer lab "projects", is rare in the international landscape, as the best-known schools are more focalised on a particular time and length scale level of description.

This school will benefit both from the exceptional central Paris environment, and from the local concentration of young and confirmed experts-teachers in each specific theme of the school.

This school is held with the support of Labex Matisse and Sorbonne Universités.



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Organizers

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PLANS / MAPS

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Amphi 15: Morning sessions – Lunch – Coffee break – Poster sessions Best poster prize & Closing Party

22-23 – 1st floor, rooms 109-111-112-114: Computer labs







Housing and accommodation Résidence Internationale de Paris

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Program

Courses: Amphi 15 Flash presentations: Amphi 15 Computer Lab: computer rooms TBC Lunch/coffee breaks: patio Amphi 15

	Monday 26	Tuesday 27	Wednesday 28	Thursday 29	Friday 30
9 :00	9 :00-10 :30 Molecular Dynamics	9 :00-10 :30 Density Functional Theory	9 :00-10 :30 Mesoscopic methods	9 :00-10 :30 Monte-Carlo method	9 :00-10 :30 Ab initio Molecular Dynamics
10 :00	Mathieu Salanne	Ari P. Seitsonen	Benjamin Rotenberg	Rodolphe Vuilleumier	Ari P. Seitsonen
	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
11 :00	11 :00-12 :30 Free energy	11 :00-12 :30 Density Functional Perturbation	11 :00-12 :30	11 :00-12 :30 Quantum Monte-	11 :00-12 :30 Path integral simulations
12 :00	Fabio Pietrucci	Theory Michele Lazzeri	Benjamin Rotenberg	Félix Mouhat	Rodolphe Vuilleumier
10.00	12 :30-13 :30 Lunch	12 :30-13 :30 Lunch	12 :30-14 :00 Lunch	12 :30-14 :00 Lunch	12 :30-14 :00 Lunch
13 :00		13 :30-14 :30			
14 :00		Flash présentations 2	14 :00-17 :30	14 :00-17 :30	14 :00-17 :30
	14 :30-17 :30	14 :30-17 :30	Computer labs	Computer labs	Computer labs
15 :00	Computer labs	Computer labs			
16 :00					
17 :00					
			17 :30-19 :00	17 :30-19 :00	
18 :00	18 :00-20 :00		Poster session 1	Poster session 2	
	Welcome cocktail				18 :30-19 :30 Best poster price
19 :00					18 :00-20 :00
20 :00					Closing cocktail







Abstracts – Courses & Computer Labs

MONDAY 26th August

Mathieu Salanne – 9h-10h30 – Amphi 15

Molecular Dynamics Simulations

Classical molecular simulations are now one of the main tools for interpreting experiments and predicting physico-chemical properties of condensed matter systems. Indeed, they provide a very useful picture of the materials at the microscopic scale. Their popularity is also due to their easy access, even for non-specialists, with a huge variety of simulation codes available.

In this lecture, we will introduce Molecular Dynamics (MD). In MD, the trajectory of the molecules is gathered by solving iteratively the Newton's equation of motion. The related algorithm, its limits and approximations, success and failures, will be detailed. The various thermodynamic and dynamic quantities that can be extracted from the simulations will also be overviewed.

Fabio Pietrucci – 11h-12h30 – Amphi 15

Free-energy calculations

Plain molecular dynamics simulations cannot sample efficiently rare events like chemical reactions, phase transitions, and many other activated processes that require overcoming free energy barriers. This lecture will present two very successful techniques employed to enhance the sampling of low-populated regions in configuration space and reconstruct free energy profiles: umbrella sampling and metadynamics. Starting from the connection between probability histograms and free energy landscapes as a function of collective variables, umbrella sampling will be discussed as a practical way to focus the computational effort in selected regions of the configuration space. The weighted histogram analysis method will then be introduced to combine together in an automatic way the statistics obtained in independent simulations. Next, the basic principles and advantages of metadynamics will be presented, together with practical considerations (by means of examples) about the choice of parameters and the convergence of the algorithm. A brief introduction to the Plumed plugin will demonstrate how to perform actual free energy calculations in the hands-on session. The last part of the lecture will focus on topics at the core of all free energy calculation approaches: how to choose appropriate collective variables, the definition of reaction coordinates by means of committor probabilities and the nature of transitions states.







Computer Lab – 14h30-17h30 – Rooms 22/23 1st floor

Search for structural minima in carbon nanotubes and clusters

Exercise 1

We will study the Stone-Wales transformation in a carbon nanotube (CNT) employing classical molecular dynamics (LAMMPS code) in combination with metadynamics (Plumed code). We will adopt simple collective variables like distances between atom pairs. The aim is setting up a simple metadynamics simulation and evaluate the effect of the different parameters (e.g., Gaussian width, height, and deposition rate) on the reconstructed free energy landscape. The tasks will include:

choose atoms involved in collective variables from a CNT structure, using VMD

 adjust a Plumed input file to define collective variables and parameters of the simulation

run a molecular dynamics simulation with LAMMPS + Plumed

analyze the trajectory of collective variables to detect transitions

 plot the reconstructed free energy landscape at different times: find the "filling time", evaluate convergence, compare barriers with literature

Exercise 2

We will explore many different geometries of Lennard-Jones clusters exploiting metadynamics in combination with topological collective variables (SPRINT). These variables characterize the network of interatomic bonds and drive the system to change topology without specifying in advance the final states, thus allowing to discover new geometries. The tasks will include:

– build initial structure of the cluster ("by hand", or with VMD)

adjust a Plumed input file and run a simulation with LAMMPS + Plumed

analyze the trajectory of collective variables to spot out the metastable structures

 based on the trajectory of the potential energy, rank structures and find the global minimum







Ari P. Seitsonen – 14h-17h – Amphi 15

Density Functional Theory

This class will establish the "common basis" of Density-Functional Theory, which will be then useful in the following of the school. After introducing the electronic density as the central quantity of the theory, the variational principle and the Hohenberg-Kohn theorem, we will follow the Kohn-Sham approach to obtain the minimization self-consistent equations, within the local-density and the generalized-gradient approximations. We will then we will briefly illustrate some practical implementation aspects, including pseudopotentials, plane-wave expansion, periodic boundary conditions, Brillouin zone sampling.

We will then consider a few basic examples of DFT calculations, from the band structure of semiconductors and metals, to charge distributions and bonding properties, to the optimization of internal coordinates and/or unit cell, to structural phase transitions, to surfaces, interfaces and low-dimensional systems. Each of these examples will feature some practical implementation techniques and exploitation of results.

Michele Lazzeri – 11h-12h30 – Amphi 15

Linear response & Density Functional Perturbation Theory

DFT is a powerful tool for the calculation of the ground-state properties of materials. In practice, however, materials are experimentally probed by measuring their response to several external perturbations. Therefore, their computation has a tremendous importance.

This can be achieved through Density Functional Perturbation Theory (DFPT), which is related to the DFT as usual perturbation theory to the Schrödinger equation. The aim of this lecture is to describe the fundamental theorems at the basis of DFPT in the case of static perturbations: the Born-Oppenheimer approximation, the Hellmann-Feynman theorem and the systematic derivation of formulas to compute nth order derivatives of the total energy. Then, we will show some examples of the calculation of first- and second-order derivatives of the total energy and relate them to some selected physical examples. The lecture will be complemented by a hands-on-computer tutorial on the linear response theory applied to the study of the para-electric to ferro-electric phase transition.





Computer Lab – 14h-17h – Rooms 22/23 1st floor

Structural Instability and Soft Phonons of cubic BaTiO₃

In this tutorial, we study the structural phase transition of the cubic, para-electric phase to the ferro-electric tetragonal phase of $BaTiO_3$, by using Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT). The numerical results will be complemented by simple analytical models, when possible.

The cubic structure of BaTiO₃ is unstable with respect to a transverse optic longwavelength mode (see Figure). This mode thus corresponds to a negative squared frequency that clearly shows up in the computed phonon dispersion $\omega(\mathbf{q})$ for \mathbf{q} vectors close to zero.

