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Abstract book

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Conceptual theoretical methods to address the challenge of energy density in Li-ion batteries

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To meet the challenges of our society in terms of energy, the autonomy and lifespan of Li-ion batteries must be considerably improved. This implies increasing the energy density of electrode materials and controlling the electrochemical reactions at the electrode/electrolyte interfaces. The energy density depends on the electrochemical potential and the specific capacity of the electrode materials. These quantities are not intrinsic properties of a given material but response properties to a change in lithium composition. For this reason, high-throughput and/or combinatorial theoretical approaches such as those developed in this field over the 20 past years have not yet made it possible to design new efficient materials for Li-ion batteries. In contrast, more conceptual approaches, based on chemical bonding and electronic structure have proven their effectiveness in identifying the chemical, structural and electronic descriptors at the origin of the electrochemical properties of a material, therefore enabling more rational design of electrode materials. This research has contributed to the discovery of a new class of positive electrodes presenting record energy densities thanks to a dual cationic and anionic redox activity (1,2) but has led to numerous controversies in the literature over the past 10 years (3). This presentation will propose an overview of the different theoretical approaches and models used to address the challenge of high-energy-density in Li/Na-ion batteries and will raise questions on the methodological issues associated with energy storage materials.

(1) M. Sathiya, et al. *Reversible anionic redox chemistry in high-capacity layered-oxide electrodes* **Nature Materials** (2013) 12, 827-835.
(2) M. Ben Yahia, et al. *Unified Picture of Anionic Redox in Li/Na-Ion Batteries* **Nature Materials** (2019) 18, 496-502.
(3) X. Gao, et al. *Is Molecular O2 Just a Mirage in Oxides Cathodes* **Nature Materials** (2024) in review

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Investigating the effect of particle size and polydispersity on NMR spectra of ions diffusing in disorder porous carbons through a mesoscopic model

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Ion adsorption and dynamics in porous carbons is crucial for many technologies such as energy storage and desalination. Nuclear Magnetic Resonance (NMR) spectroscopy is a key method to investigate such systems thanks to the possibility to distinguish adsorbed (in-pore) and bulk (ex-pore) species in the spectra. However, the large variety of magnetic environments experienced by the ions adsorbed in the particles and the existence of dynamic exchange between the inside of the particles and the bulk renders the interpretation of the NMR experiments very complex.

In this work, we implement and optimise a lattice-gas model that can predict NMR spectra of ions diffusing in particles of various sizes. The new software, implemented using pystencils, shows an efficient parallelisation with fast calculations, compared to the old software written as a serial code in C (1).

We apply this mesoscopic model to the simulation of NMR spectra of ions in systems where carbon particles of different sizes can be considered. Two types of systems, monodisperse and polydisperse, are considered in this study. In order to investigate deeply the exchanges process between bulk and particles, we modify the ion dynamics (fast – intermediate – fast regime) by tuning the residence time of ions in a given site. We show that representing polydisperse systems is necessary in order to recover some of the features observed experimentally (2).

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(2) A. Sasikumar, C. Merlet, Solid State Nucl. Mag., 126, 101883 (2023)
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Multi-scale modeling of the dissolution/growth dynamics of metallic copper clusters during synthesis or catalysis processes

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Copper nanoparticles (Cu NPs) are well known and widely used for their catalytic and plasmonic properties. In both cases, the control of size and shape is essential for a good control of the physicochemical properties. Understanding the processes involved in the synthesis of these NPs is attractive as it could open the way to rational control. However, this is a complex task because many synthetic processes take place at high temperatures, which allow many competitive reactions to take place. In this context, the recent results published by Vrancken et al. (1) are interesting because they described a synthetic process that takes place close to room temperature. It is based on the thermal decomposition of an alkyl copper reagent leading to a Cu precursor, which then evolves towards the formation of Cu NPs after stabilization with thiolates. Whereas the stabilization step is extensively reported, the formation of Cu(0) precursors is unusual in the context of Cu NPs synthesis. The decomposition reaction itself has been known for a long time, having been first described in 1970 by Whitesides et al. (2) It is proposed to take place in a two-step mechanism. A first copper alkyl reacts by β-hydride elimination to form an alkene and a Cu-hydride intermediate. A second copper alkyl then reacts with the intermediate copper hydride by reductive elimination to give an alkane and Cu(0). This mechanism highlights the formation and reactivity of the intermediate copper hydride, a chemical species of high added value for its many applications, particularly in the field of energy conversion. It is indeed proposed as a reaction intermediate in CO_2 conversion and methanol upgrading. Kinetic studies by Kochi et al. (3) have shown that the reaction is accelerated by the introduction of metallic seeds in the reaction medium, among which Cu(0) seeds, demonstrating an autocatalytic behavior. In particular, they propose the formation of multinuclear mixed valence Cu(I)-Cu(0) intermediates during the course of the reaction, which can act as catalytically active species. In addition, the reaction can occur with or without phosphine additives in the reaction medium, the role of which is not clearly understood. In this presentation, we will examine the effects of adding metallic copper to the reaction medium, as well as the effects of ligands on the relative stability of the species involved.

