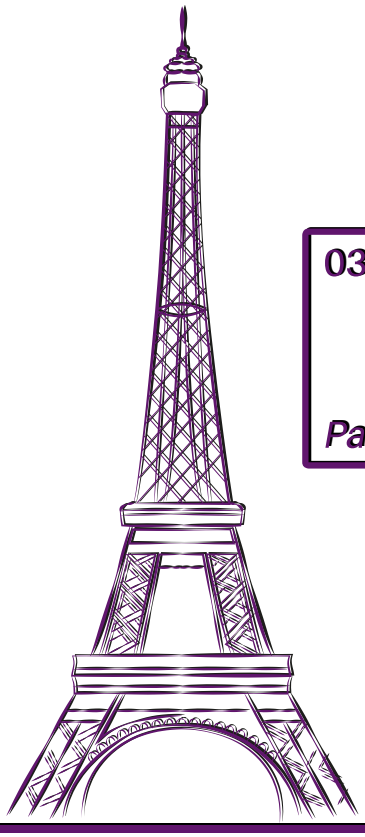

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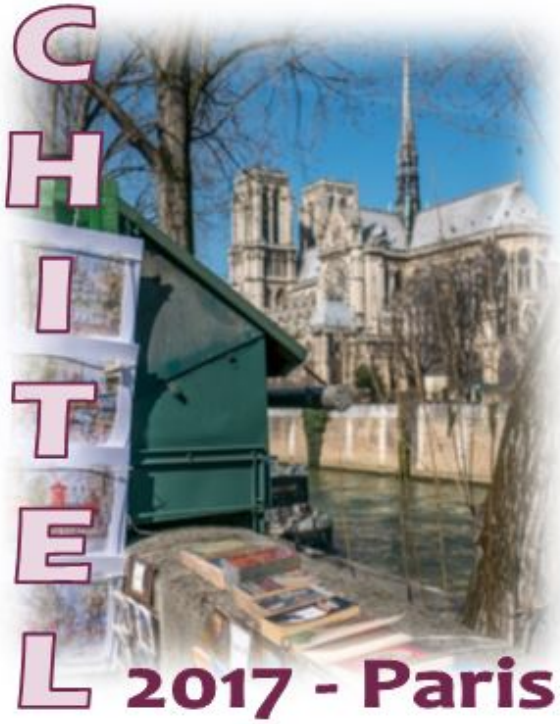
XLIIIème Congrès des

Chimistes Théoriciens d'Expression Latine



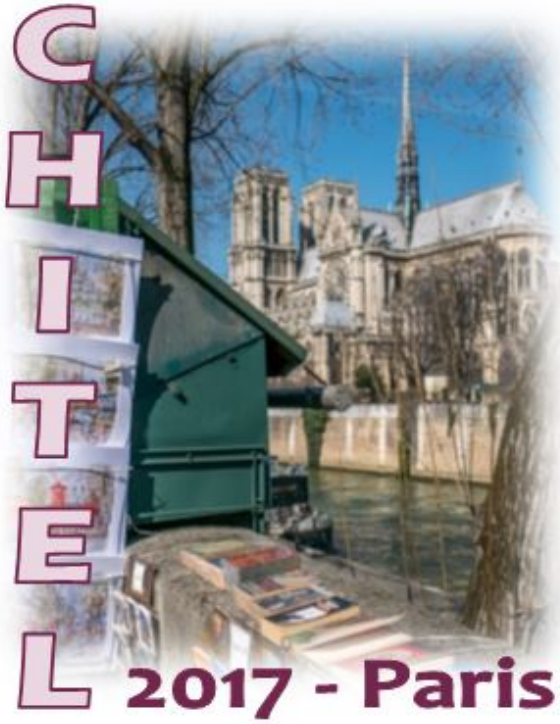
Le Congrès des Chimistes Théoriciens d'Expression Latine, dont l'acronyme s'orthographie alternativement CHITEL ou QUITEL, consiste en une réunion annuelle et historique dédiée à la chimie théorique. Initié en 1969 par Pullmann et Del Re, ce congrès a pour objectif la promotion des collaborations et de l'amitié entre chimistes théoriciens d'expression latine.