The aim of this tutorial is to compute and analyze the phonon dispersion, to relate the mode that is responsible for the instability to a structure having small atomic displacements and to understand the physical origin of the instability itself. The tutorial consists of several distinct steps:



1. Determine the optimal computational parameters (cutoff energy, Brillouin-zone sampling, etc.)

2. Compute the theoretical equilibrium lattice parameter and compare it to the experimental one.

3. Run a phonon calculation at the center of the Brillouin Zone ($\mathbf{q} = 0$) and analyze the character of the soft mode by looking at the computed eigenvectors and the atom effective charges. (Be careful, this calculation could take about an hour on a small PC - launch the corresponding job and go ahead with the tutorial in the meanwhile!)

4. Run two ground-state calculations: the first for a cubic structure with atoms slightly displaced from the high-symmetry positions; the second for a tetragonal phase where atomic positions are numerically optimized. Compare the total energies of the high-symmetry cubic phase, the cubic phase with atom displaced by hand and the optimized tetragonal phase. Deduce the relative stability of those structures.







5. If time allows, compute the phonon dispersion along selected points in the Brillouin Zone. Plot the computed dispersion and compare it to experimental data.

All along this tutorial, you will use the package *Quantum Espresso*, which is based on the DFT and the DFPT. The doc is available on the website www.quantum-espresso.org.

For the ground-state properties, you will use the pw.x module, while the dielectric response and the vibrational modes will be computed via phonon.x. The analysis is done through dynmat.x and the suite xcrysden. All modules are pre-installed, no need to download! Remember also that 1 Ryd = 13.6057 eV.

This tutorial is largely inspired by the Ph.D. Thesis work by Philippe Ghosez, which is available as a pdf file in the pre-installed directory. I highly recommend reading chapter 7 and some of the quoted references.

WEDNESDAY 28th August

Benjamin Rotenberg– 9h-10h30 – Amphi 15

Mesoscopic hydrodynamics

After introducing different situations involving the transport of simple and complex fluids, with applications in basic research, as well as in various industrial and environmental contexts, we will recall the most important notions in hydrodynamics. Starting from the standard macroscopic description (conservation equations, hydrodynamic regimes, etc), we will show how coming back to the microscopic and mesoscopic scales allows overcoming some fundamental and computational limitations of Direct Numerical Simulation (i.e. solving the Navier-Stokes equation with finite elements or finite volume methods).

We will consider in particular small objects (colloids, nanoparticles) suspended in a fluid or fluids confined down to the micrometer or sub-micrometer scale, and discuss the effect of thermal fluctuations, the simulation of hydrodynamic interactions, complex fluids, etc that play a key role in soft matter systems or fluids in porous media. We will introduce several mesoscopic simulation techniques allowing for the description of such systems beyond the reach of molecular simulation, including Dissipative Particle Dynamics or Stochastic Rotation Dynamics.









Benjamin Rotenberg – 11h-12h30 – Amphi 15

Lattice Boltzmann methods

In this second lecture, we will focus on a specific mesoscopic method for the simulation of simple and complex fluids. We will first introduce some basic notions of Kinetic Theory, on which the Lattice-Boltzmann (LB) method is grounded. We will sketch the derivation of the LB algorithm from continuous kinetic theory and illustrate how macroscopic hydrodynamics may emerge from a set of simple local rules. We will then extend the discussion to complex fluids such as fluid mixtures, colloidal suspensions, fluids in charged porous media, adsorption/desorption at solid/liquid interfaces. If time permits, we will also describe another related lattice-based method (Moment Propagation) that allows for the computation of time-dependent properties such as the time-dependent diffusion coefficient of tracers.

Computer Lab – 14h-17h30 – Rooms 22/23 1st floor

Transport of fluids in porous media

The students will use a Lattice-Boltzmann code developed by members of the PHENIX and PASTEUR laboratories, to investigate the transport of a simple fluid through porous media under an applied pressure gradient. Starting with the case of the Poiseuille flow in a slit pore, we will examine several aspects of LB simulations and of the hydrodynamic simulations in general: steady-state velocity profiles, linear response and permeability, transient regime and associated time scales, effect of discretization...

We will then move to the more complex case of a capillary filled with obstacles, mimicking a chromatographic column: The students will visualize the streamlines through the complex porous material and analyse the effect of the obstacles on the permeability of the column.

Finally, the driving and dispersion of tracers through the column will be considered, in the absence and in the presence of interactions between the solutes and the surface of the material.







THURSDAY 29th August

Rodolphe Vuilleumier – 9h-10h30 – Amphi 15

Monte-Carlo Methods

In this lecture, we will introduce an alternative way for sampling molecular configurations, the Monte-Carlo method. This method, which allowed the first evaluation of the equation of state of a fluid by Metropolis et al. as early as 1953, aims at generating a representative set of random configurations according to a specified distribution. While we lose information about the dynamics of the system, it is possible to design very efficient methods for sampling phase space. After introducing the fundamentals of the method, we will discuss the sampling of different thermodynamics ensembles and the use of biases to accelerate convergence.

Michele Casula – 11h-12h30 – Amphi 15

Quantum Monte-Carlo methods

The term "quantum Monte Carlo" refers to a large variety of methods using a Markov chain to sample the quantum partition function or the wave function. By playing with random numbers the N-body problem becomes tractable and, in some cases, exactly solvable, within the statistical noise which is inherent in any stochastic approach.

In this lecture, we will introduce the quantum Monte Carlo methods used to sample the wave function of a quantum many-body problem from first principles, i.e. by including electrons, ions, and the Coulomb interaction among all particles. The task is to find the exact ground state of any *ab initio* Hamiltonian by random numbers. In the lecture we will explain what are the different approaches to reach (or get close to) this goal, namely the variational Monte Carlo (VMC), Monte Carlo optimization, and diffusion Monte Carlo (DMC). For each, the related algorithm, its limits and approximations, success and failures, will be detailed.



Computer Lab – 14h-17h30 – Rooms 22/23 1st floor

Quantum treatment of water dimer: Potential Energy Surface

In this practical session and that of the following day, the students will investigate the quantum aspects of the hydrogen bond in a water dimer. First, the potential energy surface (PES) will be investigated using QMC.

The students will be introduced to the TurboRVB QMC code to perform QMC calculations of the water dimer. This session will be a practical guide to basis set, one-body orbitals generation, wave function ansatz, and energy minimization of the system under study. Once the setup is ready, a series of calculations will be carried out to study the QMC PES along the OH bond-stretching coordinate in the water dimer geometry. Comparison will then be made with a dissociative force-field along the same reaction coordinate.

FRIDAY 30st August

Ari P Seitsonen – 9-10h30 – Amphi 15

Ab Initio Molecular Dynamics

In this lecture, we will present the molecular dynamics approach, where the forces on the ionic cores are derived from the explicit solution of the electronic structure at each time step, or *on the fly*. In particular, we will discuss the Car-Parrinello and Born-Oppenheimer molecular dynamics approaches and their respective specificities on convergence, time-steps, equilibration, statistical averages *etc*. We concentrate on DFT-based methods, but review also the other latest developments in the field. We will then focus on their implementation in practise, with specific physical target quantities, such as vibrational dynamics and density of states, structural properties of disordered systems, thermodynamics, and diffusion, and explain how experimentally accessible observables can be evaluated, for example in neutron, infra-red, Raman and sum-frequency generation vibrational spectroscopies, NMR and EPR spectroscopies and so on. In the last part of the lecture we will present AIMD-based demonstration studies of chemical properties and structural transformations from a wide field of scientific disciplines.



Rodolphe Vuilleumier – 11h-12h30 – Amphi 15

Path-integral methods

Path-Integrals are a reformulation of quantum dynamics proposed by Feynman. In the context of statistical mechanics, the quantum canonical partition function of a system is shown to be equivalent to the classical canonical partition function of a system where every atom of the original system is represented by a closed polymer. The path-integral formulation of quantum mechanics then allows for the numerical computation of statistical quantities even for large systems in gas phase or in condensed phase.