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(2) G. M. Whitesides, E.R. Stedronsky, C.P. Casey, J San Filippo Jr., J. Am. Chem. Soc., 92, 1426-1427, 1970
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*Speaker

Studying the phase behavior of clay sheets using a flexible coarse-grained model

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The phase behavior of clay sheets suspensions can be analyzed with experimental methods such as neutron scattering or small angle spectroscopy, but to have a precise understanding of the microscopic structure of the suspension, theoretical methods can be necessary. A good way to get detailed microscopic insight is to perform molecular dynamics simulations of clay sheets. To make sure that the simulations are accurate while keeping computation time to a relative low, we decided to use a coarse-grained model. Previous studies have explored clay suspensions using simulations at different ionic forces and volume fractions (1), but they didn't include a property inherent to clay sheets : their flexibility. In this work, we incorporate in the model a flexibility parameter that allows to replicate the mechanical properties of real clay sheets (2). This flexibility could be an important factor in the phase separation, particularly in the isotropic-nematic phase transition (3), which can be observed in certain types of clay, but not all.

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(3) E. Paineau et al, *Liquid Crystals Reviews*, 2013, 1:2, 110-126

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Colloid aggregation simulations at high particle density using Fast Lubrication Dynamics

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Colloidal systems with high particle densities exhibit collective behaviors, such as aggregation, that are of significant interest in both theoretical research and industrial applications (electrophoresis deposition for the generation of protective coatings for instance). For almost five decades, molecular dynamics-type simulations have been developed to study systems of colloids (1)(2)(3). While a pair potential can often be satisfactorily derived from DLVO theory, accurately capturing the interaction with the surrounding liquid medium remains challenging, particularly at high particle concentrations. Several approaches have been developed to address this issue, but they tend to be computationally intensive, impractical, or difficult to implement. The Fast Lubrication Dynamics (FLD) method, introduced by Kumar (4) and implemented in LAMMPS, offers a promising alternative. Intuitive to apply, it maintains computational efficiency even at high densities (3).

We investigated the aggregation behavior of colloidal particles interacting through DLVO-derived pair potentials, one featuring an energy barrier and the other not. Particles are subject to hydrodynamic forces modeled by the FLD algorithm, across a range of high particle densities. We generated and analyzed a range of non-equilibrium trajectories to examine the aggregation behavior of these systems, such as tracking the number of aggregates over time. For systems with a pair potential featuring an energy barrier, coagulation is slow. We simulated such systems in constant-volume conditions at several densities and compared these results with those obtained from trajectories in a shrinking simulation domain. Additionally, we examined systems without an energy barrier to better understand the rapid coagulation dynamics of the colloid model.

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*Speaker

Adapting chemical reaction kinetics of biomass fast pyrolysis to fluidized-bed reactor model

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Fast pyrolysis has been the subject of intense fundamental research activity over the last 30 years. However, bioenergy industry is still limited and needed design improvement. Improving the process requires to consider the thermal and chemical decomposition of biomasss at molecular scale, thermal and mass transfer at particle scale and finally fluidised bed hydrodynamics at the reactor scale. This work presents a numerical model describing the devolatilization of light and heavy volatiles fractions. The chemical kinetics of biomass fast pyrolysis are predicted with the distributed activation energy model (DAEM) via a stoichiometric approach in order to take into account the complex reactivity of lignocellulosic biomass. Non-isothermal and heterogeneous reactions are assumed and the biomass sample temperature is considered. In a second phase, the direct coupling of global chemical kinetics and reactor model is considered. Preliminary tests are conducted in the scope of ideal reactor assembly. The main advances of this work is to coupled CFD with DAEM with an estimated distribution via a stoichiometric approach to incorporate realistic molecular details.

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*Speaker

Non-adiabatic dynamics investigation of $Cr(CO)_4bpy$ photodissociation

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Transition metal complexes with a d-6 electron configuration exhibit rich chemistry and photophysics. They have been extensively studied and used as luminescent probes (eg. $(Ru(bpy)_3)^{2+}$, bpy = bipyridine) and photocatalysts (eg. $W(CO)_6$). A d-6 complex with both carbonyl and an alpha-diimine ligand show simultaneous triplet state emission and ligand-selective photodissociation from MLCT states. Studying this photodissociative mechanism is challenging for experimental approaches due to an ultrafast femtosecond timescale and spectral overlap of multiple photoproducts. Understanding this mechanism on a theoretical level would contribute to the design of better transition metal catalysts and luminescent probes. In this presentation, I'll showcase the theoretical investigation of a prototypical system, $Cr(CO)_4bpy$, with non-adiabatic dynamics simulations. Using the surface hopping method on CASSCF potential energy surfaces, evidence of a ballistic mechanism of photodissociation was observed, which is in contrast to previous experimental interpretation of competitive dissociation and intersystem crossing to emissive states.

