Table of contents

Author Index   **34**

New interpretation of the reduced density matrices

Thierry Deutsch [*]

Modélisation et Exploration des Matériaux – Commissariat à l'énergie atomique et aux énergies alternatives : DRF/IRIG, Université Grenoble Alpes – France

In this talk I give a new interpretation of reduced density matrices based on the set of excitations of a system. The first step is to show that these sets of excitations are isomorphic to wave functions and form a Hilbert space with a new parameterization of two-body reduced density matrices based on a pair of anti-commutation matrices (ACMPs). The interest is that the density matrices are more easily interpretable and do not appear as an array of numbers.

This new formalism allows to reduce, in a second step, the complexity of the conditions of N-representability, and the calculation of the total energy by using a number of parameters of $O(n^4)$. The idea is to consider these excitations as intrinsic degrees of freedom of the system, a bit like energy band diagrams. I will show where I am in the implementation, notably with SDP optimization.

[*]Speaker

Reference energies for cyclobutadiene: Automerization and excited states

Enzo Monino [*][†] [1], Martial Boggio-Pasqua [1], Anthony Scemama [1], Denis Jacquemin [2], Pierre-Francois Loos[‡] [1]

[1] Laboratoire de Chimie et Physique Quantiques (LCPQ) – UMR5626 – France
[2] Chimie Et Interdisciplinarité, Synthèse, Analyse, Modélisation (CEISAM) – UMR 6230 – France

Cyclobutadiene is a well-known playground for theoretical chemists and is particularly suitable to test ground- and excited-state methods. Indeed, due to its high spatial symmetry, especially at the D4h square geometry but also in the D2h rectangular arrangement, the ground and excited states of cyclobutadiene exhibit multi-configurational characters and single-reference methods, such as adiabatic time-dependent density-functional theory (TD-DFT) or equation-of-motion coupled cluster (EOM-CC), are notoriously known to struggle in such situations.

In this work, using a large panel of methods and basis sets, we provide an extensive computational study of the automerization barrier (defined as the difference between the square and rectangular ground-state energies) and the vertical excitation energies at D2h and D4h equilibrium structures. In particular, selected configuration interaction (SCI), multi-reference perturbation theory (CASSCF, CASPT2, and NEVPT2), and coupled-cluster (CCSD, CC3, CCSDT, CC4, and CCSDTQ) calculations are performed. The spin-flip formalism, which is known to provide a qualitatively correct description of these diradical states, is also tested within TD-DFT (combined with numerous exchange-correlation functionals) and the algebraic diagrammatic construction (ADC[2]-s, ADC[2]-x, and ADC[3]) schemes. A theoretical best estimate is defined for the automerization barrier and for each vertical transition energy.

---

[*]Speaker
[†]Corresponding author: enzo.monino@irsamc.ups-tlse.fr
[‡]Corresponding author: loos@irsamc.ups-tlse.fr

Non-adiabatic coupling in trajectory surface hopping: How approximations impact excited-state reaction dynamics

Isabella Merritt [*] , Denis Jacquemin , Morgane Vacher[†]

Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation – Centre National de la Recherche Scientifique : UMR6230 – France

Photochemical reaction dynamics are very often modelled using trajectory surface hopping (TSH), first described in 1971 and extended to more than 2 states in 1990 [1,2]. The fundamental idea behind TSH, illustrated in Figure 1(a), is that fully-quantum wavepacket dynamics through a branching region on potential energy surfaces can be modelled using an ensemble of semi-classical trajectories. The nuclear motion is described classically, on a single potential energy surface at a given time using Newton's equations of motion, while an electronic wavefunction is simultaneously propagated quantum mechanically. At certain times this electronic wavefunction triggers "hops" of the nuclear trajectory from one electronic state to another [3]. TSH has been used to great success, in most cases well-reproducing the correct excited state dynamics at a much lower cost than fully quantum dynamics: since each trajectory is fully independent, an ensemble can be run entirely in parallel, resulting in good affordability.

Despite its relative simplicity, there are in fact a large number of methods which implement TSH differently. In this presentation, I will focus on the usage of different methods to assess the non-adiabatic coupling between the electronic states: this coupling describes the transfer of electronic population between adiabatic states, and as a result guides whether/when trajectories will "hop". In more detail, four different implementations of TSH [1,4,5], outlined in Figure 1(b), have been investigated on a selection of reactions; including photoisomerisation around N=N bonds, and ring-opening reactions. Comparing to "exact" TSH, I will assess three more approximate variants, one of which (Hammes-Schiffer-Tully: biorthonormal wavefunction overlaps) has been developed and implemented in OpenMOLCAS during this work. In particular, I will highlight and rationalize certain test-cases where certain approximations lead to incorrect dynamics, as well as demonstrate the capabilities of our new HST implementation to consistently reproduce reference dynamics at a much-reduced cost.

[1] J. C. Tully and R. K. Preston, *J. Chem. Phys.*, 1971, **55**, 562–572.
[2] J. C. Tully, *J. Chem. Phys.*, 1990, **93**, 1061–1071.
[3] L. M. Ibele and B. F. E. Curchod, *Phys. Chem. Chem. Phys.*, 2020, **22**, 15183–15196
[4] G. Granucci, M. Persico, A. Toniolo, *J. Chem Phys*, 2001, **114**, 10608.
[5] S. Hammes-Schiffer and J. C. Tully, *J. Chem. Phys.*, 1994, **101**, 4657–4667

[*]Speaker
[†]Corresponding author: morgane.vacher@univ-nantes.fr

Poly-epoxy amine polymer surfaces: simulation of XPS spectra and insights in their metallization mechanisms

Fatah Chiter [*†] , Kanika Anand , Jérôme Esvan , Thomas Duguet , Corinne Lacaze-Dufaure[‡]

Centre interuniversitaire de recherche et d'ingénierie des matériaux (CIRIMAT) – Institut National Polytechnique de Toulouse - INPT, CNRS : UMR5085 – France

Metallization of polymer surfaces gives them new properties, e.g. electromagnetic shielding, permeation barrier, electrical conductivity, useful for numerous technological applications. These properties are widely requested in the aeronautical/aerospace industry for the substitution of metallic or ceramic materials. However, the metal-polymer interfaces, and thus surface metallization mechanisms, must be controlled to achieve the desirable properties. Our studies deal with the surfaces of poly-epoxies and the formation of an interface with metals (M = Cu, Al, Co). According to the deposit metals, they can interact strongly with different C, O and N exposed reactive sites on the poly-epoxy polymer surfaces.

Experiment works were combined with computational studies that proposed several numerical models of the pristine and metallized poly-epoxy polymer surfaces. A numerical model close to reality, has been obtained combining classical Molecular Dynamics (MD) calculations on a pre-mix of monomers (DGEBA/EDA) with a polymerization process. From this complex poly-epoxy polymer numerical model and taking structural 'motifs', we also proposed more simplistic molecular models. DFT simulated XPS spectra using the complex model and using the 'motifs' models agreed well with experimental counterpart and validated the computational approaches.

Therefore, the two models, 'motifs' model and extended model, are used to investigate the early stages of polymer surface metallization in terms of adsorption energy of the metal atoms and clustering. We studied the adsorption of one to several metal atoms to investigate their wetting or clustering properties after deposition. A clustering behavior was observed for Cu, Al and Co, however the reaction mechanisms depend on the adsorbed metal and the size of the formed cluster. Simulated and experimental XPS spectra again compared well. These results complement our previous works based on the adsorption of metal atoms on a dimer model for Cu [1,2] and Al [3].

We combined in these studies experimental and theoretical approaches to analyze metal/polymer interfaces, by employing atomistic models at different scales, thereby promoting understanding of early stage metallization of polymeric surfaces.

[1] T. Duguet, et al., J. Phys. Chem. C, 2019, 123, 30917. [2] A. Gavrielides, et al., J. Chem. Phys., 145 (2016) 074703. [3] K. Anand, et al., ACS Appl. Mater. Interf. 2020, 12, 19616.