In these lectures, we will introduce the path-integral reformulation of quantum mechanics and the classical isomorphism to a system of polymers for the computation of the canonical partition function. Numerical aspects of the sampling of the path-integral will then be discussed.

After quickly presenting some applications of the path-integral formalism to liquid water and isotope fractionation, we will discuss extension of the path-integral techniques to time-dependent quantities and, if time allows, Bose-Einstein statistics.

Computer Lab – 14h-17h30 – Rooms 22/23 1st floor

Quantum treatment of water dimer: Nuclear Quantum Effects

In this second part of this mini-project on the water dimer, the analytical forcefield will be used to model the PES and the students will use the Path-Integral engine of CP2K to investigate the role of quantum effects on the structure of a water dimer. We will examine several aspects of Path-Integral simulations: initialization, convergence with number of beads, thermostating... Then we will investigate the role of quantum effects on the hydrogen bond strength and geometry by comparison with classical simulations. We will amply use visualization with VMD of the path-integral polymers to observe the effect of quantum delocalization and we will try to determine the probability that the water dimer be observed in a HO-...HOH2+ configuration with a spontaneous protontransfer.



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Poster abstracts









On the calculation of spectroscopic properties in complex environments

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The response and the optical properties of a molecular system can be strongly affected by the structural and electronic properties of the surrounding environment [1], however the development of theoretical approaches able to account for such effects still poses open issues. The most general computational viable approaches resort to hybrid models. The latter describe the solute molecule at the Quantum Mechanical (QM) level, whereas the environment is treated classically, through the use of force fields defined within the Molecular Mechanics (MM) framework [2]. The most reliable QM/MM methods belong to the so called polarizable QM/MM family, where mutual polarization effects between the QM and the MM portions of the system are considered [3]. In this poster, the differences between standard continuum approaches, which are widely exploited to describe environmental effects and a newly atomistic picture developed in our group are highlighted. In particular, a QM/MM model based on fluctuating charges (FQ), that can greatly improve the description of properties and molecular spectroscopies is discussed [4-7]. The performances of our model and the quality of the comparison between calculations and experimental measurements will be also discussed for selected systems [8, 9].

[1] Morzan, U. N., et al. Chem. Rev., 118, 4071 (2018).

- [2] Warshel, A., Levitt, M. J. Mol. Biol., 103, 227-249 (1976).
- [3] Senn, H. M., Thiel, W. Angew. Chem. Int. Ed., 48, 1198-1229 (2009).
- [4] Cappelli. C., Int. J. Quantum Chem., 619, (2016)
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- [6] Lipparini, F., Cappelli, C., Barone, V. J. Chem. Theory Comput., 8, 4153 (2012).
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[8] Giovannini, T., Ambrosetti, M., Cappelli, C, Theor. Chem. Acc., 137, 74 (2018).

[9] Giovannini, T., Macchiagodena, M., Ambrosetti, M., et al., Int. J. Quantum Chem., e25684 (2018)









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Oxygen is the only elemental molecule which carries a magnetic moment. At low temperature and/or high pressure, these moments order to give various antiferromagnetic ground states which have been investigated recently by neutron scattering [1,2]. The aim of this work is to describe the structural and electronic properties of solid oxygen by first principle methods. Contrary to previous DFT calculations [3] the focus of the current work is on the "low" pressure range in the 0-12 GPa range where the magnetic phases α -O2 and δ -O2 are stable. This part of the phase diagram has up to present only been modelled by classical MD simulations using empirical force fields [4]. Here, we present preliminary results on the low pressure α -O₂ phase. It is found that with increasing pressure, the cell parameters sharply decrease at around 0.5 GPa with an angular modification of the cell size, whereas the equation of state exhibits a rather satisfying agreement with experimental data. The sensitivity of the DFT related parameters is discussed, and the difference with previous results analyzed.



Fig 1: Phase diagram of solid oxygen

[1] S. Klotz, Th. Strässle, A. L. Cornelius, J. Philippe, and Th. Hansen. Physical Review Letters, 2010, 104, 115501-101514

[2] S. Klotz. Journal of Low Temperature Physics, 2018, 192, 192:1–18

[3] Y. Crespo, M. Fabrizio, S. Scandolo, and E. Tosatti. PNAS, 2014, 111, 10427– 10432

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A MODULAR MOLECULAR MODEL FOR Ln(III) TEMPERATURE-SENSING COMPLEXES

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ABSTRACT: a simple yet effective model describing the temperature dependence of Ln(III) emission in molecular complexes is presented. Non-radiative deactivation channels are described by thermally activated energy transfer processes and can be included in a modular way. This model takes into account the energy differences between the various excited states, modulated by fixed, one-size-fits-all parameters and one single variable parameter γ weighing the contributions of the deactivation channels.



Figure 1. Energy level scheme representing the sensitization process of Eu(III) via an antenna ligand and the non-radiative decay pathways.





Simulation of ionic liquids-based supercapacitors

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Objective: Understand the adsorption of ionic liquids at the interface with carbon electrodes of different geometries when varying the applied voltage.

Energy storage is one of the major technological and societal challenges of the 21st century. In this context supercapacitors are among the most efficient storage devices. They have a high power density, a long cycle-life, but a lower energy density compared to batteries. Thus, these two systems have properties that are complementary for a number of applications. Current researches on supercapacitor focus on improving the energy density, particularly by increasing the capacitance. The adsorption mechanism at the interface between the electrolyte and the electrode when different electrical potentials are applied is not completely understood yet but it has a significant impact on the capacitance. Among electrolytes, ionic liquids are considered as a promising solution to improve the performances. In order to analyse the microscopic behavior at the interface, molecular dynamics simulations can be performed. Several simulations are carried out with different electrodes geometry (planar and nanoporous carbon), with different ionic liquids (EMIM-TFSI and EMIM-BF4) and for different applied voltage. By computing ions coordination number, electrical double layer properties or number of ions adsorbed as a function of the pore size, the influence of the ionic liquid or electrode geometry will be revealed.

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Figure 1: Example of a simulation of a supercapacitor





[EMIM][BF4]

Figure 3 : Ionic liquids studied









Figure 2: Example of a nanoporous electrode



The water behavior at electrochemical interfaces by electrochemistry and molecular dynamics.

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Since a few years, we can see a renew of interest in aqueous lithium-ion batteries. Although these electrolytes are safer and eco-friendlier than the organics ones, their use is limited by the small electrochemical window of water. Indeed, it plays a double role, as solvent or as solute. One interesting and still open question is whether there is a change of the electrochemical window of water when it acts as a solute only, and not anymore as a solvent. In order to better understand the water-water interactions in the case of water solute, we here study water dissolved in small amounts in an organic solvent, i.e. acetonitrile, and in presence of a lithium salt.

By combining electrochemistry and molecular dynamics on three systems, with different amounts of salt and water, we can characterize the effect of both in contact with graphite electrodes. In particular, this study highlights the critical role played by the water organization at medium range on the structural and electrochemical properties of our mixtures.

This study opens new avenues for tuning the redox activity of water in organic solvents, by directly playing on water content and water solvation, and for designing new batteries chemistries.



Figure 1: Representative snapshot of a system made of acetonitrile, lithium perchlorate and water in presence of electrode graphite, from a simulation at a constant applied









Fully atomistic classical model for the optical properties of graphene

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Graphene has demonstrated to be an ideal platform for photonic and optoelectronic applications. Graphene plasmons [1] exhibit several advantages with respect to noble metal plasmonics, in particular due to their high electromagnetic confinement and the tunability of the plasmonic resonance frequency via electrostatic doping. Plasmonic excitations have been usually described by resorting to classical electrodynamics, thus clearly neglecting nonlocal and quantum finite-size effects occurring in the smallest graphene nano-island (size under 10 nm), which are instead well described by first-principles calculations [2]. Here we propose a fully atomistic classical description of the linear optical response of carbon-based nanostructures, by extending what has already been successfully proposed for metal nanoparticles by some of us [3]. Our model is able to return the same results obtained by QM calculations for graphene nanostructures of different shape and dimensions. Furthermore, our approach can be used to treat large systems, not affordable by QM approaches, so to allow a direct comparison between calculations and experiments.