Nous sommes heureux d'organiser la 43ème édition du CHITEL / QUITEL à Paris dans le Quartier Latin, au cœur du Vème arrondissement à l'Ecole Nationale Supérieure de Chimie de Paris (ENSCP, Chimie ParisTech).
L'organisation de ce congrès est assurée par un comité local issu de 4 laboratoires : deux laboratoires de l'Université Pierre et Marie Curie (MONARIS et LCT), l'équipe Théorique et Modélisation (Chimie ParisTech) et le laboratoire COBRA (Université de Rouen).

Au nom de tout le comité d'organisation, je vous souhaite un excellent séjour à Paris.

Paris, le 21 juin 2017

Esmaïl ALIKHANI



Sur les deux sessions de posters, quatre d'entre eux ont été récompensés par le comité de sélection.
Nous avons attribué à chacun des lauréats un prix de 125 € grâce au sponsoring de "Springer Publisher", représenté par le Dr. Svetlana Zakharchenko.

Les lauréats sont :

Aurelio Alvarez-Ibarra : Poster P1_20
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- Zhu Jingwen
- Zins émilie-Laure

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Plenary Lectures

PN_01 - Quantum Theoretical Methods for the Design of Functional Materials

Ria Broer *† [1]

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Theoretical and computational studies become more and more important for the design of functional materials. In this contribution three examples of such studies, which require the accurate computation of energies as well as wavefunctions, for various electronic states, are discussed.
Spin crossover processes may occur in metal-organic complexes of d4 ... d7 transition metal ions. Spin crossover complexes have two low-energy states, one with maximum electron pairing and one with a maximum number of unpaired d electrons. A transition between these states may lead to "excited spin-state trapping", which is of technological importance. The crossover mechanism may involve various intersystem crossings and internal conversions. By combining time-dependent DFT and CASSCF/CASPT2 calculations with a time-dependent formalism for calculating intersystem crossing rates the mechanism can be unraveled.

The modeling of core excitation spectra is especially challenging because electronic relaxation, electron correlation and often also relativistic effects are important. CASSCF/CASPT2 can be used to estimate the effects of electron correlation on the electron binding and excitation energies. A conceptually attractive nonorthogonal CI method to account for electronic relaxation and static electron correlation is also discussed. We employ the normalized elimination of the small component method to account for scalar relativistic effects, while spin-orbit coupling is included *a posteriori* employing a spin-orbit extended Hamiltonian. The intensities in X-ray absorption spectra are computed using transition dipole moments, XPS intensities are estimated using the sudden approximation.
The last example concerns the electron-hole separation in organic donor-acceptor blends for photovoltaic purposes. Relevant for this field is singlet fission, a process enabling *one* high-energy photon to generate *two* electron-hole pairs. Studying the efficiency of such processes requires knowledge of the potential energy surfaces, vibrational frequencies and of the electronic and adiabatic coupling elements, so we combine DFT, CASSCF/CASPT2 and nonorthogonal CI with molecular dynamics.

Mots-Clés: many electron methods, nonorthogonal CI, spin states, core spectra, singlet fission, functional materials

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PN_02 - Noncollinear spins in Density Functional Theory: Ground state formulation and linear response

Giovanni Scalmani *† [1]

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Noncollinear Spin Density Functional Theory (SDFT) holds the promise for describing electrons whose spins are not constrained along a common arbitrary direction. Electron distributions involving noncollinear spins can be the consequence of relativistic effects such as spin-orbit interactions or they may be required to explain the properties of magnetic materials, including phenomena like spin-dynamics.
In this contribution we present the formal development and implementation of a two-component General Kohn-Sham (2c-GKS) ground state method. Our approach describes noncollinear spins preserving a full spatial and spin rotational invariance. It has the expected collinear limit and it is free of numerical instabilities in regions of small magnetization density. All functionals already developed for collinear GKS can be used in 2c-GKS calculations, including GGAs and meta-GGAs and both global and range-separated hybrid functionals. Moreover, for functionals beyond the local density approximation, a non-vanishing exchange-correlation (XC) local magnetic torque is present, while the Zero Torque Theorem (ZTT) remains satisfied globally.

We further introduce a proper linear response (LR) approach starting from a 2c-GKS ground state. In this formalism the linear response XC kernel involves the same functional used to produce the unperturbed ground state density. Moreover, to ensure proper invariance both the Hermitian and anti-Hermitian components of the transition density in the atomic orbital basis are involved in the response kernel. The LR-2c-GKS approach is the prerequisite for two interesting methodological developments: a very useful stability test for the 2c-GKS ground state itself, and a single-particle excited states method via a Time-Dependent (TD) 2c-GKS approach.
We will discuss some technical details involved in achieving a robust implementation of LR-2c-GKS in the case of closed shell systems, and we will present the results of some prototypical calculations which showcase the richness of details in the description of the single-particle excitations provided by the LR-2c-GKS approach.