[*]Speaker
[†]Corresponding author: fatah.chiter@toulouse-inp.fr
[‡]Corresponding author: corinne.dufaure@ensiacet.fr

Computational characterization of the non-linear optical properties in solution and preliminary analysis in cluster of molecular photoswitches

Angela Dellai *

Université de Bordeaux – Institut des Sciences Moléculaires, The French National Centre for Scientific Research, Bordeaux, France – France

Molecular photoswitches have been widely studied in the development of optoelectronics and photonics, as in optical memories. Exploiting the non-linear optical (NLO) response of the molecules in the reading process, in particular second harmonic generation (SHG) allows the utilization of near infrared wavelength confering a non-destructive readout process. Two families of photochromic compounds have been investigated from a computational viewpoint. Those are the well known Azobenzene derivatives and a new class, the so-called donor-acceptor Stenhouse adducts (DASA), first synthesized in 2014. Azobenzene derivatives stands as the most commonly used for surface functionalization, while for DASA it has never been reported so far and their interest extends by virtue of their reverse photochromism. The alteration of the π-electron conjugation within the molecules provoked by the photoisomerization induces a significant change in the NLO response between the two forms. That finds potential application in photoresponsive NLO material and device.

A first study concerns the simulation of the optical properties in solution of a series of Azobenzene and DASA compounds which differ by substitution patterns, in particular playing with electron donor (D) and acceptor (A) units strength, in order to capture structure-to-properties relationship. The calculations are carried out with time dependent density functional theory (TD-DFT) in chloroform simulated with the Polarizable continuum model. The theoretical results are validated by the good agreement with experimental data and the SHG responses of the harmonophoric forms are rationalized by the two-state approximation (TSA).

As a first step toward the simulation of photoresponsive NLO surfaces, which is the perspective of the project, we have characterized clusters of azobenzene functionalized with alkyl chains. The impact of intermolecular interactions on the NLO has been investigated by calculating the SHG of clusters of increasing size, extracted from previously reported MD trajectories, with particular interest in the contrast in the first hyperpolarizability. In order to characterize such large systems, a new and simplified method, the so-called sTD-DFT has been utilized. Its interest is the possibility to treat at a quantum level the entire system.

---

*Speaker

Understanding the conformational flexibility of large aromatic ligands of organolanthanides

Valeriu Cemortan * [1], Grégory Nocton [2], Carine Clavaguéra[†] [1]

[1] Institut de Chimie Physique – Université Paris-Saclay, Institut de Chimie Physique, UMR 8000 CNRS, Paris, France – France
[2] Laboratoire de chimie moléculaire – Centre National de la Recherche Scientifique : UMR9168, Ecole Polytechnique, Institut Polytechnique de Paris, Centre National de la Recherche Scientifique : UMR9168 – France

The organometallic chemistry of lanthanides has long been dominated by the use of the classical aromatic 5-membered monoanionic cyclopentadienyl (Cp^-) ligand and the dianionic, larger cyclooctatetraenyl (COT^{2-}), as well as their derivatives.Our group has helped expand the family organolanthanide complexes featuring large aromatic ligands using the monoanionic 9-membered cyclononatetraenyl (Cnt) ligand.

Of particular interest is the different coordination modes that the Cnt affords. Depending on the coordination environment and the lanthanide ion, anything from a full $\eta 9$ coordination pattern in linear sandwich complexes to more bent structures, where fewer C atoms interact with the lanthanide, can be observed (Figure 1). *Ab initio* molecular dynamics (AIMD) simulations were performed at the DFT/PBE/zora-def2-TZVP level of theory, using a scalar relativistic ZORA Hamiltonian, to understand the dynamic behaviour of the ligand and to explain the variety of coordination modes that are observed.

Individual snapshots, displaying different coordination modes, are recovered from the AIMD runs and are examined (mainly at the DFT and CASSCF level) to investigate whether the strength of the interaction between metal and ligand, the orbital interaction and the aromaticity of the Cnt ligand are modulated by the hapticity. Further work will include topological analyses and Energy Decomposition Analyses to better gauge the interaction between the lanthanide and the Cnt ligand.

*Speaker
[†]Corresponding author: carine.clavaguera@universite-paris-saclay.fr

Atomic scale simulation of intricate aluminosilicate catalysts: Structural and mechanistic sources of complexity

Céline Chizallet *

Catalysis, biocatalysis and separation division – IFP Energies Nouvelles – France

Heterogeneous catalysis is linked to industrial considerations from its origins, so is computational heterogeneous catalysis. The impact of first principles calculations on discoveries made for industrially relevant systems is growing year after year. The present talk will discuss and illustrate these various stages of the catalyst understanding and performance prediction where computational catalysis has a crucial role to play, with a focus on the simulation of complex zeolite catalysts of industrial relevance. Most calculations discussed were performed in the framework of the periodic density functional theory (DFT). Comparison with experimental spectroscopic or catalytic feature is key to get advance knowledge and to validate the prediction procedures, making use of micro-kinetic models based on DFT calculations.

Regarding zeolite catalysts in their proton exchanged form, several challenges needs to be addressed. First, most of the time, the location of the acid site in the framework is unknown. DFT investigation of the respective reactivities of each kind of site is fruitful to locate the most active sites, which we will illustrate in the case of ethylcyclohexane hydroisomerization by a bifunctional catalyst, with the EU-1 zeolite as the zeolite phase. Static approaches are insufficient to capture the good order of magnitude for the rate constants of elementary steps in large pores zeolites, as we will show in the case of the hydroconversion of n-heptane. But once accurate enough rate constants are obtained, microkinetic models can be built, based on the findings from first principles calculations, with a satisfactory prediction ability. However, taking into account the reactivity of the bulk sites only may not be representative enough of the real catalyst, for which efforts need to be dedicated in terms of simulation of defects, external surfaces, and interaction with additives present in the course of the preparation and shaping of the catalyst.

Future directions will also be suggested, based on the need for ever more exhaustive and accurate models of catalytic sites and catalytic reactions representative of industrial systems, and for speed up in catalyst understanding and discovery.

---

*Speaker

Isomerization and cracking of alkenes catalyzed by zeolites: From ab initio molecular dynamics to machine learning perturbation theory

Jérôme Rey * , Céline Chizallet [1], Pascal Raybaud [2], Mauricio Chagas Da Silva [3], Dario Rocca [4], Michael Badawi† [3], Tomas Bucko‡ [5]

[1] Catalysis, biocatalysis and separation division – IFP Energies Nouvelles – France
[2] IFP Energies nouvelles (IFPEN) – IFP Energies Nouvelles, Solaize, France – France
[3] Laboratoire de Physique et Chimie Théoriques (LPCT) – Institut de Chimie du CNRS, Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique – Boulevard des Aiguillettes - B.P. 70239 F-54506 Vandoeuvre-les-Nancy, France
[4] Laboratoire CRM2 – Université de Lorraine, CNRS : UMR7036 – France
[5] Comenius University – Bratislava, Slovakia

Cracking and isomerization reactions via cationic intermediates are building blocks of many chemical transformations for valorization of long chain paraffins coming from plastic waste, vegetable oils, Fischer-Tropsch process or crude oils.

We have performed the first characterization of the transition state of a type B1 cracking reaction (from secondary to tertiary cations), starting from C7 alkenes in acidic chabazite at T = 500 K by enhanced ab initio molecular dynamics, at the PBE+D2 level of theory. A free energy barrier of $\Delta A = 60.1$ kJ/mol was found, starting from a π-complex (the relevant kinetic intermediate) [1]. The complexity of the system may require more accurate levels of theory that are computationally more expensive. Higher levels of theory have been made affordable by the application of Machine Learning Perturbation Theory (MLPT)[2,3] which make possible the first calculation of a free energy barrier at the RPA level of theory.

Low variations of the free energy barrier are found for GGA functionals while the barrier computed at the RPA level is in excellent agreement with the experimental one [4] (Fig 1.b). Current efforts are devoted to the investigation of the effect of the level of theory for isomerization reaction barriers.

[1] Rey, Bignaud, Raybaud, Bučko, Chizallet, Angew. Chem. Int. Ed. 2020, 59 (43), 18938–18942.
[2] Chehaibou, Badawi, Bucko, Bazhirov, Rocca, J. Chem. Theory Comput, 15, 6333-6342 (2019)
[3] Bučko, Gešvandtnerova, Rocca, J. Chem. Theory Comput, 16, 6049–6060 (2020)
[4] Schweitzer, Rey et al, *ACS Catal,* **2022**, 12, 1068–1081.