Figure 1: Charge distribution associated with the plasmonic mode of a graphene nanodisk of 4 nm

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Selective adsorption of propanol and toluene in DAY zeolite in the presence of water.

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The dealuminated Y-zeolites (DAY) described by chemical formula SiO₂ is hydrophobic. It is often used when there is a competitive adsorption with water, this is the case for the adsorptive waste gas purification, the recovery of organic solvents and also for the adsorption of Volatile Organic Compounds (VOC) in aqueous phase. In this work, adsorption isotherms of toluene, 1-propanol and their binary mixtures with water have been computed on Y-zeolites. The adsorption isotherms were calculated by grand canonical Monte Carlo (GCMC) simulations at 300K and 310K for partial pressures between 0.00001 and 10^5 Pa. The simulations were conducted using molecular models from the literature [1,2].

The results obtained for pure 1-propanol and toluene show that DAY traps propanol and toluene molecules at low pressures. It does not promote the adsorption of water because of the hydrophobic behavior of the adsorbent material. The adsorption isotherms of propanol-water and toluene-water mixtures show that the zeolite DAY is selective for the adsorption of propanol, in the presence of water, at low pressures. The results also show that the presence of propanol favors the adsorption of water due to the hydrophilic group (OH) of propanol. By increasing the temperature, the zeolite becomes more selective compared to propanol. In the case of the toluene-water mixture, it is found that the dealuminated Y-zeolites preferably adsorb toluene.

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Theoretical Modelling of Water Oxidation Mechanism in Photosynthetic catalytic cycle

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The reaction centre of the Photosystem-II, named Oxygen Evolving Complex, is a fundamental catalyst for most of the earth life, indeed it provides the driving force for the carbon fixation and evolve as side product the oxygen that nowadays compose our atmosphere. Its efficiency and simplicity are inspiration for artificial mimic structures whom could achieve similar catalytic properties in inorganic environment. An extensive and deepen comprehension of peculiar traits of the reaction centre and the performed mechanism is crucial for such task. Theoretical elucidation aims to eventually connect the points in the foggy panorama of many experimental evidences which seems to disprove each other. The catalytic process performing water oxidation is called Kok-Joliot's cycle, composed of 5 states named S0 to S4, and the main characters is the MnCa complex. The crucial steps in the mechanism resides in the supplying of substrate water molecules (S2,S4) and in the bond formation between such substrate oxygens (S4). The huge advancements in the crystallographic techniques provided all the data necessary for an extensive theoretical study. Using DFT based methods involving QM/MM dynamics and gas phase calculation of Minimum Energy Paths, we built a comprehensive pathway of intermediate steps, starting from the S2 state up to the O-O bond formation and including the delivery of the substrate water molecules. The proposed mechanism involves interconversions between two isomers of the MnCa cluster allowing the consecutive charging of oxidation potential up to critical point in which the peroxide bond is formed. Employing both dynamic and static computational methods, we estimated an energy pro-file accordant with the experimentally measured timescale and providing molecular basis for a preferential reaction mechanism in water oxidation.



Fig.1: MnCa cluster, core of the PSII reaction center just before O-O bond formation (S4 state).

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F-RESP: a new and fast polarizable force field

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F-RESP (Fluctuating-Restrained ElectroStatic Potential) is a new polarizable model for classical molecular dynamics that considers atomic charges to be function of the electric fields exerted along the bonds of the molecule they belong to by the other particles of the system. The main advantage of this technique is that electric fields along bonds are calculated using fixed "generating" charges, which are obtained from RESP[1] ones during the parametrization procedure along with coefficients for charge variation function, thus avoiding the slow self-consistent process that would have been necessary using real charges. The calculation of fictitious electric field (whose name is given by the use of fictitious generating charges) can be performed using Ewald summation[2] technique or Fennell's potential[3]. Both models have been implemented in LAMMPS[4] and parallelized; for the latter, corrections to the virial are calculated, enabling to perform NPT simulations. Good results have been obtained with simulations on water with respect to the classical TIP3P model, while the application of the technique on more complex molecules that have until now represented a challenge for classical MD, like ionic liquids, is underway.



Fig. 1: Water O-O RDF comparison

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Band Edge Alignment at NiO/H₂O and Ni₂P/H₂O Interfaces

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The search for semiconductor co-catalysts requires the calculation of the alignment of valence and conduction bands of the co-catalyst with respect to the redox levels of liquid water. In this context, we analyze two transition metal-based co-catalyst, namely NiO and Ni₂P, which have been proven to exhibit high hydrogen evolution rates when used in conjunction with metal-organic frameworks, acting as photo-catalysts.^[1] We perform hybrid-functional calculations to compute the band structure of the two semiconductors. Both a molecular and a dissociative model of the water adsorbed at the semiconductor surfaces are considered. Finally, molecular dynamics simulations of the NiO/H₂O and Ni₂P/H₂O interfaces are used to determine the band edge alignment. Our results aim at giving an explanation for the role of NiO and Ni₂P as co-catalysts for the photo-catalyst MIL-125-NH₂.



Figure 1: Band alignment at the NiO/H₂O interface and at the Ni₂P/H₂O interfaces

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Configurational Entropy in High-Entropy Alloys: Matrix Formulation from Ab Initio Based Cluster Expansion Hamiltonian and Application to the FCC Cr-Fe-Mn-Ni System

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High-Entropy Alloys (HEAs) were brought to attention through the work of Cantor et al. [1] and have been shown to have excellent mechanical properties including strength and ductility [2]. In Cantor's alloy, the single phase stability was attributed to high ideal entropy of mixing in the alloy. Until recently [3], most phase formation rules used to predict HEA stability assumed that these systems were in the fully random solid solution state following the well known Boltzmann equation. Known HEAs were reported to form when configuration entropy of mixing ranged between 1.4 and 2.1kB, and intermetallics lower entropies than HEAs in the 1.3-2.0kB range [2]. The overlap of configuration entropy of mixing in HEAs and in intermetallics suggests that single phase may not be always dominant in HEAs at high-temperatures.

In this work, a new matrix-based formalism built from Group Theoretical crystallographic methods and the Cluster Variation Method (CVM) is developed to combine the Cluster Expansion (CE) of the HEAs Hamiltonian with Monte Carlo (MC) simulations. The formalism is developed to predict the multi-body cluster probabilities and the configuration entropy of mixing as a function of temperature and composition [3]. The multi-body probabilities are determined as a function of temperature and composition from symmetry independent correlation functions. The formalism is applied to analyse the 4-body cluster probabilities for the quaternary system Cr-Fe-Mn-Ni as a function of temperature and alloy concentration. It is shown that the high value of probabilities for Cr-Fe-Fe and Mn-Mn-Ni-Ni are strongly correlated with the presence of the ordered phases L12-CrFe3 and L10-MnNi, respectively.

In the present work it is shown that, at high temperatures, the many-body cluster probabilities play an elucidating role in relating the configuration entropy to the atomic ordering or disordering configurations before reaching the random state of solid solution in the CrFeMnNi system. The present work will help to improve further understanding the phase stability of HEAs, specifically on the derivative phases as a function of temperature and composition from HEAs random solid solutions.

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Excitons in hexagonal Boron Nitride

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In two dimensional semiconductors and layered systems, the Coulomb interaction between conduction electrons and valence holes is poorly screened. This results in the appearance of non-negligible two-particle bound states below the band gap energy: excitons. Excitonic states tend to dominate the optical properties of such systems (fig.1), and their understanding is therefore of great importance in spectroscopy.