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*Speaker

Two-photon vibrational resolved spectra of organic dyes: insights into the role of Herzberg-Teller couplings

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Nowadays, organic dyes with substantial Two-Photon Absorption (TPA) cross sections are widely applied in diverse technological domains, such as optical data storage and bioimaging (1). The growing interest in these dyes stimulated intense theoretical research efforts, focusing on interpreting experimental measurements and rationalizing molecules with significant TPA. Any computational protocol aiming at replicating experimental TPA spectra of organic-conjugated molecules must consider the couplings between electronic and vibrational degrees of freedom. Numerous studies have demonstrated the importance of vibrational coupling within the Condon approximation in TPA spectra of push-pull chromophores. Additionally, more refined non-Condon or Herzberg Teller (HT) corrections have been shown to play a prominent role in modeling the spectra of fluorescent proteins (2). In this study, we utilized density functional theory to compute the vibrational TPA spectra of a series of common fluorescent dyes, along with model chromophores of fluorescent proteins in vacuum. Our analysis aims to offer insights into the role of vibronic coupling in such a diverse range of systems. Furthermore, it explores the possibilities and limitations of various vibronic models based on the harmonic approximation (3) for the computation of TPA spectra.

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Modeling multiple photoinduced electron transfers in covalent donor-photosensitizer-acceptor triads

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Efficient solar energy conversion is a major challenge in relation with climate change, which requires to stop using fossil fuels as primary energy sources. One solution to this problem is the development of solar fuels, among which, dihydrogen can be obtained through water photolysis (1). A key concept in this reaction, which requires the formal exchange of four electrons, is photoinduced electron transfer (PET). While this process is well understood for a single charge separation in donor-photosensitizer-acceptor (**D-PS-A**) triads, systems allowing the separation of two charges are uncommon (2), and no covalent non biological D-PS-A triad able to undergo double PET has been yet reported in the literature. The current challenge and the purpose of our work is to better understand multi-electron processes in these systems. The initial design of covalent molecular triads D-PS-A takes advantage of potential inversion (3), a phenomenon that is observed only with certain types of two-electron donors and acceptors, for which the second redox process is less demanding than the first one, mostly due to structural variations. The photosensitizers used are earth-abundant high-potential molybdenum complexes (4).

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*Speaker

Neural network-based sum-frequency generation spectra of pure and acidified water interfaces with air

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Understanding the acidity of the air-water interface is key for rationalizing many processes of great importance in atmospheric chemistry or microdroplet catalysis. Recent simulations employing neural network potentials (NNPs) trained to reproduce the hybrid DFT level of theory predict that the acidic hydronium cations $H3O^+$ are stabilized at the air-water interface, while the alkaline hydroxide anions HO^-» are repelled (1). Although these simulations agree with the conclusions obtained from Sum-Frequency Generation (SFG) experiments (2), a surface-specific non-linear vibrational spectroscopy, the interpretation of these complex measurements is still highly debated. We have therefore employed a dual neural-network-based strategy to compute SFG spectra of the pure and acidified air-water interfaces at the same level of theory used to probe the surface affinity of water self-ions. First, we employ the same NNPs to obtain several ns-long molecular dynamics (MD) simulations of these two interfacial systems. Then, we train complementary neural-networks able to predict molecular dipoles and polarizability tensors based on the displacements of the Wannier centers associated with each molecule (3). The predictions of these neural-networks on the long NNP-MD configurations are used to obtain converged SFG spectra of the pure and acidified air-water interfaces. Our simulations correctly reproduce the spectral changes induced by acidification on the phase-resolved SFG spectrum of the air-water interface, thus providing a strong validation of our simulation methodology. Decomposing this signal into spatial and molecular contributions yields a detailed interpretation of these spectral changes, which are due to both an electrostatic polarization of deeper layers of water molecules and to low-frequency vibrations of the interface-lying hydronium cations, which had not been previously observed in simulations due to the challenge posed by the reactive proton transfer events (4). The methodology employed in this work can be extended to calculate vibrational spectra of any reactive system in the condensed phase.

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Dynamics of hydrogen interaction on tungsten surfaces: quantum or classical?

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Because of its fundamental role in natural and technological processes, surface reactivity has been intensively studied both experimentally and theoretically for decades. Currently, understanding the microscopic mechanisms in the interaction of hydrogen with the surface of tungsten is a major challenge for nuclear fusion technologies.

With this in mind, we study the collision dynamics of hydrogen on tungsten via classical and quantum molecular dynamics approaches, using a multidimensional Potential Energy Surface (PES) interpolated from Density Functional Theory (DFT) energies based on the vdW-DF2 functional.

We also implement quantum corrections based on semi-classical considerations to reach an agreement between quantum and classical calculations. In particular, we focus on the sticking probability, which has been previously measured experimentally. Preliminary results show a considerable improvement concerning the quantitative agreement between theory and experiment with respect to previous work using the PW91 functional, pointing out the decisive role of the density functional on the sticking dynamics. Existing quantum corrections have also also been refined to reach quantum-like accuracy from classical calculations, which lead to a deeper understanding of the physics underlying the reaction.