---

*Speaker
†Corresponding author: michael.badawi@univ-lorraine.fr
‡Corresponding author: tomas.bucko@uniba.sk

Why silver zeolites are efficient for radioiodine capture ? A mechanistic description by ab initio molecular dynamics

Michael Badawi * [1], Tomas Bucko [2], Siwar Chibani [1], Laurent Cantrel [3]

[1] Laboratoire de Physique et Chimie Théoriques – Institut de Chimie du CNRS, Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique – France
[2] Comenius University in Bratislava – Slovakia
[3] Institut de Radioprotection et de Sûreté Nucléaire (IRSN) – Institut de Radioprotection et de Sûreté Nucléaire (IRSN) – CE Cadarache – Bât 328 – 13115 Saint-Paul-lèz-Durance, France

The radioactive iodine species belong to the most dangerous components of nuclear effluents and waste produced in nuclear facilities and this fact motivates a significant effort in development of technologies for their efficient trapping in case of severe accident. In this work we performed theoretical simulation at the periodic DFT level [1] to investigate dissociative adsorption of iodomethane on silver exchanged mordenite, which is among the most effective sorbents of iodine species available as of today [2,3]. The structural models for the Ag-MOR have been selected on the basis of systematic analysis of energetics of diverse Ag sites [4]. The structure, energetics, and mobility of complexes Ag-(CH3I)n formed upon adsorption of iodomethane on Ag+ sites are investigated using the molecular dynamics approach (MD). The free-energy profiles for the reaction CH3I + Ag-MOR → AgI + CH3-MOR are determined using MD bluemoon ensemble technique [5] and compared with the results of static approach. The AgI species formed as a product of dissociative absorption are shown to combine spontaneously into small clusters (AgI)m with the size and geometry restricted by the size of confining void. The geometry and energetics of the (AgI)m species are analyzed in detail and our findings are shown to agree well with the available experimental results [3,6]. The internal energy of formation of clusters in mordenite is shown to contribute significantly to the shift of equilibrium from the undissociated to dissociated form of adsorbed CH_3I. The influence of the Ag content on the mechanism of dissociative adsorption is also discussed [6].

[1] T. Bučko, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, *Phys. Chem. Chem. Phys.* **19**, 27530 (2017).
[2] K.W. Chapman, P.J. Chupas, T.M. Nenoff, *J. Am. Chem. Soc.* **132**, 8897 (2010)
[3] T. Ayadi, M. Badawi, L. Cantrel, S. Lebègue, *Molecular Systems Design and Engineering* **7**, 422 (2022)
[4] S. Chibani, M. Chebbi, S. Lebègue, T. Bučko, M. Badawi, *J. Chem. Phys.* **144**, 244705 (2016).
[5] T. Bučko, *J. Phys.: Condens. Matter* **20**, 064211 (2008).
[6] T. M. Nenoff, M.A. Rodriguez, N.R. Soelberg, K.W. Chapman, *Micropor. Mesopor. Mater.* **200**, 297 (2014).
[7] S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Phys. Chem. Chem. Phys.* **18**, 25574 (2016).

*Speaker

Critical comparison of molecular dynamics simulations of amorphous metal–organic frameworks

Nicolas Castel * [1,2], François-Xavier Coudert[†] [1]

[1] Institut de Recherche de Chimie Paris (IRCP) – CNRS : UMR8247, Chimie ParisTech, Paris Sciences et Lettres (PSL) – France
[2] École des Ponts ParisTech – Ministère de la Transition écologique et de la Cohésion des territoires – France

There is an increasing interest in the amorphous states of metal-organic frameworks (MOFs), which can be produced by various routes (under the application of pressure, temperature, etc). Amorphous MOFs can exhibit useful physical and chemical properties, distinct from those achievable in the crystalline states, along with greater ease of processing, and intrinsic advantages over crystals and powders, such as high transparency and mechanical robustness. However, these amorphous states are particularly challenging to characterise, and the determination of their framework structure at the microscopic scale is difficult, with only indirect structural information available from diffraction experiments. As of today, an array of methods coexists to model these disordered materials, with a lack of direct and in-depth comparison in the existing literature.

One strategy consists in simulating the phase transition from a crystalline MOF to the amorphous state using molecular dynamics (MD). While ab initio MD has successfully been used to model the melting of MOFs and their liquid phases, its significant computational cost has limited its use to small systems on rather short time scales (tens to hundreds of ps), calling for the development of more computationally tractable approaches. Classical MD simulations, routinely used for crystalline MOFs, are not a straightforward option as they are unable to simulate bond breaking or reformation, two processes inherent to the formation of most amorphous MOFs. ReaxFF reactive force fields have been proposed in several studies to generate models of MOF glasses by melt-quenching.

In our work, we have compared the existing methodologies to generate and study amorphous MOFs, with an interest in methods more economical than ab initio. In particular, we have critically investigated the use of ReaxFF, highlighting its extreme sensitivity and showing that the glass models it generates are markedly different from their ab initio counterparts. Finally, we demonstrated the possibilities offered by each MD scheme to compute several mechanical properties of interest, contrasting the results, and highlighting the challenges.

---

[*]Speaker
[†]Corresponding author: fx.coudert@chimieparistech.psl.eu

Trapping properties of iodine in actinide oxides: a DFT+U study

Mathieu Gascoin * [1], Vincent Klosek [1], Michel Freyss [1], Ibrahim Cheik Njifon [2]

[1] CEA, DES, IRESNE, DEC, Cadarache – Centre de recherche du Commissariat à l'Energie Atomique - CEA Cadarache (Saint Paul-lez-Durance, France) – France
[2] Canadian Nuclear Laboratories, Chalk River Laboratories – Canada

UO_2 and $(U,Pu)O_2$ actinide oxides are the most used nuclear fuels. Under irradiation in a reactor, new elements are created in these materials due to the fission of uranium and plutonium atoms. Some of these fission products, especially iodine, caesium and tellurium may chemically react together to form compounds which can be corrosive to the cladding that contains the fuel pellets. In accidental conditions, the release of these corrosive species towards the cladding may lead to its failure, induced by stress corrosion cracking, and subsequently to a contamination of the primary circuit by radioactive elements such as iodine 131 or caesium 137.

In order to improve the safety and performance of reactors, a line of research aims at avoiding the cladding corrosion by preventing the formation and migration of corrosive species within the fuel. In this context, it is necessary to prior determine the most stable chemical forms of iodine, caesium and tellurium in the fuel as well as the trapping and mobility mechanisms of these elements in the actinide oxides.

We perform electronic structure calculations, using a combination of the Hubbard-corrected density functional theory (GGA+U) with X-ray absorption spectra simulations (using the FDMNES code [1]), to evaluate the preferred location of I and I_2 in UO_2 and $(U,Pu)O_2$ crystals. To that aim, we determine the stability of I and I_2 in various point defects, followed by the computation of their XANES spectra in each considered defect. The comparison of the computed spectra with the experimental spectra contributes not only to the identification of the chemical forms of iodine in UO2 and $(U,Pu)O_2$, but also of the corresponding trapping sites for these species. This approach had already been successfully applied to Kr [2] and Xe [3] in UO_2.

The use of a Hubbard term (GGA+U) allows us to take into account the strong correlations of actinide 5f electrons. To avoid the metastable states inherent to this method, we use the occupation matrix control (OMC) procedure [4], which also allows us to control the valences of each species in the simulation. This particular point makes our approach extremely reliable with respect to the determination of iodine incorporation energies in the various studied defects.

---

*Speaker

Computation of vibrational circular dichroism in the periodic gauge

Sascha Jähnigen *† [1], Rodolphe Vuilleumier‡ [1], Anne Zehnacker-Rentien [2]

[1] Processus d'Activation Sélective par Transfert d'Energie Uni-électronique ou Radiatif (UMR 8640) – École normale supérieure - Paris, Sorbonne Université, Centre National de la Recherche Scientifique
[2] Institut des Sciences Moléculaires d'Orsay (ISMO) – Université Paris-Sud - Paris 11, Centre National de la Recherche Scientifique : UMR8214

Vibrational Circular Dichroism (VCD) is the chiral form of IR absorption spectroscopy and an important analytical tool to study absolute configurations of chiral systems. Being bound to vibrational transitions, it delivers very rich spectra that also contain information of how a molecule interacts with its environment. In this context, VCD measured in solid-state is becoming ever more popular in academic research as well as in pharmaceutical industry, because the resulting spectra can not only be deployed to determine absolute configurations of molecules, but also the absolute structure of the entire chiral crystal and polymorph. Furthermore, it circumvents the necessity of substrate solubility and is therefore easily accessible experimentally.[1] In order to interpret VCD spectra, accurate computations are required, but, unlike conventional IR absorption spectroscopy, they cannot be attained within the Born-Oppenheimer approximation. This is because VCD needs the magnetic response of electrons bound to the nuclear motion (*i.e.*, vibrations). Nowadays, these properties are obtained *via* quantum linear response theory and have become in the last decades standard features of many quantum chemistry codes.