We investigate theoretically the prototype 2D system hexagonal Boron Nitride (hBN), a wide band gap semiconductor which has attracted great attention for its strong excitonic effects and UV luminescence properties. We employ both *ab initio* methods and a semi-empirical model which maps the two particle excitonic problem (Bethe-Salpeter equation) onto an effective single particle tight binding Hamiltonian.[1]

We thus obtain a precise characterization of the excitonic states in single and multi-layer hBN in terms of their symmetries and optical selection rules. Further, using a simple 1D model, we investigate the splitting of the main peak in the absorption spectrum with increasing number of layers and show that in multilayers, the lowest bound excitonic states are actually localized on the surface layers and can be optically active.[2]



Figure 1: ab initio absorbtion spectrum of single-layer hBN. The dotted line marks the band gap.

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Not Wave, Not Particle: Polaronic Charge Carrier Propagation Through Organic Crystals.

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Exciting new technologies such as organic light emitting diodes, photovoltaics and nanoelectronics rely on organic semiconductors. While important progress has been made in recent years towards theoretical and computational modelling of organic semiconductors (OSs), understanding the charge transport (CT) mechanism in these materials is still very challenging because the parameters determining the dynamics are typically outside the regime of validity of existing theories (e.g. Hopping or Band theories). On the other hand, non-adiabatic molecular dynamics simulations are in principle free of model assumptions permitting a realistic view into the CT mechanism. We have recently developed an efficient decoherence-corrected surface hopping methodology (denoted FOB-SH) which allows us to propagate the coupled electronnuclear motion in realistic condensed phase systems [1-3]. Here we present the first application of FOB-SH (blue symbols Fig.) to the calculation of room temperature charge mobility for a series of eight molecular organic crystals. We obtain very good agreement with experimentally measured mobility values over three orders of magnitude successfully bridging the regime where hopping (green symbols) and band models (red symbols) are invalid as shown in Fig. We find that the mechanism of transport critically depends on the ratio between electronic coupling and reorganization energy (electronphonon coupling), V/ λ . At small ratios, as found in p-MSB, the charge carrier is delocalized over no more than 1-3 molecules and diffuses through the crystal via slow hopping. For values exceeding the critical threshold $V/\lambda > 1/2$ as found in pentacene, the charge carrier forms a polaron delocalized over 15 molecules concomitant with a strong increase in mobility. Implications of our work for the search of new organic materials with be high room temperature mobility will discussed.

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Quantum dynamics with sinks (or sources) in a constant-temperature bath

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Open quantum system dynamics is ubiquitous in physics [1]. One well-known example is provided by the energy transport in photosynthetic systems [2][3].

Having in mind to model such systems, we adopt an approach based on the evolution of the density matrix operator by means of non-Hermitian Hamiltonians [4]. This enables us to describe the presence of sinks in our model. Moreover, we generalize previously introduced equations, based on mathematical deformation of quasi-Lie brackets [5], upon modeling thermal fluctuations of the system environment by means of a Nosé-Hoover Chain thermostat [6].



Figure 1: Diagram a) represents an isolated two-level quantum system. In b) a probability sink is added to the system. Finally, in c) we add a constant-temperature bath.



Figure 2: The figure represents the mechanisms entering quantum energy transport in photosynthetic systems. In addition, our theory considers a probability sink (picture taken from A. I. Nesterov, G. P. Berman, and A. R.

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Phase transitions between (meta)stable phases in alumina

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In this work, we present a computational study on alumina phase transitions. The study is based on molecular dynamics, enhanced sampling simulations and free energy calculations [1,2]. Our approach relies on the PathCV-PIV collective variables [3] and allows tracking transitions among liquid, amorphous and crystalline forms of alumina providing transformation mechanisms and free energy landscapes. We present results on (i) the simulation of the crystallization of amorphous alumina at different temperatures, (ii) the connection between stable and metastable crystalline phases of alumina and (iii) the effect of temperature on the free energy landscape of alumina at ambient pressure. *Figure:* (a) amorphous structure of Al2O3 (b) crystal structure obtained from



metadynamics (to be investigated) (c) alpha-like crystal structure of Al2O3 (d) Uncongerved Free Energy Lanscape from metadynamics

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A Density Functional Theory Study of Gas Adsorption in Nitrogen-Doped Carbons

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Porous nitrogen-doped carbons are known to have several applications, in which the adsorption of polar gases play a significant role. We investigated the adsorption of water (H_2O), ammonia (NH_3) and carbon dioxide (CO_2) in a recently synthesized well organized nitrogen-doped carbon with C_2N stoichiometry[1] using Density Functional Theory based geometry optimizations. In order to analyze the impact of the nitrogen-doping, the results are compared to those of a carbon material without nitrogen-doping.

We found that the adsorption in C₂N is energetically favored for all three molecules. The nitrogen-doping increases the water affinity where the water molecules occupy vacant sites in between the C₂N layers. The adsorption affinity for ammonia in C₂N is even more enhanced. As a result of its high oxidation potential, C₂N is found to also support the formation of dihydrazinium ions, N₂H₆²⁺, on its surface. However, the final adsorption configuration contains both, ammonia and dihydrazinium ions, which are alternatively located between the layers. The adsorption of carbon dioxide molecules occurs in the C₂N layers with an angle of 90° with respect to these surface layers. The phenomenon of CO₂ adsorption is observed only in the nitrogen-doped system.



Figure 1: Adsorption state of ammonia at C₂N materials where C₂N is able to form $N_2H_6^{2+}$. Carbon: black, nitrogen: blue, hydrogen: white.

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Comparison of the Structural and Electronic Properties of Fe-Phthalocyanine Adsorbed on Cu(111) and Ag (111)

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M-Phthalocyanine (MPc) is a large organo-metallic molecule (M=3d Metal) that attracted many researchers because of the mixture of its properties leading to various applications at low cost, starting from dyes in the industrial field to numerous applications in several fields such as oncology, catalysts, spintronic devices and optoelectronic devices ...

Some applications require the deposition of these molecules on supporting metallic surfaces. Therefore, in this work, we use Density Functional Theory DFT calculations with Van der Waals interactions to investigate the contact of MPc molecules (where M is Fe) on metallic substrates Cu(111) and Ag (111) in order to fully understand their effect on geometric, electronic and magnetic properties. We also present a complete comparison of the obtained results of the adsorption of FePc/ Cu (111) and FePc/Ag(111) systems.

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First passage algorithms for sink strength calculations: Application to vacancy emission and absorption

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Kinetic Monte Carlo techniques are extensively used to simulate the evolution of defects in materials and to study irradiation effects in particular. All these methods are based on a master equation involving a transition rate matrix. Transition rates are derived from an energetic model in which defects and atoms may either occupy substitute and interstitial sites of a crystalline lattice or exhibit off-lattice in a continuous space. Unfortunately, KMC methods become inefficient when the transition rate matrix exhibits a broad spectrum of frequencies. Vacancies perform a huge number of transitions between a few atomic configurations connected to each other by small energy barriers. These connected configurations form trapping basins from which the typical escape time for a particle is much higher than the typical time to cross the small barriers inside the basins. The system remains stuck in metastable thermodynamic states. Acceleration techniques based on the theory of absorbing Markov chains are currently being used in Kinetic Monte Carlo simulations to overcome kinetic trapping in low energy basins . This is achieved by drawing escaping events to distant locations from the exact first passage and no-passage distributions. These two distributions can be formally expressed through the eigenvalue decomposition of the transition rate matrix. Assuming reversible diffusion processes, a property usually satisfied by defects in metals and alloys in and out of equilibrium, we show that the involved linear and eigenvalue problems to be solved can be symmetrized. The slowest modes associated with the smallest eigenvalues contribute the most to the first passage and no-passage distributions. As a result, Krylov subspace projection techniques implementing reverse iterations provide us with an efficient tool for accurately approximating the two desired distributions at a relatively low cost. We discuss the convergence, scalability and range of applicability of the approach. We demonstrate its efficiency by computing sink strengths and transition currents for the emission and absorption of vacancies from and to cavities in Aluminium at low defect concentrations.