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Point defects and diffusion mechanisms in titanium nitrides (TiN and Ti$_2$N) including oxygen insertion

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Titanium alloys are widely used in aerospace applications due to their high specific strength. In environments subject to high thermomechanical stress, titanium alloys can replace steels and nickel-based alloys to reduce aircraft engine weights. However, titanium alloys are limited to temperatures below 600∘C due to insufficient creep (1) and oxidation resistance due to oxygen embrittlement (2). In a previous study, we showed that the presence of tungsten in titanium alloys promotes the formation of a continuous Ti$_2$N-titanium nitride layer below the oxide scale (3). The presence of this layer reduces the oxygen dissolution in the alloy. The observed decrease in oxygen dissolution in the metal may be attributed to the presence of an oxygen diffusion barrier effect exerted by the nitride layer. Alternatively, it may be attributed to a decrease in oxygen solubility resulting from a change in the thermodynamic equilibrium of the metal/oxide interface. A study of oxygen diffusion in titanium nitrides (TiN and Ti$_2$N) was therefore conducted to confirm or refute the first aforementioned hypothesis. A preliminary first-principles investigation into point defects in TiN and Ti$_2$N was undertaken, including the insertion of oxygen (4). This demonstrated that the majority of defects in TiN were consistently nitrogen or titanium vacancies, dependent on the stoichiometry of the nitride. Additionally, the insertion of oxygen invariably substituted the nitrogen. In the case of Ti$_2$N, nitrogen vacancies remain the main defect for Ti$_2$N$_{1-x}$ nitride. However, for the super-stoichiometric nitride, the nitrogen in the interstitial sites becomes the main defect. When oxygen is introduced into the system, it replaces the nitrogen in the sub-stoichiometric nitride. Nevertheless, once stoichiometry is reached, the oxygen is also located in the interstitial site. In the light of these findings, an investigation was conducted into the diffusion mechanisms of the different species (Ti, N and O) in the two titanium nitrides. In both cases, nitrogen diffuses only through nitrogen vacancies and vice versa, thereby demonstrating the independence of the titanium and nitrogen sub-lattices. Diffusion along interstitial sites is also possible; however, in the case of TiN, it has been shown that self-interstitial atoms (SIAs) are not possible. In the Ti$_2$N nitride, a strong anisotropy along the basal plane or the (001) direction has been demonstrated for all three elements.

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*Speaker

Computation of exchange couplings in photogenerated excited states in DFT-KS

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Optically excited states of three-spin molecules have recently attracted much attention to manipulate magnetooptical properties, with possible application in spintronics or quantum technologies. They consist of a stable radical linked to a chromophore, which once excited, creates a three-spin system magnetically coupled. However, unlike exchange couplings in ground states, little is known about them in excited states, and their study is challenging from both experimental and theoretical points of view.

Determination of magnetic exchange couplings usually resorts to DFT with the computation of high spin and broken symmetry determinants, which are ground states of their given spin symmetry. This strategy cannot be directly applied to excited states due to the inherent variational collapse, and the first computations in this context are based on time-consuming wave-function-based methods or Spin Flip TD-DFT.(1,2)

In this communication, I will show how the recently developed decomposition/recomposition method offers an affordable and unequivocal strategy to compute exchange couplings in excited states.(3) This method allows decomposing magnetic exchange couplings in their three main physical contributions, which once summed up, offers a rigorous evaluation of the coupling. (4,5) This strategy is based on a selective relaxation of the orbitals involved in the different mechanisms, and these controlled relaxations prevent the question of variational collapse. The method is applied to study couplings in a series of mono- and diradical-based molecules recently synthesised.(6,7)

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*Speaker

Ni surfaces and nanoparticles functionalized with trimethylphosphine: A DFT study of structure sensibility, magnetization and topological analysis

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Understanding the multiple effects that determine the catalytic performance of materials is a key step towards the rational design of more effective, efficient, and greener catalysts for specific applications. In particular, Ni nanoparticles (NPs) functionalized by phosphyne ligands have shown a significantly better catalytic performance in hydrogenation reactions, however, experimental limitations hinder the our comprehension of catalytic effects of the Ni-phosphyne interactions. Density Functional Theory (DFT) allows the exploration of catalytic systems at the molecular scale, but require a carefull selection of methods and models that properly represent the experimental systems. In this work we studied the adsorption properties of trimetylphosphine (PMe_3) on Ni catalysts. Spin polarized calculations were carried out for clean and adsorbed Ni extended surfaces with (111), (100) and (110) terminations of different sizes to explore coverage effects. These were directly compared with the PMe_3 monoadsorption and self-assembly of a PMe_3 monoshell on NP of five different morphologies (icosahedral, ino-decahedral, cubo-octahedral, truncated octahedral and Marks) with moderate sizes (Ni146–147, around 1.4 Å diameter). PMe_3 adsorption is favorable and appears to be stronger on extended surface models compared to NPs models for a wide range of coverages. Moreover, the combination of covalent and dispersion contributions on PMe_3 covered NPs can not be reproduced by extended surface models. On NPs, the icosahedral morphology appears to be the more stable even after the self assembly of a PMe_3 monoshell. A Quantum theory of Atoms in Molecules (QTAIM) analysis indicates an electronic donation from PMe_3 towards Ni upon formation of the σ Ni–PMe_3 bond, which can be identified from their Electron Localization Function. Counterintuitively, the Ni–PMe_3 bond length decreases with increasing coverage, which also helps reducing the interaction between adsorbates on the NPs. On NPs, Ni magnetization strongly depends on the atomic configuration and is locally affected by the surface adsorption of PMe_3 according to the NP symmetry. Our analysis evidences the differences between the commonly used extended surface models and a nanoparticle approach that is aimed to more closely represent experimentally synthesized NPs. More specifically, this work opens the door to study the reactivity of alkyl and aryl phosphines on Ni catalysts using NP models of moderate sizes.