However, the magnetic dipole moment is a pseudovector and its magnitude depends on a reference origin. Solid-state VCD has therefore long been considered unfeasible due to periodic boundaries imposed by the crystal structure. Under these conditions, the positions of atoms or molecules, required for the calculation of non-local VCD, are only defined modulo the lattice constant, which unavoidably leads to jumps of the induced magnetic dipole moment. Disregarding periodic boundaries, in turn, would only yield boundary effects that are too significant to be ignored. Consequentially, non-local VCD resulting from a true bulk crystal system has long been inaccessible computationally.

This contribution discusses the computation of solid-state VCD and points out the limitations of the conventional theoretical framework used for the definition of VCD in solution or gas phase. We show that it is possible to formulate VCD with an explicit account for periodicity, which re-connects the theoretical model to the (finite) physical system. [2] Several applications are presented together with the general workflow to obtain a solid-state VCD spectrum from computed molecular properties, for which we employ our python package ChirPy.[3]

[1] Jähnigen, S.; Scherrer, A., Vuilleumier, R., Sebastiani D. *Angew. Chem. Int. Ed.* **2018** *57*, 13344-13348. [2] Jähnigen, S.; Zehnacker, A.; Vuilleumier, R. *J. Phys. Chem. Lett.* **2021** *12*, 7213-7220. [3] Jähnigen, S.; *ChirPy*; Zenodo **2022** https://doi.org/10.5281/zenodo.4775330.

---

*Speaker
†Corresponding author: sascha.jahnigen@ens.psl.eu
‡Corresponding author: rodolphe.vuilleumier@ens.psl.eu

A selected configuration interaction study of ground- and excited-state dipole moments and oscillator strengths

Yann Damour [*][†] [1], Michel Caffarel [1], Denis Jacquemin [2], Fabris Kossoski [1], Anthony Scemama [1], Pierre-Francois Loos[‡] [1]

[1] Laboratoire de Chimie et Physique Quantiques – Institut de Chimie du CNRS – France
[2] Laboratoire CEISAM – Université de Nantes – France

In UV/Vis spectroscopy, the dipole moments, the transition dipole moments and oscillator strengths are valuable quantities that allow to have a better understanding of the underlying excitation processes. However, from a computational point of view, obtaining accurate values of such one-electron properties is very challenging, since they highly depend on the basis set, the underlying formalism, and also the gauge in the case of oscillator strengths [1]. The usual way to compute these properties is to rely on high-order linear-response (LR) or equation-of-motion (EOM) coupled-cluster (CC) calculations. Furthermore, obtaining near complete basis set limit (CBS) values requires calculations with an increasing number of one-electron basis functions. As a consequence of the computational cost of high-order CC methods, like CCSDTQ, the calculations in large basis sets can only be done with low-order CC methods, like CCSD or CC2. Unfortunately, these latter methods generally provide results with a non-negligible difference compared with CCSDTQ [2]. Thus, even if CCSD is generally taken as reference to benchmark cheaper computational methods (like time-dependent density-functional theory for example)[3], it is not always the best option since it inherently carries an error. In the present poster, we investigate the range of applicability of a selected configuration interaction (SCI) method known as CIPSI [4,5] for the computation of near full CI quality ground- and excited-state dipole moments and oscillator strengths.

[1] Chrayteh, A.; Blondel, A.; Loos, P.-F.; Jacquemin, D., *J. Chem. Theory Comput.* **2021**, *17*, 416–438. [2] Sarkar, R.; Boggio-Pasqua, M.; Loos, P.-F.; Jacquemin, D., *J. Chem. Theory Comput.* **2021**, *17*, 1117–1132. [3] Hait, D.; Head-Gordon, M., *J. Chem. Theory Comput.* **2018**, *14*, 1969–1981. [4] Giner, E.; Traore, D.; Pradines, B.; Toulouse, J., *J. Chem. Phys.* **2021**, *155*, 044109. [5] Garniron, Y.; Applencourt, T.; Gasperich, K.; Benali, A.; Ferté, A.; Paquier, J.; Pradines, B.; Assaraf, R.; Reinhardt, P.; Toulouse, J.; Barbaresco, P.; Renon, N.; David, G.; Malrieu, J.-P.; Veril, M.; Caffarel, M.; Loos, P.-F.; Giner, E.; Scemama, A., *J. Chem. Theory Comput.* **2019**, *15*, 3591.

[*]Speaker
[†]Corresponding author: ydamour@irsamc.ups-tlse.fr
[‡]Corresponding author: pierrefrancois.loos@gmail.com

Theoretical study of the vibrational energy redistribution in CO and CO:N$_2$ aggregates

Samuel Del Fré [*] , Alejandro Rivero Santamaria[†] , Céline Toubin[‡] , Denis Duflot[§] , Maurice Monnerville[¶]

Laboratoire de Physique des Lasers, Atomes et Molécules – Université de Lille, Centre National de la Recherche Scientifique : UMR8523 – France

In the coldest regions ($\sim$10 K) of the interstellar medium (ISM), most molecular species apart from H$_2$ accrete on dust grains to form ice mantles, acting as particularly rich molecular reservoirs. Nevertheless, large amounts of gas phase species are also detected in these regions and their existence can be explained by desorption processes at the ice surface. Among these processes, the desorption induced by UV radiations, known as UV photodesorption, has been the subject of several experimental studies on different compounds, such as CO, the second most abundant species in the interstellar medium. It has been shown that the UV photodesorption in pure CO and mixed CO:N$_2$ ices follows an indirect "Desorption Induced by Electronic Transition" (DIET) mechanism. In this astrochemical context, the theoretical work presented here aims to understand, at the molecular level, the vibrational energy redistribution mechanism in pure CO and binary CO:N$_2$ ices. The chosen approach is the molecular dynamics one, either ab initio (AIMD) with the VASP software or based on classical force fields. In particular, the focus is on the end of the DIET mechanism where the electronic energy of the excited molecule, redistributed on some high vibrational states of its electronic ground state, is transferred to neighbouring molecules inducing or not a desorption. To do this, an aggregate approach is used to model the amorphous structure of the simulated ice. These aggregates, initially created, optimised, and then thermalised at temperatures similar to those of the ISM, are then used in molecular dynamics simulations in which a randomly selected CO or N2 molecule is excited at given vibrational levels. The energy redistribution in translational, rotational, and vibrational modes taking place in the aggregate, after a single molecule vibrational excitation, is analysed and compared for the two molecular dynamics approaches used in this study.

---

[*]Speaker

[†]Corresponding author: alejandro.rivero@univ-lille.fr

[‡]Corresponding author: celine.toubin@univ-lille.fr

[§]Corresponding author: denis.duflot@univ-lille.fr

[¶]Corresponding author: maurice.monnerville@univ-lille.fr

Ultrafast calculation of solvation in supercritical CO$_2$ with classical DFT

Antoine Carof * [1], Mohamed Houssein [1], Francesca Ingrosso [1], Daniel Borgis [2], Luc Belloni [3]

[1] Laboratoire de Physique et Chimie Théoriques – Institut de Chimie du CNRS, Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique – France
[2] Maison de la Simulation – Université de Versailles Saint-Quentin-en-Yvelines, Institut National de Recherche en Informatique et en Automatique, Commissariat à l'énergie atomique et aux énergies alternatives, Université Paris-Saclay, Centre National de la Recherche Scientifique : UAR3441 – France
[3] Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire – Nanosciences et Innovation pour les Matériaux, la Biomédecine et lÉnergie (ex SIS2M) – France

Supercritical CO$_2$ is a powerful solvent for different industrial applications. The supercriticality permits to precisely control the solubility and the density by small variations of pressure and temperature, which allows to develop efficient extraction of organic molecules, impregnation of polymer matrices for medical applications, and synthesis of nanoparticles [1]. Supercritical CO$_2$ is also an environmental-friendly solvent: it is abundant, non-toxic, non-flammable, and accessible at mild thermodynamical conditions. To increase its solvation power, supercritical CO$_2$ is often used with a polar co-solvent (e.g., water, acetone, or methanol).