Figure 1: Residence times and fluxes associated with a single vacancy emission from a spherical cavity

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Impact of intermolecular vibrational coupling effects on the sum-frequency generation spectra of the water/air interface

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In our recent work^[1], we have examined the impact of intermolecular vibrational coupling effects of the O-H stretch modes, as obtained by the surface-specific velocity-velocity correlation function approach^[1,2], on the simulated sum-frequency generation spectra of the water/air interface. The water/air interface was developed by means of adiabatic centroid molecular dynamics simulations in conjunction with a flexible q-TIP4P/F force-field^[3], which was augmented by explicit three-body effects^[4]. Our work clearly demonstrates that the inclusion of intermolecular coupling effects within the first three water layers, i.e. from the water/air interface up to a distance of 6 Å towards the bulk, is essential to reproduce the experimental SFG spectra. In particular, we find that these intermolecular vibrational contributions to the SFG spectra. In particular, we find that these molecules vibrational contributions to the SFG spectra of the water/air interface are dominated by the coupling between the SFG active interfacial and SFG inactive bulk water molecules. Moreover, we find that most of the intermolecular vibrational contributions to the spectra originate from the coupling between double-donor water molecules only, whereas the remaining contributions originate mainly from the coupling between single-donor and double-donor water molecules.



Figure 1: A snapshot of simulated water/air interface at ambient conditions, illustrating different water layers (Left figure) and its corresponding sum-frequency generation spectra (Right figure). All hydrogen atoms are shown in white, while the oxygen atoms are colored according to the different layers they are associated with, i.e. L₁ (blue), L₂ (green), L₃ (yellow) and bulk water (red).

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The impact of sulfur on the transfer of platinoids by geological fluids

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Knowledge of the mobility of platinum group elements (PGE) in magmatic-hydrothermal fluids is a key to understanding PGE deposit formation and fractionation. Yet, existing data on aqueous chloride, sulfate, and hydroxide PGE complexes predict far too small metal contents (<ppb) in fluids from most geological settings [1, 2, 3], thus calling upon an important role of the sulfide and, potentially, trisulfur ion ligands in PGE transport. In an attempt to quantify the effect of sulfur in PGE mobility, we combined solubility measurements, in-situ X-ray absorption spectroscopy (XAS), thermodynamic, and molecular dynamics modeling based on recent advances of our knowledge of S speciation in crustal fluids [4, 5]. Our solubility and spectroscopic measurements performed at 300°C and 500 bar demonstrate enhanced solubility of Pt in H₂S/SO₄/S₃⁻ hydrothermal solutions over a wide pH range (4-7), with Pt concentrations as high as 10s ppm, which is ~5 orders of magnitude higher than the Pt average lithospheric abundance. Our solubility and XAS data suggest formation of Pt-HS-S₃⁻ complexes, similar to those proposed for gold [4], and the presence of species of tetravalent Pt(IV), which have never been considered in previous experimental studies and thermodynamics models [5, 6], postulating divalent Pt(II) as the major oxidation state in geological fluids. Thus, our new data highlight the role of previously ignored sulfur complexes in PGE transport and fractionation by S-bearing ore-forming fluids in the Earth's crust.

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Point defects in PbS: An ab-initio study

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Lead chalcogenides (PbX, X = S, Se, Te) are an important family of narrow band-gap IV-VI semiconductors that are the subject of intensive research due to their wide range of application, such as thermoelectric conversion, infrared lasers, thermal photovoltaic devices and light-emitting diodes. In addition, PbX systems in the form of heterogeneous nanocrystals are extensively used to formulate new materials with tunable and novel physical properties.

Defects exist in crystals both by the physics and by the processes of their formation, and play a vital role in crystal synthesis, growth and properties. Point defects and impurities, in particular, have a strong impact on the physical properties of materials and affect their performance in applications [1].

The energetics and electronic properties of point defects in PbS are studied using first principles methods. In particular, intrinsic defects are compared with oxygen defect states. For the intrinsic defects it is found that the lowest formation energies are associated with Schottky defects and with lead and sulfur vacancies. Interstitials, Frenkel pairs and antisite defects are all found to have much larger defect formation energies. The electronic band structure is affected by the presence of intrinsic defects. For the Schottky dimer it is found that the bandgap is narrowed, whereas for the lead vacancy the Fermi level is shifted below the valence band maximum indicating p-type conductivity. Finally, sulfur vacancies introduce levels deep in the band gap which may affect the electronic properties significantly. It is found that the formation energies of oxygen defects are highly competitive with respect to those of intrinsic defects and therefore oxygen point defects are expected to play a significant part in determining material properties.

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First principles lattice thermal conductivity using an approximation of averaged phonon-phonon interaction strength

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Recent progress in computational power has enabled us to calculate third-order force constants within a realistic wall-clock time and let us calculate lattice thermal conductivity from phonon-phonon interaction strengths. In this paper, we investigated the general tendency of phonon-phonon interaction strength toward lattice thermal conductivity within the framework of linearized phonon Boltzmann equation with single-mode relaxation time approximation (RTA). We used 37 rocksalt- and 33 zincblende-type compounds, which already showed satisfactory agreements between experimental and calculated results[1]. For calculating lattice thermal conductivity, we employed phonopy and phono3py software packages. For first principles calculations, we used VASP code[2].

In linearized phonon Bolzmann equation with RTA, lattice thermal conductivity of the isotropic compound is written as $\kappa = 1/V \sum_{\lambda} C_{\lambda} v_{\lambda}^2 \tau_{\lambda}$. C_{λ} , v_{λ} and τ_{λ} are heat capacity, phonon group velocity and phonon lifetime of phonon mode λ . Phonon lifetime is

calculated from phonon-phonon interaction strengths. We employed an approximation of phonon-phonon averaged interaction strength[3], which is the averaged interaction strength value of the three phonon interaction strenaths which satisfy the momentum conservation. Fig. 1 shows the comparison between lattice thermal conductivities with and without using an approximation of averaged phonon-phonon interaction strengths. In Fig. 1, lattice thermal conductivities using averaged phonon-phonon interaction strengths show systematically lower values than the values without usina averaged phonon-phonon interaction strenaths. rocksaltand and zincblende-type compounds are clearly separated, which means there is a different phonon-phonon interaction mechanism in the two crystal structures. This result shows that three phonon scattering phase space mainly describes microscopic structure of the lattice thermal conductivity.



FIG. 1. Comparison between lattice thermal conductivities with and without using the phonon-phonon interaction approximation.

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Optimization of drug-membrane selectivity from free-energy calculations

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Current virtual screening approaches reduce the computational cost by using simplified representations and approximations, while statistical mechanical effects are excluded. We investigate one way to include the effects determining the selectivity of a molecule to a specific target in virtual screening by using physics-based models. Coarse-grained simulations are introduced as a preliminary step to allow the effective screening of a large number of molecules. In the coarse-grained representation, the bead types at selected positions of a small molecule are changed and the difference in binding affinity between the original and modified structures are determined by free energy calculations. As a next step, the information lost in the coarse-graining process is reintroduced to the most promising subset of the screened molecules by repeating the free energy calculations in atomistic detail.

As a test case, the physical and chemical properties of the fluorescent dye 10-N-nonyl acridine orange are modified to increase its binding affinity to Cardiolipin. Cardiolipin is exclusively found in the eucaryotic inner mitochondrial membrane, making it an interesting object of research.



Figure 1: Virtual high throughput screening

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A mechanistic study of the HF pulse in the thermal atomic layer etch of HfO2 and ZrO2

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Thermal atomic layer etching (ALE) of HfO2 and ZrO2 uses sequential and self-limiting fluorination reactions using HF as the reactant. This modern approach for ALE is the reverse of atomic layer deposition (ALD) and leads to isotropic etching that removes the modified layer. Each cycle of thermal ALE consists of two precursor pulses. In the first pulse the precursor reacts with the surface atoms of the substrate material and forms a stable and non-volatile layer, this surface modification is self-limiting in nature. We present a first principles study of the hydrogen fluoride pulse in the first step in thermal atomic laver etch of monoclinic hafnium dioxide and zirconium dioxide using density functional theory (DFT) calculations. HF molecules adsorb on the surfaces of these metal oxides by forming hydrogen bonds and may remain intact or dissociate to form, Hf-F and O-H for hafnium dioxide and Zr-F and O-H for zirconium dioxide. The adsorption of one HF molecule at the bare surface of both metal oxides results in dissociative adsorption at all binding sites. The adsorbed H atom can migrate to other O sites on the bare surface depending on energetic barriers. For multiple HF adsorption at coverages ranging from 1/16 to 1 monolayer we find mixed molecular and dissociative adsorption of HF molecules at the bare surfaces.