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*Speaker

Prediction of very large skyrmion stability in monolayer MnSeTe: Interplay between Dzyaloshinskii-Moriya interaction and higher-order exchange interactions

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Magnetic skyrmions in atomically thin van der Waals (vdW) materials provide an ideal playground to push skyrmion technology to the single-layer limit. The Dzyaloshinskii-Moriya interaction (DMI), which prefers canted spins of adjacent magnetic atoms, is often recognized as the key ingredient in forming magnetic skyrmions. However, the role of underlying higher-order exchange interactions (HOI) has been overlooked in 2D magnets. Here, using first-principles calculations combined with atomistic spin simulations, and taking a Janus monolayer as an example, we present a comprehensive study on the interplay between DMI and HOI affecting skyrmion energy barriers (which protect against annihilation) and their collapsing mechanisms. We show that these nanoscale skyrmions have high energy barriers due to strong DMI. Also, we unravel that including HOI along with DMI slightly decreases the energy barriers and alters the collapse mechanisms.

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Study of the microscopic interactions underlying the properties of spin liquids in Kagome lattice of spin 1/2

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Herbertsmithite is a key material in the study of spin liquids. It is characterised by a spin frustration that gives rise to very interesting magnetic properties. The aim of our study, based on ab initio calculations (WFT and DFT), is to determine the magnetic interactions at the origin of these properties. We will focus in particular on extracting the magnetic coupling constant J and the Dzyaloshinskii-Moriya interaction, which is thought to play a crucial role in this type of system.

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Mechanisms of pyrite formation in marine sediments and implications for isotope fractionation in the presence of trace elements

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The elemental and isotopic compositions of sedimentary pyrites provide insights into the chemical evolution and redox state of the oceans over geological timescales. In particular, iron isotope ratios are proxies for the progressive increase in atmospheric oxygen during the Archean and Paleoproterozoic (1). However, the interpretation of the isotopic signatures is subject to large uncertainties arising from the limited understanding of the mechanisms and kinetics of pyrite formation. Notably, the presence of other trace elements has been shown to modify significantly the nucleation and growth of pyrite, and presumably its precursors.

The objective of this work, conducted in tandem with experimental approaches, is to identify the likely mechanisms involved in the growth of sedimentary pyrite and how these are affected by the presence of trace elements, such as nickel and arsenic. To this end, density functional calculations and molecular dynamics will be applied to build an understanding of how sedimentary pyrite is formed. A comprehensive study of the solid iron sulphide phases that might be implicated in these mechanisms, such as mackinawite and greigite as well as amorphous and partially deconstructed structures will tackle the problem from one perspective. A detailed study of iron-sulphide clusters in aqueous solution will identify the likely contributions of these species to the eventual pyrite. The distribution of iron isotopes between the various phases can be determined from fractionation factors based on the contribution to the free energies of the thermodynamic partition functions calculated using linear-response density functional calculations and molecular dynamics.

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*Speaker

Modeling biomimetic calcium phosphates using density functional theory

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Calcium phosphates are the primary inorganic component of biological hard tissues in living organisms, such as bones and teeth where they crystallize in an apatitic structure (1). Calcium phosphates have thus been a key focus in biomaterials research aimed at producing bioactive/bioinspired bone substitutes but also for enhancing the biocompatibility of other medical implants to ensure their osteointegration, thereby improving their functionality and longevity within the body. **In tooth enamel,** the calcium phosphate phase is known to be very close to stoichiometric hydroxyapatite (HAP, $Ca_{10}(PO_4)_2(OH)_2$). However, in bone mineral, the apatite phase is nonstoichiometric, and exhibits very peculiar structural features that significantly differ from those of regular HAP. Indeed, several studies, mainly based on FTIR and ssNMR spectroscopy techniques, have shown that biological apatite nanocrystals (or their synthetic analogs) are constituted by a sub-stoichiometric apatitic core and a non-apatitic hydrated ionic layer on their surface (2-3). This hydrated ionic layer is responsible for the high surface reactivity of bone/biomimetic apatites. Its structure significantly varies from the bulk HAP structure and exhibits an FTIR vibrational response close to – but not strictly identical to – that of another hydrated calcium phosphate phase, namely octacalcium phosphate (OCP, $Ca_8(PO_4)_4(HPO_4)_2 \cdot 5H_2O$, triclinic). OCP was reported to be involved in dental processes and is thought to be an intermediate phase during apatitic precipitation during some biomineralization events (4).