Mots-Clés: noncollinear spins, two component methods, linear response DFT, TD DFT

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PN_03 - Spectroscopy of relevant non-rigid molecules of astrophysical interest: ethylen glycol and methyl isocyanate

Maria Luisa Senent Diez *† [1]

[1] CSIC (CSIC) – Espagne

I present my own methodology for the spectroscopic study at low temperatures of non-rigid organic molecules detected in star formation regions of the interstellar medium. The last works on ethylen glycol[1] and methyl isocyanate[2] are detailed. The former was identified in 2002[3], and the latter in 2015 and 2016[4-5]. For methyl isocyanate, previous assignments of many rotational lines are ambiguos. Ethylene glycol is an example of organic molecule whose Far Infrared Spectrum is specially tricky given the role of intramular bonds on the internal dynamics.
Non-rigid molecules show more than one minimum on the ground electronic state potential energy surface. The conformers interconvert through very anharmonic large amplitude vibrational motions without bond breaking or bond formation. The analysis of their very complex spectra requires specific theoretical models assuming the non-rigidity. Thus, we use a variational procedure implemented in my code ENEDIM using ab initio geometries and energies as inputs.

These studies are relevant to molecular astrophysics since levels corresponding to the vibrational motions responsible for the no-rigidity are of very low energy and can be populated at very low temperatures. The calculations search to help rotational spectra assignments. They can provide an initial set of parameters necessary for assignments of experimental spectra using effective Hamiltonians.

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Mots-Clés: astrochimie, Far IR

*Intervenant
†Auteur correspondant: reinh@lct.jussieu.fr

PN_04 - Extreme chemistry: simulating the fate of simple molecules at extreme conditions of pressure and temperature

Sandro Scandolo *† [1]

[1] The Abdus Salam International Centre for Theoretical Physics – Strada Costiera, 11 I - 34151 Trieste Italy, Italie

Extreme conditions of pressure and temperature such as the ones found in the interiors of planets induce dramatic chemical changes in simple molecules, including dissociation, ionization, and polymerization. Understanding such changes has far-reaching implications in chemistry, physics, planetary sciences, geophysics, and materials science. I will illustrate strengths and limitations of density-functional-theory based molecular dynamics in three case studies: the polymerization of CO_2, the dissociation of the planetary mixture CH_4/H_2O, and the collapse of magnetism on O_2.

Mots-Clés: DFT, MD

*Intervenant

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PN_05 - Quantum Mechanics illuminating experimental results

Elson Longo *† [1]

[1] Federal University of São Carlos (UFSCar) – Brésil

The scientific advance of today has as a fundamental axis the theoretical-experimental association. The semiconductors that constitute the basis of multifunctional materials, have evolved exponentially due to a better understanding of the electronic structure of solid materials. Theoretical interpretation of the morphology of solids based on quantum mechanical calculations, considering a solid order-disorder of clusters at short range. The interaction of these clusters is fundamental for the interpretation of the optical and electronic properties of the solids, as well as the surface phenomena. Thus, experimental results of silver growth on the surface of semiconductors Ag_2MO_4, M = Cr, W and Mo, when irradiated by electron beam using scanning or transmission electron microscopy or when irradiated by laser in femtoseconds will be reported. These experimental data are interpreted using ab initio simulations method, using density functional theory (DFT) in the framework of QTAIM, were undertaken to complement the experimental results.This fact demonstrates that electrons irradiation or laser irradiation produces a new reaction kinetics for the synthesis of semiconductors

Mots-Clés: Matériaux, DFT, QTAIM

*Intervenant

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PN_06 - Conceptual Approaches to High-Energy-Density Materials for Li-Ion Batteries

Matthieu Saubanere* [1,2], Ying Xie [1], Mouna Ben Yahia† [1], Marie-Liesse Doublet ‡§ [1]

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[2] Réseau sur le stockage électrochimique de l'énergie (RS2E) – CNRS : FR3459 – France