Chemical ordering transformations in nanoalloys studied by molecular dynamics and metadynamics

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In most experiments metal nanoparticles are initially produced in out-of-equilibrium states; they then evolve towards thermodynamic equilibrium undergoing transformations in geometric structure and, in the case of nanoalloys, in chemical ordering. Here we study the evolution at constant temperature of AuCo, AgNi and AgCu nanoparticles by molecular dynamics (MD) simulations. Nanoparticles sizes of about 2.5 nm are considered, in the temperature range from 300 to 700 K. These nanoparticles present the same tendency to phase separation and to surface segregation of either Au or Aq, which lead to the same type of core@shell equilibrium structures [1]. In spite of these similarities, the simulations reveal significant differences in the equilibration pathways from chemically disordered configurations [2]. These differences are both quantitative (equilibration time scale) and gualitative (presence or absence of geometric structure transformations, formation of different types of three-shell metastable arrangements during the evolution). In the case of AuCo we also study the evolution of smaller nanoparticles from reverse core-shell Au@Co to core-shell Co@Au at room temperature. Due to the long time scale of this process, it is not possible to study the complete evolution by standard MD simulations; therefore we use a recently developed form of metadynamics [3], which turns out to be very efficient in the study of the chemical ordering transformations of nanoparticles.



Figure 1 : Equilibration stages of chemical ordering in AuCo nanoparticles starting from randomly intermixed structures. Evolution of the surface (top row) and of the interior (bottom row)

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DFT Calculation of Pressure-Induced Semiconductor-Metallic Transition in Tin Oxide

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Tin oxide SnO is an attractive material candidate for inclusion in semiconductor and optoelectronic applications. SnO electronic properties are strongly affected by temperature and pressure conditions, because of the metastable layered structure of the tetragonal phase and the high hole mobility. A pressure-induced semiconductor to metallic phase transition of SnO has been confirmed by both experiments and theoretical approaches [1-4]. Theory has predicted that this transition is associated with a tetragonal-orthorhombic structure transformation [3,4]. However, experiments show controversial results about whether an orthorhombic phase is formed or not [1,2]. Altogether, a clear explanation of the pressure effect on the electronic properties of SnO is still lacking and the high pressure metallic phase remains to be explored.

In this study, we examine the effect of high pressure on both the structure and physical properties of SnO via density functional theory methods. Thermodynamic relationship of tetragonal and orthorhombic phases in high-pressure region is carefully examined and several pseudopotentials and exchange correlation approximations are applied within the Quantum Espresso code [5], to clarify the true nature of this phase transition. We found that the tetragonal phase is the stable high pressure phase under hydrostatic conditions. Further, we verified that the distorted orthorhombic structure under non-hydrostatic conditions is not the main reason for the semiconductor-metallic transition in SnO. In addition, at high pressure over 80 GPa an interlayer Sn-Sn bond forms accompanied by a dramatic change of the band structure and the local density of states on the interlayer Sn atoms. In addition, effects of high pressure condition on the Sn-O, Sn-Sn bonds and electronic mobility are significant. Hence, SnO potential application in thermoelectric converter and solar cell may be improved under appropriate pressure conditions.

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Ru-doped and Ru-passivated ε-TaN as combined Barrier and Liner materials for Copper Interconnects

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With ever decreasing transistor size, materials that combine both diffusion barrier and liner material properties are needed to successfully electroplate Cu and thus beat the current interconnect bottleneck. In order to facilitate coating of high aspect ratio vias, the material should be as thin as possible. One possibility to achieve this is presented in this study, where we investigate through density functional theory, the behavior Cu on Rudoped and Ru passivated ϵ -TaN (1 1 0). Initially, the adsorption, diffusion and association of one and two Cu atoms on the different surfaces was studied in order to probe the early stages of film growth. This showed that, while surface diffusion of atoms was more favourable on the Ru-passivated surface, the Ru dopant acts as a nucleation site for Cu, with atoms preferentially diffusing towards it.

In order to understand the mechanism of film growth on this surface in more detail and to fine-tune the barrier and liner properties of the material, the effect of different percentages of surface doping were studied. Further, the behavior of Cu_{13} and Cu_{29} clusters on different doped surfaces and on the passivated surfaces was investigated. In particular, the study focused on the pathways toward agglomeration as well as the associated activation energies. We find that on a Ru doped surface the atoms agglomerate spontaneously to form a two-layer film, whereas they remain in a monolayer on Ru-passivated TaN (1 1 0).









Cross-linked cellulose nano-sponges: a small angle neutron scattering (SANS) study

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Cellulose xerogels prepared using 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) oxidized and ultra-sonicated cellulose nanofibers (TOUS-CNFs) as three-dimensional scaffolds, and branched polyethyleneimine (bPEI) as the cross-linking agent [1], underwent to a systematic Small Angle Neutron Scattering (SANS) investigation, by varying the amount of cross-linker and the water content. The aim was to provide an experimental evidence of nano-porosity in these cellulose nano-sponges (CNS) by investigating the water nanoconfinement geometries in the adsorbent material. Moreover, we also verified how the breaking/reformation of specific intermolecular hydrogen bond interactions between water and the chemical groups present in the architecture of the CNS can contribute to regulate the water adsorption process observed at macroscopic level. The analysis of the experimental data was performed in terms of a Correlation Length Model (CLM) [2], whose parameters turned out to be all sensitive to the structural variations induced by the progressive uptake of water on the bPEI/TOUS-CNFs xerogels with different CNS ratios. Finally, the effect of the addition of citric acid in the CNS formulation was also investigated.



Figure 1: Scattering intensity as a function of q for CNS (0.2:1) (a), CNS (0.5:1) (b), CNS (1:1) (c), and CNS (2:1) (d) sponges, in the dry state and swollen at different hydration values h.

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Insights on the decomposition mechanism of MoDTC by QM/MM simulations

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Simulating tribochemical reactions, i.e. the chemical reactions occurring at the interface under the effect of mechanical stresses, allows a better understanding of the phenomena relative to friction. wear and their reduction at the atomistic level. MoDTC is a well-known base oil additive capable of forming lubricating tribolayers of molybdenum disulfide, after molecular dissociation [1]. However, the process leading to the formation of this beneficial tribolayer is still debated [2-4]. We perform QM/MM simulations to describe the dissociation processes of the MoDTC additive by employing a coupling between the Quantum ESPRESSO [5,6] and LAMMPS [7] packages to consider realistic tribological conditions. We find that oxygen atoms present in MoDTC play a major role in stabilizing the reaction products and modulate the kinetics of the dissociation [8,9].



Figure 1: Chemical structure of MoDTC



Figure 2: Typical system for QM/MM simulations.Vertical (horizontal) arrows represent normal load (shear stress).

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Interaction of small molecules with cobalt spinel nanocrystals

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Cobalt spinel nanocrystals (Co₃O₄) are excellent redox-tunable model catalytic nanomaterials of well-defined shape (Fig. 1a and 1b) and widespread applications. In particular, these materials exhibit an exceptional performance in the low temperature decomposition of nitrous oxide (N₂O). However, catalytic performance of Co₃O₄ can be significantly diminished due to the presence of inhibitory gases, especially nitric oxide (NO). Despite the critical role of NO in the deactivation of Co₃O₄, a comprehensive molecular-level description of its interaction with the catalyst surface is still lacking.