All these compounds, and specially HAP and biomimetic apatites, have been extensively experimentally studied in our laboratory for decades. However, for a better understanding of biomineralization phenomena *in vivo* or for the development of innovative bioactive bone biomaterials, it is important to explore further the surface state of these biologically-relevant calcium phosphates as well as their ability to interact with (bio)molecules and ions of interest in aqueous medium. DFT studies were thus performed in the present work on HAP surfaces with different slab terminations, considering the (010) face of biological relevance: one stoichiometric and two non-stoichiometric (either rich in Ca or in P). By using the chemical potential method and an implicit solvent (water) model, we determined the thermodynamically most stable (010) surface in aqueous environment, *i.e.* the Ca-rich one. To model synthetic biomimetic apatites that mimic bone mineral, more complex models including an apatitic core ($Ca_{16}(PO_4)_{10}(OH)_2$) and a hydrated ionic layer ($Ca_2(HPO_4)_2 \cdot nH2O$) with different amounts of water molecules (n = 3, 5, 7) were then originally developed. The latter layer was built considering an initial compositional

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similarity with the hydrated layer in OCP crystals (5).

The models built for HAP and biomimetic apatites were further used to simulate FTIR spectra: vibrational frequencies were determined using phonons calculations based on the finite differences approach, and their corresponding peak intensities were drawn from the Born charge effective tensor. The good agreement observed between our simulated and experimental spectra is a first validation of the models proposed for HAP and, for the first time, for biomimetic apatites.

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Structural Analysis of the Drosophila Melanogaster's GSTome

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Glutathione transferase (GST) is a superfamily of ubiquitous enzymes, multigenic in numerous organisms which generally presents an homodimeric structures. For instance, GSTs are involved in numerous functions as chemical detoxification as well as chemoperception in mammals and insects. GSTs catalyze the conjugation of their cofactor, the reduced glutathione (GSH) to xenobiotic electrophilic centers. To achieve this catalytic function, GSTs are made of a ligand-binding site and a GSH binding site per subunit. The GSH-binding site (G-site) is very specific and the hydrophobic substrate binding site (H-site) allows the binding of diverse substrates. In addition, the G-site presents a high conservation among GSTs. The chemical diversification in plant during the evolution was probably an important evolutive driver leading to the GSTs diversification, especially in insects. This encourages the study of insect GSTs to understand how spontaneous mutations/insertions/additions in the sequences modify the stability, selectivity, and the catalytic efficiency of this superfamily of enzymes. The Universal Protein Database (UniProt) registers 36 GST sequences in the fly, Drosophila melanogaster's (D. mel), which are distributed in 6 classes and composing its GSTome. GST subunit structures are characterized by a thioredoxin-like fold in its N-terminal part (Domain I) and an helical domain in its C-terminal part (Domain II). Domain I is quite conserved among GSTs and contains specific residues critical for GSH binding and catalytic activity whereas Domain II is quite variable both in sequence and structure, and this diversity determines the ample and distinct hydrophobic substrate specificities observed for the different enzymes. Finally, the interface of dimerization between the two subunits also plays a crucial role in the stability and catalytic activity of GSTs.

The goal of the present work is to study the complete GSTome of D. mel from its 36 sequences and structures to determine how changes in the amino-acid sequence modifies the structural characteristics of GSTs, particularly in the binding sites and in the interface of dimerization. First, we predicted 3-D atomic structures of each GST using the AlphaFold program developed by DeepMind and compared them with existing X-ray crystallography experimental structures (7 over 36 of them have been resolved). We also characterized their global and local fold using secondary structures predictions and free-energy landscape analysis of internal coordinates such as backbone and side-chain dihedral angles. Second, we used Multiple Sequence Alignment (MSA) technique coupled with AlphaFold predicted 3-D structures to characterize the relationship between sequence and structural fingerprints of GST enzymes,. Finally, we applied Normal Mode Analysis using the Anisotropic Network Model to compute the thermal B-factors of all GSTs of D. mel. Particularly, we extracted the flexibility profiles of GST enzymes and identify key residues that are systematically involved in the ligand binding/dimerization processes and thus playing a crucial role in the catalytic function. This methodology will be extended to guide the in silico design of GST enzymes with new/optimal properties for detoxification applications.

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Molecular Electron Density Theory study on the mechanism and selectivity of the 1,3 dipolar cycloaddition reaction of N-methyl-C-(2-furyl) nitrone with activated alkenes

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We have investigated the underlying molecular processes involved in the (3+2) cycloaddition (32CA) reactions between N-methyl-C-(2-furyl) nitrone and three acetylene derivatives: 4b, 5b, and 6b. For this investigation, we utilized molecular electron density theory (MEDT) and density functional theory (DFT) methods at the B3LYP-D3/6 31G (d) computational level. These 32CA reactions, which exhibit a zwitterionic (*zw-type*) nature, proceed through a one-step mechanism with activation enthalpies ranging from 8.80 to 14.37 kcal mol–1 in acetonitrile and ethanol solvents. When the nitrone reacts with phenyl methyl propiolate (4b), two regioisomeric pathways lead to the formation of two products: P1,5-4b and P1,4-4b. On the other hand, when the nitrone reacts with dimethyl acetylene dicarboxylate (5b) and acetylene dicarboxylic acid (but-2-ynedioic acid) (6b), it results in the formation of a single product. Through topological analysis, we can categorize nitrone as a zwitterionic three-atom component (TAC). Furthermore, the analysis of conceptual density functional theory (CDFT) indices classifies the 32CA reactions of the nitrone with 4b, 5b, and 6b as forward electron density flux (FEDF) reactions. The study of bond evolution theory (BET) reveals that the formation of new C-C and C-O covalent bonds does not initiate in the transition states, as the intermediate stages of these reactions display pseudoradical centers of the atoms already involved in bonding.