The development of new industrial processes requires to know accurately the solvation properties (free energy, enthalpy, partial molar volume and structure). These properties depend on numerous factors: fraction of co-solvent, nature of the solute, pressure, and temperature. To determine solvation properties, the current methods are experiments, molecular simulations, and parametric approach. Both experiments and molecular simulations provide accurate estimation of the solvation properties but remain too costly (in term of human resources and time) to explore an extensive range of thermodynamical conditions, co-solvent fractions, and families of solute [2]. Industrial companies usually rely on the parametric methods, where solubility data for each solute are fitted on empirical equations, obtained from equation of state or from crude description of the microscopic solvation. Although these parametric approaches are relatively accurate, they need a new fit for each solute and each co-solvent fractions – they cannot be used to predict the solubility.

We propose a new strategy based on classical density functional theory (cDFT). cDFT is an analogue of the well-known electronic DFT, where the solvation free energy is minimized in function of the solvent density around the solute. Contrary to molecular dynamics simulations, cDFT only focuses on a small subset of solvation properties that permits it to be very efficient - at least 4 orders of magnitude faster! We face three challenges for the development of a cDFT in supercritical CO$_2$: (i) building a temperature and pressure dependent functional, (ii) including the molecular nature of CO$_2$ and (iii) incorporating the large density fluctuations near the critical point. We developed a new functional in the near critical region using classical molecular dynamics simulation of bulk supercritical CO$_2$ [3]. Using this functional, our first results show a particularly good agreement between molecular dynamics simulation and cDFT for several simple and molecular solutes in supercritical CO$_2$.

[1] A. Eckert, B. Knutson, et P. Devenedetti, *Nature* 383 (1996) 313-318. [2] F. Ingrosso, et M. Ruiz-Lopez *ChemPhysChem* 18 (2017) 2560-2572. [3] S. Luukkonen, M. Levesque, L. Belloni, et D. Borgis *J. Chem. Phys.* 152 (2020) 064110.

---

*Speaker

Simulating the birth of a cellular organelle: Molecular mechanism of lipid droplet budding

Vincent Nieto [1], Jackson Crowley [1], Luca Monticelli *†[1]

[1] Molecular Microbiology and Structural Biochemistry – Centre National de la Recherche Scientifique - CNRS, Université Claude Bernard - Lyon I (UCBL) – France

Lipid droplets (LDs) are organelles regulating lipid storage and metabolism in cells. LD biogenesis takes place mostly in the endoplasmic reticulum (ER), and starts with the synthesis of neutral lipids, such as triglycerides. When the concentration of neutral lipids reaches a certain threshold, oil droplets form by phase-separation, yielding a lens-shaped nascent lipid droplet – a process known as nucleation. As more neutral lipids are synthesized, the lens grows and eventually buds out of the ER membrane, generally towards the cytosol, at sites marked by a specific protein named seipin. Several open questions remain regarding the mechanism of LD budding, because the initial steps of LD biogenesis are extremely difficult to observe experimentally. Notably, the roles of ER topology, leaflet asymmetry, and membrane composition in the budding mechanism are substantially unknown. Here we present a new, simple methodology allowing to simulate the generation of lipid droplets in membranes mimicking the topology and composition of the ER, and explore possible mechanisms of LD budding. Molecular dynamics simulations at the coarse-grained level are performed out of equilibrium, as in real life experiments. First, we build ER tubular membranes with realistic size and different compositions, including a realistic ER composition, then we progressively increase the number of triglyceride molecules in the system to mimic the effect of triglyceride synthesis and induce budding. We explore different possibilities for the driving forces of the budding process, including LD volume and ER leaflet asymmetry, and observe LD budding with different mechanisms depending on the specific conditions imposed on the system. The simulations allow us to make prediction on the role of seipin, the localization of phospholipid synthesis, and the stability of the ER-LD connection. Our methodology pushes the limit of biological simulations allowing, for the first time, simulations of organelle biogenesis.

---

*Speaker
†Corresponding author: luca.monticelli@inserm.fr

In vivo stability of 211At-radiopharmaceuticals: On the impact of halogen bond formation

Thibault Yssartier * [1,2], Nicolas Galland† [1], Jean-Yves Le Questel [1], Gilles Montavon [2]

[1] Laboratoire CEISAM – CNRS : UMR6230, Nantes Université – France
[2] Laboratoire SUBATECH – CNRS : UMR6457, IMT Atlantique, Nantes Université – France

Astatine (At), Z=85, is both the heaviest halogen element (below iodine) and a radioelement. The At-211 radioisotope is particularly promising for applications in nuclear medicine, owing to (i) its short half-time period, 7.2 hours, and (ii) the high energy of its emitted alpha-particles.[1] However, ^{211}At must be guided towards cancerous cells through its binding to carrier-targeting agents: ^{211}At is labelled on an organic molecule which is then coupled to a biomolecule. Until now, most labelling protocols rely on the formation of an Caryl–At bond with prosthetic groups as in N-succinimidylastatobenzoate (SAB) and in N-succinimidylastatoguanidinomethylbenzoate (SAGMB). However, this bond type in SAB presents an insufficient *in vivo* stability, leading to the SAB degradation. In contrast, SAGMB has been shown to be suitable for *in vivo* applications. In order to develop more effective labeling strategies, the understanding of these different behaviors is mandatory.[1] In case of iodinated aryls, an *in vivo* deiodination mechanism of Caryl–I bonds has been previously identified, which is initiated by a halogen bond (XB) formation.[2] Since astatine is the strongest XB donor atom,[3] we propose to investigate the possibility of a similar dehalogenation mechanism for SAB.

Because At is the rarest natural element on Earth, spectroscopic tools are not enough sensitive to characterize its compounds and molecular modeling is very helpful for such studies. Two-component relativistic DFT calculations were therefore performed on model systems. On one hand, astatobenzene (At–Ph) mimics the SAB, *i.e.* the XB donor, and, on the other hand, fragments of amino acids have been selected as basic components of protein receptors (XB acceptors). The B3LYP hybrid and the PW6B95 meta-hybrid GGA functionals have both been used and associated to the dhf-TZVPD-2c basis set. These levels of theory have been previously demonstrated to be accurate for studying At-mediated XBs.[4]

The increase of the XB interaction energy according to the nature of the amino acid (AA) sites notably leads to a lengthening of the At–Caryl bond, which might correspond to a first step in the possible dehalogenation mechanism. Such results underline the significance of XBs involving anionic groups of AA residues. Focusing on the second step of the mechanism, ruled by the nucleophilic character of the C atom bearing the halogen, we computed some reactivity descriptors. The natural charges and condensed dual descriptor values confirmed the significance of the anionic AAs, *i.e.* aspartate and selenocysteine. A further thermodynamic analysis helped to decipher that among the two, selenocysteine might be the key contributor in the SAB deastatination process. The study for SAGMB shows that XB interactions with the selenocysteine residue are unlikely to happen. This result goes along with the hypothesis that XB-mediated interactions might cause the Caryl–At bond breaking in At-labelled radiopharmaceuticals.

[1] F. Guérard, C. Maingueneau, L. Liu, R. Eychenne, J.-F. Gestin, G. Montavon, N. Galland, *Acc. Chem. Res.* 54 (2021), 3264–3275. [2] C. A. Bayse, E. R. Rafferty, *Inorg. Chem.* 49 (2010) 5365–5367. [3] N. Guo, R. Maurice, D. Teze, J. Graton, J. Champion, G. Montavon, N. Galland, *Nat. Chem.* 10 (2018) 428–434. [4] L. Liu, S. Rahali, R. Maurice, C. Gomez Pech, G. Montavon, J.-Y. Le Questel, J. Graton, J. Champion, N. Galland, *Chem. Sci.* 12 (2021) 10855–10861.