Increasing the energy density of cathode materials is a central goal of the ongoing research Li-ion batteries. This implies improving simultaneously the capacity and the potential of the materials used at the positive electrode of the electrochemical device. On the one hand, the amplitude of the electrochemical potential of an electrode material is relatively well-controlled through an appropriate choice of the redox centre involved in the Li-driven electrochemical reactions. One the other hand, the increase of capacity for high-potential materials appears more difficult to achieve without penalizing the material structural stability. So far, materials showing the highest energy densities are the Li-rich layered transition metal oxides for which a cumulative cationic and anionic redox activity has been demonstrated. [1-3] We review the different methodologies to address the fundamental questions of increasing both the potential and the capacity of current positive electrodes and show that conceptual rather than computational approaches help in clarifying the relationship between the material electronic structure, the potential, the (extra)-capacity and the consequences of high energy density on the material structural stability. [4-6] This unified picture gives a clear description of the structural and electronic features of a host structure that govern the potential and the capacity of insertion materials and clearly highlights that a trade-off needs to be found for increasing the performance of the next generation of Li-ion batteries. [7]

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Mots-Clés: batteries, Li ion

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PN_07 - Recent Advances in Enzymatic Reaction Mechanisms and Structural Proteomics

Pedro Fernandes *† [1]

[1] UCIBIO@REQUIMTE, Faculdade de Ciências, Universidade do Porto, Portugal – Portugal

I will summarize several quasi-related developments that are taking place within our group.
The talk will not focus on specific applications but instead in will give an overview of the fields we are working in, with selected examples to illustrate the concepts.
The calculation of enzyme reaction mechanisms with QM/MM techniques will be addressed [1-3], emphasizing the methodological aspects that have to be taken into consideration to achieve accurate results [4]. The role of enzyme flexibility on catalytic rates will be discussed as well [5]. The influence of ultra-fast nanosecond timescale conformational changes on the reaction rate will be discussed in detail.
Some of our work is structural proteomics will be discussed as well. Methods for rapid calculation of the effect of mutations in binding free energies [6], as well as improved protocols and scoring functions for protein-protein docking [7].

ACKNOWLEDGEMENTS: This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/00 7728and NORTE/01/0145/FEDER/000024) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia, Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/MULTI/04378/2013,and grants INCENTIVO/EQB/LA0006/2014

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Mots-Clés: DFT, QM/MM, Reaction Mechanisms, Free energy calculations, Protein, Protein docking

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Keynote Lectures

KN_01 - Baird's rule of aromaticity and antiaromaticity

Miquel Solà *† [1], Ouissam El Bakouri [1], Jordi Poater [2], Ferran Feixas [1]

[1] Universitat de Girona (UdG) – Espagne
[2] Universitat de Barcelona (UB) – Espagne

From the discovery of benzene in 1825 to the present day, the concept of aromaticity has experienced several revolutions that have fueled the interest of both theoretical and experimental chemists. Very recently, several works [1-3] have highlighted the importance of aromaticity in excited states. Aromaticity is essential to understand and predict many photochemical processes. This renaissance of excited state aromaticity represents an important revolution in the field of aromaticity. Although aromaticity is a property usually linked to the ground state of stable molecules, certain excited states are unquestionably aromatic. This is especially the case of annulenes in the lowest-lying triplet states whose aromaticity follows the 4N Baird rule [4]. In this work, we apply this rule to discuss the aromaticity and antiaromaticity of all-metal clusters, we discuss the existence of Hückel-Baird hybrid aromatic species [5], and we show how Clar's rule can be extended to the lowest-lying triplet excited states of certain polycyclic aromatic molecules.

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Mots-Clés: Aromaticity, excited states, Baird rule, photochemistry, molecular clusters, polycyclic conjugated hydrocarbons

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KN_02 - A Novel Mixed Quantum/Classical Method for Nonadiabatic Quantum Dynamics in Explicit Solvent Models: Decay of Thymine in $\pi\pi^*/n\pi^*$ Water

Fabrizio Santoro *† [1]