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Ab initio molecular dynamics calculations on NO oxidation over oxygen functionalized Highly Oriented Pyrolytic Graphite (O-HOPG)

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Nitrogen monoxide (NO) belongs to the group of the most polluting gases in the atmosphere. It serves as a critical precursor for the formation of smog and acid rain, which currently pose significant environmental and human health challenges. Understanding the molecular interactions between NO and models of carbonaceous surfaces is essential for developing effective strategies to mitigate its adverse effects on the environment. We presented here ab initio molecular dynamics (AIMD) calculations on the NO oxidation over oxygen functionalized Highly Oriented Pyrolytic Graphite (O-HOPG) surface. We examined the impact of four different NO incidence energies and two orientations of incidence on the reaction. Our simulation results indicate that the probability of the oxidation reaction (O – HOPG + NO(g) $\rightarrow$ HOPG + NO_2(g)) varies between 10-30 %, depending on these initial conditions. Notably, the reaction occurs even at the lowest incidence energy studied (0.025 eV) which corresponds approximately to room temperature (300 K). The angular distribution of the products and the energy losses during the reaction were also analyzed. The scattered NO molecules (non-reactive channel), loses 50-60 % of their initial translational energy and are vibrationally cold but rotationally excited. The detected NO2 molecules share the same angular distribution as the scattered NO molecules, suggesting a swift and direct reaction dynamic for NO oxidation characterized by effective energy transfer. These findings provide important insights into the reaction mechanism of NO oxidation on activated carbonaceous surfaces, contributing to the potential development of applications to mitigate environmental pollution.

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Theoretical study of NV centers in diamanes

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Recent advances in quantum technologies have led to quantum computers that surpass classical computation limits (1). Transmons, using superconducting loops, are the main qubit technology but require constant cryogenic cooling and have issues with noise sensitivity and scalability (2). An alternative is to use negatively charged NV-centers in diamond lattices (3) (cf. Fig. 1), where replacing a nitrogen atom next to a vacancy creates a two-level quantum system within the band gap, possibly acting as qubits, with transitions between bright and dark exciton states tunable by electromagnetic fields (4, 5). Two-dimensional semiconductors may be even better hosts for NV-centers due to more isolated defects, higher radiative rates, and smaller Bohr effective radii (6, 7).

This work aims at studying theoretically diamanes, a 2D version of diamond built form hydrogenated bi-,tri-layer and few-layers of graphene (8, 9, 10). In last years, several evidence of partial hydrogenation of such systems with a soft approach have been proposed by some of our close collaborators (11, 12). Our first goal is to determine using the first-principle calculations, the different thermal and optical properties of host materials. And in second part how NV-centers behave in them. We report thanks to phonon studies thermal properties such as the thermal expansion, heat capacity and thermal conductivity of various freestanding layers that are shown to be stable thanks to phonon dispersion behavior. Optically, diamanes have direct, wide band gap at the Γ point and shows a decrease of the fundamental gap value as function of graphene layer numbers. Furthermore, the electronic dispersion including NV-centers shows the emergence of different localized states within the band gap at the Γ point, there details will be presented. The nature of strongly bind excitons in such systems will be discussed as well. This project is funded by ANR (through GLADIATOR project) and EUR-NanoX, and supported by CALMIP, GENCI-IDRIS and GENCI-TGCC for computational time.

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Gold fluorocarbenes: Bonding situation and reactivity

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Chemists long neglected gold because it was considered as a noble and therefore chemically inert metal. The interest for gold rose in the late 1990s and gold catalysis is currently undergoing major development. First, gold chemistry was limited to its Lewis acid properties, but the design of chelating (P,P) and hemilabile (P,N) ligands has enabled new reactivities such as oxidative addition, migratory insertion... and opened the way to new unusual bonding situations such as gold(I) carbene complexes (P,P)AuC=R1R2+.

In this work, we further studied this chemistry by considering gold fluorocarbene complexes LnAu=CF2+. As fluorinated compounds find important applications in numerous fields (pharmaceutical, agrochemicals, materials science...), the introduction of fluorine atoms in organic derivatives is of particular interest. Difluorocarbenes are however very reactive, and coordination to gold may enable to tame reactivity and develop synthetically useful transformations.

In collaboration with the team of D. Bourissou, we carried out calculations to help understanding the bonding situation and reactivities of gold(I) fluorocarbene complexes. The bonding studies were carried out using Natural Bond Orbital analysis (NBO) and Energy Decomposition Analysis (EDA) on the two main gold fluorocarbene complexes involving (P,N) and Cy-JohnPhos ligands. Other ligands ((P,P) and monodentate ligands) were also investigated. Special attention was given to the relative contributions of Au→carbene backdonation and F→carbene pi-donation. In presence of alkene and 1,3-dienes, these carbenes undergo unusual reactions, *i.e.* formal (2+2) and (2+4) cycloadditions, respectively. The mechanistic paths possibly accounting for these transformations have been investigated using Density Functional Theory (DFT).