*Speaker
†Corresponding author: nicolas.galland@univ-nantes.fr

Molecular simulation of CH_4 adsorption in kerogen: Effects of maturity and poromechanics

Kévin Potier * , Amael Obliger , Jean-Marc Leyssale[†]

[1] Institut des Sciences Moléculaires – CNRS : UMR5255, CNRS UMR 5255 – France

Molecular simulations allow us to overcome experimental constraints and facilitate the characterization of fluid adsorption in porous carbons. However, for practical reasons, these simulations are often performed by neglecting the deformations of the carbon induced by adsorption. We present here hybrid Grand Canonical Monte Carlo simulations coupled with isothermal-isobaric molecular dynamics to simulate methane adsorption in kerogen under unjacketed conditions, i.e., where the kerogen is embedded into a fluid at fixed P and T. Kerogen models obtained by simulating the geological evolution of organic residues [1][2] and spanning a wide range of maturities (atomic H/C ratio) are considered and simulated at 318 K and pressures ranging from 1x10-2 to 500 bar. The results are compared to the usual approximation in which no deformation of the carbon is taken into account.

It is observed that the consideration of poromechanical couplings has very little effect at low pressures. On the other hand, at higher pressures, the rigid matrix approximation leads to a significant underestimation of the adsorbed amount for immature kerogens. This underestimation decreases as maturity increases, which reflects a change in the matrix, going from an ensemble of flexible alkyl chains to a single rigid aromatic ring cluster. This transition has a considerable impact on porosity. Indeed, unlike mature carbons, immature carbons show little to no porosity at rest; adsorption at higher pressure is associated to the creation of pores, highlighted by the important increase in volume (swelling) of the matrix.

[1] L. Atmani *et al.*, *Chem. Sci.*, **8**, 8325–8335 (2017)
[2] L. Atmani *et al.*, *Energy Fuels*, **34**, 1537–1547 (2020)

---

*Speaker
[†]Corresponding author: jean-marc.leyssale@u-bordeaux.fr

Molecular dynamics investigation of non-Fickian effects on desorption from source rocks' organic matter

Amael Obliger [*] [1]

[1] Institut des Sciences Moléculaires – CNRS : UMR5255, CNRS UMR 5255 – France

Shale-gas recovery from unconventional reservoirs is a very slow process that exhibits "anomalous" behaviour at large scales such as non-Fickian productivity declines [1] (i.e. the recovery curves evolve at early times as tˆa with a < 0.5). Such non-Fickian behaviors have also been observed experimentally on methane desorption from coal samples [2]. Recent numerical studies, focusing on the microporosity of the organic matter called kerogen (where the hydrocarbons are produced and trapped during maturation), has been carried out to elucidate transport properties [3,4,5] using various atomistic reconstructions of kerogens' microporosity and by neglecting or not the effects of flexibility of the carbonaceous microporous structure that can lead to important swelling due to fluid adsorption. Despite those results, the underlying quasi-stationnary assumption usually made to upscale the obtained transport properties imposes a Fickian desorption regime in contrast with the observations.

By using Non Equilibrium Molecular Dynamics (NEMD) we show that the kinetics of desorption from an amorphous microporous structure lead to non-Fickian effects similar to those observed on the fields and in experiments. We highlight that the general scaling ta for the early regime of the recovery curve might not be unique as the exponent adepends on the portion of the curve we fit and that this exponent depends on the rigidity of the carbon microstructure while always remaining below 0.5 as observed. By confronting the NEMD results with a Fickian diffusion model solved numerically we show that the Fickian desorption regime (a=0.5) is very robust, e.g,. a concentration dependent diffusion coefficient still lead to a Fickian desorption regime. By investigating the equilibrium mechanism of diffusion we suggest a qualitative explanation of the non-Fickian effects revealed by NEMD, thus sheding light on observations made on the fields and in experiments.

[1] Monteiro *et al.*, *PNAS*, *109* (50), 20309–20313, (2012).
[2] Kang *et al.*, AIP Advances 5, 127119-6, (2015).
[3] J. Collell *et al.*, Journal of Physical Chemistry C, 119(39):22587–95, (2015).
4] A. Obliger *et al.,* Langmuir, 34(45):13766–80, (2018).
[5] A. Obliger *et al.,* Journal of Physical Chemistry B, 123(26):5635–5640, (2019).

---

[*]Speaker

A density-based basis set correction for wave function methods: Overview of recent developments and results

Emmanuel Giner *

Laboratoire de Chimie Théorique – CNRS : UMR7616 – France

One of the main problems of wave function theory (WFT) many-body calculations is the slow convergence of the quality of the results with respect to the size of the one-particle basis set employed. This is caused by the slow convergence of the two-body density near the electron-electron coalescence point (i.e. $r_{12} \approx 0$) where the wave function has a discontinuity in its first-derivative (i.e. the electron-electron cusp). On the other hand, density functional theory (DFT) captures efficiently the correlation effects at small r_{12} due to its universal character which can be imported from known physical systems such as the uniform electron gas (UEG). In this talk, I will introduce the recently proposed 1 basis-set correction for WFT based on density functional theory (DFT). At the heart of this framework lies the realization that the Coulomb interaction, once projected in an incomplete basis set, is no longer divergent. This enables us to propose a clean mapping with range-separated DFT (RS-DFT) guaranteeing an unaltered complete basis set (CBS) limit. After reviewing the theoretical grounds on this approach, I will introduce some of its recent achievements in terms of benchmarks for weakly and strongly correlated systems, together with the latest tracks for the computation of properties .

---

*Speaker

Coupling of quantum chemical models and high performance algorithms for the global exploration of the energy landscape of atomic and molecular systems

Valentin Milia * [1,2,3], Nathalie Tarrat [4], Mathias Rapacioli [4],
Juan Cortes [1]

[1] LAAS CNRS TOULOUSE – France
[2] Rapacioli Mathias – Laboratoire de Chimie et Physique Quantiques (LCPQ), IRSAMC, UMR 5626 CNRS – France
[3] CEMES CNRS, 29 RUE JEANNE MARVIG, 31055 TOULOUSE, FRANCE – France
[4] Laboratoire de Chimie et Physique Quantiques (LCPQ) – Université Paul Sabatier (UPS) - Toulouse III, CNRS : UMR5626 – 118 Route de Narbonne Bât. 3R1 b4 Toulouse 31062 Toulouse cedex 9, France

The study of the physical and chemical properties of molecules and atomic aggregates, isolated or surrounded, requires the description of these systems at the atomic level. Theoretical chemistry provides essential information such as chemical reactivity, ionisation energy, spectroscopy... For these complex systems, this implies on the one hand (i) the calculation of the potential energy, and on the other hand (ii) the global exploration of the resulting potential energy landscape, possibly containing many local minima connected by many transition paths.

Among the theoretical chemistry models, the Density Functional based Tight Binding approach1 allows to treat certain processes such as reactivity or physics and chemisorption thanks to the explicit quantum description of the electronic system. Compared to ab initio methods, its low computational cost comes from the use of parameters derived from DFT calculations.

Exploration of the energy landscape can be carried out by many methods, the most common being based on variants of Monte Carlo or molecular dynamics simulation techniques. Despite research efforts in these areas, there seems to be no reliable and computationally efficient general method to explore the energy landscape of large systems in a comprehensive way. Algorithms used in robot motion planning have been adapted and applied as efficient methods to explore the conformational space of molecular systems2. In particular, the Transition-based Rapidly-exploring Random Trees (T-RRT) algorithm34 has been shown to efficiently explore energy landscapes. Previous work in this context was based on semi-empirical potentials, our objective is to
synergistically couple these robotics-inspired exploration methods with a DFTB-type quantum potential. As a first case study, this new approach will be applied to the study of molecules of the Phthalate family (Figure 1), which are widely used in various types of industries, and which represent a major risk for health and the environment.