[1] ICCOM-CNR – Italie

Quantum vibronic effects can play a major role in determining the photoexcited dynamics of internal conversions in molecular systems. Recent advancements in quantum-dynamical (QD) approaches, like those provided by the MCTDH method and its multilayer extension, allow a fair description of such effects, even in large systems, if they are rigid (harmonic) and in gas phase. However, we are often interested in the photophysical behavior of dyes embedded in a solvent, possibly establishing with it specific interactions, or even in more complex and heterogeneous environments. The effects of the environment are difficult to include in QD approaches, and in most of the cases this is done through the interaction with a spectral density.
Trajectory-based classical and semiclassical approaches are very powerful and well suited to deal with these scenarios, and the prize they pay is that the motion of the nuclei is considered classical. In this contribution, we present a novel mixed quantum classical (MQC) scheme, based on Ehrenfest framework, that describes the molecular degrees of freedom at quantum level (by a propagating wavepacket) and the environment (the solvent) by an ensemble of classical trajectories. In its current formulation, the method is suitable for cases where the coupled potential surfaces (and their couplings) are amenable of a description in terms of a quadratic local expansion (linear vibronic, quadratic vibronic models).

Although necessarily approximate, the proposed method has the strength to describe the quantum vibronic dynamics of the solute and how it is affected by the solvent, retaining a molecular model for the latter.
We will discuss the potentialities of this approach by investigating the quantum dynamics of the $\pi\pi^*/n\pi^*$ internal conversion of thymine in explicit water models.

Mots-Clés: excited states, internal conversion, quantum dynamics at conical intersection, solvent effects

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KN_03 - Spectroscopy and transport with TDDFT in real time

Damian Scherlis *† [1]

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In recent years, real time simulations of the electron dynamics in molecules and materials have started to be feasible from first-principles. These studies can provide an accurate, time-resolved description of non-adiabatic processes such as radiation absorption, quantum transport, excitations, or photochemistry. In this talk I will discuss our time-dependent density functional theory (TDDFT) implementation to propagate the Kohn-Sham equations in real time using Gaussian basis functions. This code runs on graphics processing units, which remarkably accelerates its performance, and can represent complex molecular environments through a Quantum-Mechanics Molecular-Mechanics (QM-MM) hamiltonian. We will show applications of this methodology to the spectroscopic characterization of elusive chemical intermediates in solution and to the calculation of molecular conductance in organic polymers.

Mots-Clés: Quantum dynamics, conductance, QMMM

*Intervenant

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KN_04 - Valence bond theory and excited states

Stephane Humbel *† [1]

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In this talk I will discuss Valence Bond description of excited states. A short introduction will be given about a Generalized Brillouin optimizer that we implemented[1] as a side-program that uses the XMVB code (Wei Wu's team, Xiamen University).[2] However, most of our talk will concern wave-functions for some excited states optimized with XMVB optimizers. These wave functions will be compared to delocalized MCSCF and MRCI wave functions on the basis of their projection onto a basis of localized structures (VB or Lewis).[3] A special focus will concern the V state of ethylene. The case of the dipole inversion in excited states and the role of Lewis structures will also be discussed using the example of methylene cyclopropene.[4]

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Mots-Clés: Valence Bond, Excited state

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KN_05 - Molecular understanding of Ice Nucleation

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The formation of ice is one of the most common phase transitions in Earth's atmosphere. Nevertheless, little is known about the microscopic pathway that leads to the crystallization of water and the role that surfaces and molecules have on the reaction coordinate and the efficiency of ice nucleation. In this presentation I will discuss our approach to modeling ice nucleation with coarse-grained models and the main insights we obtained on the nature of the reaction coordinate, the role of stacking disorder on the nucleation barrier, and the way surfaces and biomolecules promote the nucleation of ice.

Mots-Clés: ice, nucleation, coarse grained models

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KN_06 - Second-order NLO susceptibilities of organic crystals and metal-organic frameworks from a multi-scale numerical simulation approach

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In this contribution, it is shown that a multi-scale approach combining first principles evaluations of the molecular properties with electrostatic interaction schemes to account for crystal environment is reliable for predicting and interpreting the experimentally-measured electric linear and second-order nonlinear optical susceptibilities. This is illustrated by considering organic crystals including ionic crystalline salts as well as hybrid organic/inorganic metal organic frameworks. A good agreement between theory and experiment is achieved providing the electric field effects originating from the electric dipoles of the surrounding molecules are accounted for. The presentation will also i) highlight the key role of the geometry on the c(1) and c(2) responses, ii) demonstrate the impact of electron correlation on the molecular and crystal properties, iii) assess the performance of exchange-correlation functionals, iv) address the amplitude of the zero-point vibrational energy contributions, as well as v) discuss aspects related to the description of the in-crystal polarizing field (charge definition) and of the local field factors (partitioning of the polarizability tensors).