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Atomic surface site interaction point model for non-covalent interaction quantification

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Advances in theoretical chemistry allowed us to discover the equations that describe the electronic structure of the atoms, but also informed us that such accurate calculations are very expensive indeed. To look at larger systems, akin to guest-host and protein-ligand complexes, simplifications need to be introduced which compromise the quality of result, and we ought to carefully consider errors that might henceforth arise. Furthermore, in a drug design campaign the aim is not merely in learning about a single system, but discovery of one with desirable properties, hence we need a reliable way of canvassing chemical space to find a ligand of interest. This process has been entrusted to scoring functions which evaluate the relative stability of complexes formed between ligands and proteins. We have used DFT to develop the Atom Surface Site Interaction Point (AIP) approach (1)(2) to quantify all non-covalent interactions a molecule is capable of making with the environment, i.e. solvent or binding site. When two molecules interact, AIPs that are close in space are paired to calculate the free energy of binding by summing over all pairwise interactions. Each such interaction has an associated electrostatic and dispersion components. The method has been successfully applied to phase transfer energies, hydrogen bonding arrays, host-guest complexes in a variety of solvents by using SSIMPLE solvation energies (3). More recently, we used the CASF-2016 dataset of diverse X-ray protein-ligand structures (4) to develop an AIP scoring function for use in drug discovery. The method is fast and produces interpretable and accurate binding free energies, as well as AIP Interaction Maps that allow interpretation of the key contributions to binding. This knowledge can be used not only to judge promising ligand leads but to design better binding ligands overall.

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Diving into the continuum with resonances

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In quantum chemistry, the Hamiltonian spectrum contains continuum states in addition to the usual bound states. Among those continuum states can be found the so-called "resonances", which are metastable states resembling bound states. However, due to their metastability, resonances have a finite lifetime which makes them differ from the regular bound states and lead to interesting properties. For this reason, resonances are studied in various fields involving electron-molecule collisions, from biochemistry (DNA damage induced by ionizing radiation or the development of radiosensitizers against cancer) to interstellar chemistry (extraterrestrial synthesis of prebiotic molecules). The unbound nature of resonance states creates various theoretical challenges because of the necessity of accounting for the coupling of the bound part of the wave function with the continuum. Several methods have been specifically developed to describe accurately such states and notably their lifetimes. However, at the current stage, one of the state-of-the-art methodologies to describe resonances of medium-sized molecules remains the complex absorbing potential (CAP) technique (which consists in the addition of a complex one-electron potential to the usual Hamiltonian) combined with coupled-cluster with singles and doubles (CCSD). Unfortunately, the resulting errors for resonances are one to two orders of magnitude larger than obtained with state-of-the-art methods for bound states. This aspect underlines the necessity of improving the description of the electronic structure of resonances. Answering this call, we propose to combine the CAP technique with selected configuration interaction (SCI). This choice is motivated by the ability of SCI to provide highly-accurate excitation energies for bound states, allowing to faithfully benchmark more approximate methods. In this contribution, we will give a concise overview of resonance states, the CAP methodology, and the SCI method, before investigating the performances of CAP-SCI and CAP-CCSD on various ubiquitous resonance states.

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Probing Quadratic Response for ESA: From Coupled Cluster to TD-DFT

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During excited-state absorption (ESA), an electronic transition between two excited states (ESs) occurs. ESA is a crucial phenomenon for probing and understanding light-matter interactions. ESA is an essential process in, e.g., organic optoelectronics, such as solar cells or lasers, and optical power limiting devices (1). Accurate and computationally attainable ESA data are thus increasingly sought after. Quadratic-response TD-DFT (QR-TDDFT) is a promising method which can be used to obtain ESA properties at a low computational price (1, 2). Here, we present a dataset of oscillator strengths (f), in three different gauges, and vertical excitation energies of electronic transitions between the ESs of 27 small and medium molecules from the QUEST database (3). The reference values were obtained solely within the quadratic-response CC3 function formalism using a total of 8 Dunning correlation consistent basis sets. This allows to assess the performance of QR-TDDFT performed with both global and range-separated hybrids, as well as of lower-order wave function methods, e.g., CCSD, CC2, and ADC(2).

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Encodings of vibrational model Hamiltonians on a quantum computer

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In contrast to electronic structure, the simulation of the vibrational structure problem with qubit-based quantum computers is still in its infancy and encodings of second-quantized bosonic operators have been only determined recently. Those encodings are not as direct as mapping a spin-orbital occupancy to the state of a qubit (the Jordan-Wigner encoding for the fermionic particles). This is because bosons do not follow the Pauli exclusion principle and bosonic modes are not two-level systems. Hence, mapping a bosonic system on qubits is not straightforward, although some encodings have been developed to overcome this difficulty. Here, we present some of these encodings with their advantages and drawbacks. We illustrate them on systems with one-mode quartic and double-well potentials expressed in a harmonic oscillator basis set. We highlight the crucial importance of the ordering of the second quantization operators, which is a consequence of the basis truncation. However, the difference in the spectrum of Hamiltonians with different orderings is not due to lack of convergence of the eigenvalues, it is an error coming from the disruption of the closure relation. If the proper ordering is not taken into account, the final converged energy obtained from the Variational Quantum Eigensolver (known as VQE) can lead to an artificial wrong eigenvalue.

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