---

*Speaker

BSE/GW excited state surfaces: tackling the DMABN twist challenge

Iryna Knysh [*][†] [1], Ivan Duchemin [2], Xavier Blase [3], Denis Jacquemin [1]

[1] Nantes Université – Nantes Université, CNRS, CEISAM UMR 6230, 44000 Nantes, France – France
[2] Université Grenoble Alpes – Université Grenoble Alpes, CEA,
IRIG-MEM-L$_Sim, 38054 Grenoble - -France$
[3] Université Grenoble Alpes – Université Grenoble Alpes, CNRS, Institut Néel, 38042 Grenoble – France

The 4-(dimethylamino)benzonitrile (DMABN) and its derivatives are the prototypical cases for abnormal dual fluorescence as well as benchmarking the shape of excited state potential energy surfaces (PES).([1]) The accurate description of the evolution of excited state PES upon twisting of DMABN is the key to explaining its unusual fluorescence. However, a dilemma arises when choosing a method to compute ES properties: high-level wavefunction theories yield accurate results but are limited to model molecules, while the less computationally demanding TD-DFT fails to properly describe ES with charge transfer (CT) character,([2],[3]) and delivers qualitatively incorrect PES for DMABN when a GGA or global hybrid functional is used.([4])
In this communication, we present a study of PES of the two lowest excited states of DMABN using the Bethe-Salpeter Equation (BSE) and Green's function (GW) formalisms as well as TD-DFT and Coupled Cluster (CC) methods (CC2, CCSD and CCSD(T)(a)*) in both gas and condensed phases, the latter being used as a reference. Our results prove that BSE/GW formalism is able to accurately reproduce the evolution of excited state PES upon geometrical change, shows negligible starting point dependency, and provides accurate vertical ES energies while having the same computational scaling with system size as TD-DFT.

1. E. Lippert, W. Ludar, and H. Boss, Advances in Molecular Spectroscopy (Pergamon Press, Oxford, 1962).
2. D. J. Tozer. J. Chem. Phys. **119**, 12697 (2003).
3. A. Dreuw and M. Head-Gordon. J. Am. Chem. Soc. **126**, 4007 (2004).
4. P. Wiggins, J. A. G. Williams, and D. J. Tozer, J. Chem. Phys. **131**, 091101 (2009).

---

[*]Speaker
[†]Corresponding author: iryna.knysh@univ-nantes.fr

Reducing computational cost of geminal methods for strongly-correlated electrons

Patrick Cassam-Chenaï [*] [1]

[1] Lab. J. A. Dieudonné – CNRS : UMR7351, Université Côte d'Azur – France

The Lewis electron-pair picture pervades all of chemistry and a substantial domain of materials science. "Geminals" are electron-pair quantum states which are used to express approximate solutions of the Schrödinger equation of polyelectronic systems. In quantum chemistry, geminal-based methods are potentially more effective than the traditional ones based on the orbital picture where electrons occupy orbitals and experience only the average effect of each other. This is especially true for strongly correlated-systems. However, the computational cost of using general antisymmetrized product of geminals (APG) is non-polynomial in the system size.

So, in the past, the so-called "strong-orthogonality" constraint has often been imposed to APG, leading to the antisymmetrized product of strongly-orthogonal geminals (APSG) ansatz. If APSG does reduce computational cost to a polynomial one, it is too drastic to reach chemical accuracy. In this talk, we will review recent endeavours by several groups to develop geminal models relaxing such a constraint.

Actually, all these recent attemps fall into the category of seniority zero methods, that is to say, they only consider excitations of electron pairs in the same orbital, and are therefore unable to describe states involving significant contributions from open-shell configurations. In contrast, we have proposed a new APG ansatz which goes beyond both the strong-orthogonality and the seniority zero approximations (1,2). We will present the path we have followed to arrive at this model, denoted EPI2O-APG, an acronym standing for "extented permutationally invariant 2-orthogonality" APG.

References

P. Cassam-Chenai, V. Rassolov, Chem. Phys. Lett. 487, 147-152 (2010).

P. Cassam-Chenai, T. Perez, D. Accomasso, 2D-Block Geminals: a non 1-orthogonal and non 0-seniority model with reduced computational complexity, (depot hal-03763128 sur HAL)

Keywords: geminals, strongly correlated electronic systems

---

[*]Speaker

Artificial Neural Networks as Exchange and Correlations functionals for Transition Metal Complexes

Joao Paulo Almeida De Mendonca *† [1], Antonio Lorenzo Mariano [2],
Emilie Devijver [3], Noel Jakse [4], Roberta Poloni [5]

[1] Science et Ingénierie des Matériaux et Procédés – Institut de Chimie du CNRS, Centre National de la Recherche Scientifique : UMR5266, Université Grenoble Alpes, Institut polytechnique de Grenoble - Grenoble Institute of Technology – France

[2] Science et Ingénierie des Matériaux et Procédés (SIMaP) – Institut Polytechnique de Grenoble - Grenoble Institute of Technology, Institut National Polytechnique de Grenoble, Centre National de la Recherche Scientifique : UMR5266, Université Grenoble Alpes – 1130 rue de la Piscine, BP 75 38402 Saint Martin DHères, France

[3] Laboratoire d'Informatique de Grenoble – CNRS : UMR5217, Université Grenoble Alpes – France

[4] Noel Jakse – Institut National Polytechnique de Grenoble - INPG – France

[5] Science et Ingénierie des Matériaux et Procédés (SIMaP) – Université Joseph Fourier - Grenoble 1, Institut Polytechnique de Grenoble - Grenoble Institute of Technology, Institut National Polytechnique de Grenoble, Centre National de la Recherche Scientifique : UMR5266, Université Grenoble Alpes – 1130 rue de la Piscine, BP 75 38402 Saint Martin DHères, France

Recent studies have shown that by training Machine Learning (ML) models with highly accurate ab initio wavefunction data, one can construct exchange and correlation functionals in DFT that improve upon standard approximations. As such, Nagai et al. (2022) demonstrated that Artificial Neural Network (ANN) functionals can yield very accurate values of atomization energy and ionization potential of small molecules consisting of light atoms. Yet, this is an emerging approach in the field of electronic structure calculations and many questions stay open on how to adapt the ML framework to particularly challenging materials or properties, such as, for example, transition metal complexes and adiabatic energy differences. In our work, we propose a combination of ANN and non-gradient bio-inspired training methods adapted from Particle Swarm Algorithm which is trained over transition metal diatomic molecules. For some systems the traditional approach of learning energy differences and densities simultaneously doest not work locally and a quantity can be sacrificed in the detriment of the other. The obtained functional is validated against multiconfigurational calculations for predicting adiabatic energy differences, showing an improvement over several GGA and meta-GGA functionals. The training process itself is also analyzed, revealing the strong interdependence in the accurate description of density and energetic properties while describing SCO phenomena.

---

*Speaker
†Corresponding author: joao-paulo.almeida-de-mendonca@grenoble-inp.fr

Halide perovskites beyond methylammonium lead iodide

Mikaël Kepenekian * [1]

[1] Institut des Sciences Chimiques de Rennes (ISCR) – Universite de Rennes 1 – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

After only a decade, halide perovskites ABX3 (with A a cation, e.g. methylammonium or Cs+; B a metal divalent cation, e.g. Pb2+; X an halide anion, e.g. I–) have had a significant impact on the pursuit of high solar-to-electric power conversion efficiencies (PCE) with impressive milestones achieved, including PCE greater than 25% for single junction solar cells and beyond 30% for perovskite/Si tandem cells [1]. Remarkably, those performances are obtained with unexpensive abundant materials that are solution processed at room temperature, hence come with low production costs, which contributes further to the quest for renewable energy sources with low-kWh costs.

Such a success of the prototypical methylammonium lead iodide (MAPbI3) has brought increased attention to the rest of the halide perovskite family and its impressive structural variety [2]. If 3-dimensional (3D) compounds, with corner-shared (BX6) octahedra, offer limited choice over the choice of the metal or the organic cation, layered materials (2D), already known for their great optical properties, offers many opportunities for chemists to design application driven materials [3]. In between strictly 2D and 3D materials, there is a wealth of compounds with features of both dimensionality and intriguing properties. Among those, one can find the 'deficient' or 'hollow' perovskites [4], but also perovskitoids consisting of not-only corner-shared octahedra [5] down to 1D materials. Another direction recently explored aims at moving away from toxic lead using double perovskites structures [6] or even by making a side-step towards cousin structures of perovskites where (BX6) octahedra are no longer corner-shared [7].

Here, we will navigate this wide range of materials and highlight how modelling and computational investigations, in close contact with experimental approaches, can help rationalize the optoelectronic properties of compounds but also lay done rules for the design of new materials.

Best research-cell efficiencies from the National Renewable Energy Laboratory (July 2022). https://www.nrel.gov/pv/cell-efficiency.html.