Herein, periodic spin unrestricted, gradient corrected DFT calculations along with first principles thermodynamics were performed to investigate the structure and stability of various NO adspecies on the most abundant cobalt spinel (100) facet, over a wide range of temperatures and pressures. Several conceivable models of NO admolecules were examined to find the most stable adsorption mode. Then, according to the obtained results, the NO molecules were successively added to coordinatively unsaturated cobalt ions in order to obtain full surface coverage corresponding to a monolayer. The results revealed that in the pressure range of typical catalytic reactions (p/p° ~0.01 to 1), at low temperature range (below 50-100°C), two molecules of NO are bound to the surface in a top-on fashion: one to an octahedral center (Co[°]) and the other to a tetrahedral center (Co^T), as depicted in Fig. 1c. In higher temperatures (between 50-100°C and 475-600°C), the NO molecule adsorbed on Co[°] leaves the surface, and only one NO molecule remains strongly attached to the Co^T (Fig. 1d). The constructed thermodynamic diagram of NO sorption (Fig. 1e) summarizes the surface coverage as a function of pressure and temperature, providing a convenient background for understanding the harmful effect of the presence of NO on the catalytic performance of cobalt spinel.



Figure 1: A) STEM image of the cobalt spinel nanocrystal exhibiting cubic morphology. B) Gradient of the STEM image, showing the edge pattern used for morphology retrieving. Perspective view of C) two and D) one NO molecule adsorbed on the cobalt spinel (100) surface. Color coding: Co^{o} – light blue; Co^{T} – purple; O – red; and N – dark blue. E) Two-dimensional diagram of NO coverage as a function of temperature and partial pressure.

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Exciton-Phonon Coupling in Monolayer and Bilayer MoTe₂

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 $MoTe_2$ is a layered transition metal dichalcogenides (TMDs); they are a family of semiconductors whose structure is composed of two-dimensional (2D) sheets weakly bound by Van-der-Waals interactions. These materials have been extensively studied for their exceptional properties: electronic, optical and for the appearance of topological or superconducting phases. While there is a large amount of literature on molybdenum disulphide (MoS₂) and molybdenum diselenide (MoSe₂) considerably less attention has been devoted to MoTe₂.

Usually direct band semiconductors are considered efficient light emitters while the indirect ones are regarded as inefficient, but it has been showed that also an indirect gap semiconductor like hexagonal BN (h-BN) seems to defy this rule [1].

MoTe₂ shows a direct to indirect bandgap crossover when going from monolayer to few layers. This has been investigated with both experiments and simulations [2,3]. In particular, in one of the experimental works on the difference between the photoluminescence yeld by monolayer and bilayer, exciton-phonon coupling has been studied showing that MoTe₂ bilayer could be a robust light emitter due to a weak coupling with phonons [4].

We want to investigate this using Many Body Perturbation Theory (MBPT) and Density Functional Perturbation Theory (DFPT) to investigate from a theoretical point of view this behaviour. We exploit nondiagonal supercells [5] to reduce the computational cost and use innovative methods to compute spectra taking into account the coupling between excitons and phonons [6].

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Tunnelling splittings and the Kramers rate of activated processes

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In this work a novel approach to the calculation of the ground state tunnelling splitting is presented. This new technique is based on the profound isomorphic relation existing between the Fokker-Planck-Smoluchowski and Schrödinger equations that allows the use of what already done in the field of Kramers theory of activated kinetical processes, for the evaluation of the tunnelling splitting. In this context the calculation of the tunnelling splitting represents the quantum counterpart of computing kinetic transition rates. Besides the utilitarian aspect of recovering, in the limit of high potential barriers, accurate tunnelling splitting this technique allows one to look at the problem of quantum tunnelling with a new prospective possibly leading to new theoretical insights.



Figure 1: Computed tunnelling splitting value for a double gaussian probability distribution model (on the left) and the correspondent relative error in respect to the numerical value (on the right)

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Heterogeneous Catalysis in Biomass Chemistry: Determining the Surface Structure of Metallic Ruthenium in Aqueous Media Under Gas Phase Environments

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Metallic ruthenium has been found to be an efficient catalyst for carrying out many different chemical transformations involving molecules obtained from biomass-based sources in aqueous phase.¹ It has been elucidated through both experiments and first principles calculations that water plays a major role in the increased activity and reactivity of the metallic ruthenium catalysts.² Such catalytic reactions often require certain conditions of temperature and gaseous pressures e.g. a pressure of hydrogen³. However, ruthenium has a strong tendency to be oxidized in the presence of oxygen; and it has also been shown that water molecules split on the surface of ruthenium to make a wetting layer consisting of hydrogen-bonded hydroxyl groups and water molecules.^{4a-b} It is, therefore, imperative to investigate the surface state of ruthenium catalysts under the presence of all these species to be able to better understand the mechanisms of different chemical transformations taking place on the surface. Ab-initio thermodynamic⁵ studies based on the periodic Density Functional Theory (DFT) have been carried out to investigate the stability of different phases of ruthenium catalysts as a function of hydrogen and oxygen chemical potential. The phases considered include bare ruthenium surfaces, hydrogen/oxygen adsorbed on different ruthenium surfaces, OH adsorbed on different ruthenium surfaces, bulk RuO₂ and different surfaces of RuO₂. The work will provide insights into the surface state of the catalyst under realistic conditions of temperature and pressure.



Figure 1: Wulff Construction for pure ruthenium in equilibrium.

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Algorithm for enumerating crystal structures with decision diagram

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Crystal structure plays a crucial role in material science. We propose a new algorithm for enumerating crystal structures to comprehensively search for stable ones. So far, a gradient-decent-based structure optimization method or an enumeration-based method that prepares finite structure candidates in advance [1] are used for crystal structure search. These methods, however, have an inevitable problem that a search space expands exponentially with the increase of the number of atoms in a unit cell.

It is known that many ionic crystal structures can be regarded as the closest packing structure of anions with cations in their interstitial sites [2]. Therefore, we consider a model in which anions are located at lattice point sites and cations are at interstitial sites and enumerate crystal structures within this model. To reduce the number of enumerated structures, we leave only the structures satisfying Pauling's rules, which is one of the well-known empirical rules about the stability of ionic crystal structures.

If we select the part that satisfying constraint from all listed structures, listing all structures becomes a bottleneck in the total procedure, and limits the size of a unit cell which can be applied the method of structure enumeration. To avoid this, we apply a zero-suppressed decision

diagram(ZDD)[3], which is a kind of discrete algorithm and can retrieve only the part that satisfies constraints without all listing.

We show the result of enumerating FCC-derived binary oxide with composition ratio 1:1 in Table 1. This result indicates that we can largely reduce candidates for searching crystal structures by introducing prior knowledge or Pauling's rules.

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unit cell w/o w/ Pauling's w/ Pauling's size constraints 3rd rule 2nd and 3rd 1 12 3 2 2 130 15 7 3 1684 46 10 4 34087 248 43 350832 438 22 5 2836 91 6 7 5546 48 8 42746 385

[3] S. Minato, Proceedings of the 30th ACM/IEEE Design Automation Conference (1993). Table 1. the number of enumerated derivative

structures of binary oxide







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Hydrogen Activation on Rutile TiO₂ Surfaces: A therotical Study

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Titanium oxide (TiO_2) has been widely used in many fields, such as photocatalysis, photovoltaics, catalysis, sensors.^{1,2} Interaction of the H₂ molecule with the TiO₂ surface plays an important role in many reaction processes. However the activation of hydrogen over rutile TiO₂ surfaces has not been systematically studied. In this work, we use density functional theory (PBE+U) to identify the pathways for two processes: the heterolytic dissociation of H₂ as a hydride/proton pair, and the subsequential H transfer from Ti to near O accompanied by reduction of the Ti sites. Four facets were considered: (002), (100), (110), (101). We find the first process (the dissociation pathway) kinetically more favorable than the second process (H transfer), though the second process is thermodynamically more favorable. The activation barrier is low for hydrogen dissociation, 0.50-1.08 eV. For hydrogen transfer from Ti to near O, the activation barriers are higher (from 1.40 eV to 1.86 eV). The four terminations studied exhibit similar behavior, the (101) displays the smoothest overall profile.



Figure 1 The energy barriers of hydrogen dissociation on rutile TiO₂ (002), (100), (101), (110) surfaces and the energy barriers for H transfer from Ti to near O.

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