B. Saparov, D. B. Mitzi, *Chem. Rev.* **2016**, *116*, 4558.

L. Pedesseau, M.K. *et al.*, *ACS Nano* **2016**, *10*, 9776; C. Katan, N. Mercier, J. Even, *Chem. Rev.* **2019**, *119*, 3140.

A. Leblanc *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 16067; I. Spanopoulos *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 5728; A. Leblanc, M.K. *et al.*, *ACS Appl. Mater. Interfaces* **2019**, *11*, 20743.

J. M. Hoffman, M.K. *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 10661; X. Li, M.K. *et al.*, *J. Am.*

*Speaker

Chem. Soc. **2022**, *144*, 3902.

G. Volonakis *et al.*, *J. Phys. Chem. Lett.* **2017**, *8*, 772; X. Li, M.K. *et al.*, *Chem. Mater.* **2021**, *33*, 5085.

I. Turkevych *et al.*, *ChemSusChem* **2017**, *10*, 3754; B. Cucco, M.K. *et al.*, submitted.

Photochrom grafted gold nanoparticle for solar energy harvest and storage

Corentin Poidevin * , Arnaud Fihey [1]

[1] Institut des Sciences Chimiques de Rennes – Université de Rennes 1, CNRS : UMR6226, Universite de Rennes 1 – France

Molecules able to undergo reversible photoisomerization (photochroms) keep on attracting wide attention for their use in: molecular solar thermal storage (MOST), molecular switches, motors or memory. In particular, in the context of renewable energy search, MOST are considered as promising strategy for solar energy harvest and storage.[1] It has been shown that grafting photochroms on materials could lead to an increase in the stored energy.2 Additionally, large metal nanoparticle (starting at 279 atoms for Au) exhibit surface plasmon resonance band.3 Thus, we wanted to study computationally photochroms for MOST grafted on large thiolate protected gold nanoparticles to explore the effect of both steric constraints and the plasmon resonance band on the isomerization and the stored energy. As the size of these systems can easily excide the 1000 atoms, we used tight-binding DFT (DFTB) which have proven to be reliable in this context.4 We are studying both the influence of both the packing and of the size of the nanoparticles on these properties with norbornadiene/quadricyclane (NBD/QC) derivatives as MOST as illustrated in Figure 1.

Keywords: Molecular solar thermal, DFTB, gold nanoparticles

---

*Speaker

Impact of the electric field on magnetic parameters: disruptive Dzyaloshinskii-Moriya interaction

Nathalie Guihéry* , Barthélémy Pradines [†] [1], Benjamin Cahier , Nicolas Suaud

[1] LCPQ – CNRS – France

One may obviously think that the best way to control magnetic properties relies on using a magnetic field. However, it is not convenient to focus a magnetic field on a small object whereas it is much easier to do so with an electric field. Magnetoelectric coupling allows one to control the magnetization with the electric field and the polarization with the magnetic field and could therefore provide a solution to this problem. The present talk aims at quantifying the impact of the electric field on both the isotropic magnetic exchange and the Dzyaloshinskii-Moriya interaction in the case of a binuclear system of S=1/2 spins. This study follows previous works which showed that very high Dzyaloshinskii-Moriya interaction, *i.e.* the antisymmetric exchange, can be generated when close to first order spin orbit coupling. We will therefore explore this regime in a model Cu(II) complex that exhibits a quasi-degeneracy of the orbitals. This situation is indeed the one that allows to obtain the largest spin orbit couplings in transition metal complexes. We will show that both the magnetic exchange and the Dzyaloshinskii-Moriya interaction are very sensitive to the electric field and that it would therefore be possible to modulate and control magnetic properties by the electric field.

Keywords: Dzyaloshinskii, Moriya interaction, electric field, Magnetoelectric coupling

---

*Corresponding author: nathalie.guihery@irsamc.ups-tlse.fr
[†]Speaker

Unravelling the Spin-Phonon Relaxation Mechanism in a series of Co(II) and Dy(III) Single-Molecule Magnets

Sourav Mondal * [1,2], Alessandro Lunghi[†] [2]

[1] Sourav Mondal – School of Physics, Trinity College Dublin, Dublin-2, Ireland, Ireland
[2] Trinity College Dublin – Ireland

Magnetic recording is underpinned by the possibility to retain the magnetization direction of a given material in a zero-applied magnetic field. Magnetic molecules have shown such a property but only at cryogenic temperatures. As temperature increases, spin-phonon relaxation becomes the limiting factor for the spin lifetime. The experimental determination of the spin relaxation mechanism is a challenging task and a convincing interpretation is still lacking. We apply ab initio spin dynamics to understand the spin relaxation mechanism for a series of 12 molecular crystals of Co(II) and Dy(III) ions that well represent the chemical space explored so far. Our results revisit years of experimental investigations and correctly interpret the spin relaxation path in terms of Orbach and Raman mechanisms. Simulations further reveal that the spin relaxation rate depends on the crystal field splitting, while further improvements may become possible through vibrational engineering.

Keywords: Spin, phonon coupling, spin relaxation, ab initio spin dynamics

---

*Speaker
[†]Corresponding author: lunghia@tcd.ie

Rigorous Extraction of Magnetic Exchange Couplings in Compounds with Several Magnetic Centres: the Recomposition Method

Grégoire David * [1], Nicolas Ferré [2], Boris Le Guennic [3]

[1] Institut des Sciences Chimiques de Rennes (ISCR) – Université de Rennes 1, Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, 35043 Rennes Cedex – France
[2] Institut de Chimie Radicalaire – Aix Marseille Université : UMR7273, Centre National de la Recherche Scientifique : UMR7273 – France
[3] Institut des Sciences Chimiques de Rennes (ISCR) – Universite de Rennes 1, Ecole Nationale Supérieure de Chimie de Rennes, Institut National des Sciences Appliquées, Centre National de la Recherche Scientifique : UMR6226, Institut National des Sciences Appliquées – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

Molecules with remarkable magnetic properties, such as Single-Molecule Magnets, have been attracting much attention over the last decades for their potential technological applications as elementary building blocks in Quantum Technologies or Molecular Spintronics.[1] Indeed, molecules have the advantage of being highly versatile, with a possible design of compounds with predefined magnetic properties. In this aim, compounds with multiple magnetic centres, for instance with f- and d-metal ions or radical ligands, are particularly interesting since the couplings between centres may play a key role in the control of the global magnetic behaviour.[2] However, the theoretical evaluation of the magnetic exchange couplings in these systems is particularly challenging.

On the one hand, wave-function theory-based methods are the reference approach but their computational cost is most of the time prohibitive in these very large compounds. On the other hand, it is possible to compute these couplings in Kohn-Sham density functional theory (KS-DFT) by means of the broken-symmetry (BS) approach. Despite the success of this strategy over the last decades for two-centre systems, the computation of couplings in multi-centre compounds is not exempt of important pratical and theoretical questions. Among them, one may mention the problem of the spin contamination which is very often neglected, whilst at the heart of this formalism, as well as the dependence of the couplings on the choice of the determinants used to compute them.

In this communication, I will present a new method to compute magnetic exchange couplings in multicentre systems in BS KS-DFT, the so-called **recomposition method**.[3] Based on the effective Hamiltonian theory, this approach proposes to properly extract the relevant physical contributions of the coupling to rigorously evaluate an overall quantity free from spin contamination, following the strategy of our previous works in the context of two-magnetic-centres systems.(4-6) In addition, this strategy offers a powerful rationalisation tool through this decomposition to go beyond the only numerical value of the couplings. This method is applied on a series of 3 and 4 copper ions-based compounds, whilst a special attention will be paid to the influence of the spin contamination in multi-centre compounds.

E. Coronado, *Nat. Rev. Mater.*, **2019**, *5*, 87–104.

---

*Speaker

J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nat. Chem.*, **2011**, *3*, 538–542.

G. David, N. Ferré, B. Le Guennic, *submitted*

G. David, N. Guihéry, N. Ferré, *J. Chem. Theory Comput.*, **2017**, *13*, 6253-6265.

G. David, N. Ferré, G. Trinquier, J.-P. Malrieu, *J. Chem. Phys.,* **2020**, *153*, 054120.

G. David, G. Trinquier, J.-P. Malrieu, *J. Chem. Phys.*, **2020**, *153*, 194107.

Author Index