Mots-Clés: optical properties, organic crystals, metal, organic frameworks, multiscale approach

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KN_07 - CRYSTAL17, a code for dealing with huge systems and tiny effects.

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The capability of the next release of the CRYSTAL program, a quantum-mechanical ab initio code for the simulation of solids, is introduced. Its main features, with particular attention to those characterizing CRYSTAL17, the incoming version, will be briefly outlined.
Few applications to real-case systems will be presented focusing on:
(i) today's ability to tackle large systems, ranging from inorganic super-conductor as the cuprate $Bi_2Sr_2CaCu_2O_{8+x}$
to proteins, by exploiting the improved massively parallel version of the code;
(ii) the new accuracy in detecting and characterizing thin effects, as weak interactions and topological features, thanks to the refinement and optimization of existing algorithms. Application to surface chemistry and guest-host interaction as occurring in MOF structures will be provided.

Mots-Clés: ab initio QM, periodic, electronic structure, charge density

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KN_08 - Theoretical studies on the mechanism of ammonia borane and amine–borane dehydrogenation by precious and non-precious transition metal-based catalysts

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The dehydrogenation of ammonia borane (NH3BH3, AB) and its amineborane derivatives has emerged as a subject of contemporary considerable interest both for H2 production and storage and for the selective formation of B–N materials such as polyaminoboranes, the isoelectronic analogues of polyolefins. New protocols allowing the regeneration of dehydrogenation products have further stimulated this interest. In the course of the years, several catalysts for assisting AB and amineboranes dehydrogenation and dehydrocoupling have been proposed, and particularly, homogeneous second and third row transition metal catalysts have shown to possess remarkably high activity and selectivity. Although, as a result of the very numerous both theoretical and experimental studies devoted to the elucidation of the mechanism of such processes, an almost unified model in which to put in context additional information has been proposed, many important details have yet to be uncovered. Here are presented the results of our computational DFT analysis of AB and amineborane derivatives dehydocoupling and dehydrogenation processes assisted by homogeneous catalysts containing precious and non-precious transition metals. Such investigations have been performed because both inspired by and in combination with experiments.

Mots-Clés: homogeneous catalyst, amineboranes, dehydogenation, DFT

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KN_09 - Chemical Reactivity: Undertstanding Reaction Mechanisms from The Reaction Force and The Reaction Electronic Flux Perspective.

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Chemical reactivity is crucial to understand if a given chemical system will react in order to generate a single or more products and which way this reaction will undergo most favorably, obtaining their reaction mechanism. This topic has been a main interest in chemistry, and in particular to our group leading us to propose two theoretical tools to analyze and understand reaction mechanisms, the reaction force and the reaction electronic flux.[1,2]

The reaction force is the derivative of the energy with respect to the reaction coordinate, giving a rational partition of the reaction profile. This partition is very useful to identify the chemical events that are taking place along a reaction coordinate, activating the system to reach the transition state and relaxing the system to get the reaction products. Combining this partition with structural parameters and quantum reactivity indexes, it is possible to identify the origins of each activation/deactivation, and quantify the works associated along any given reaction.[1]

On the other hand, Reaction electronic flux (REF) is defined in the framework of density functional theory (DFT)[3] as the derivative of the chemical potential with respect to the reaction coordinate, and in analogy with thermodynamics, indicates the spontaneity or non spontaneity of the electron reorganization along a reaction path.[2]

In this work will be discussed representative results regarding the analysis of reaction mechanisms from the reaction force and the reaction electronic flux perspective, in combination with structural and electronic descriptors applied into different systems such as proton transfers, antiradical reactions, and carbenoid alkylations.

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Mots-Clés: Reaction force, reaction electronic flux, reactivity, DFT.

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KN_10 - Estudios teóricos sobre el origen de la eficiencia catalítica de las enzimas.

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Las estimaciones teóricas de efectos isotópicos cinéticos (KIEs) representan valiosas herramientas para derivar conclusiones sobre la acción de las enzimas, incluyendo el papel del efecto túnel, los efectos electrostáticos o la relevancia de los efectos dinámicos. Este conocimiento puede utilizarse como una guía para el diseño de inhibidores enzimáticos con potenciales aplicaciones en biomedicina, o de nuevos biocatalizadores. Mostraremos en esta comunicación varios ejemplos de KIE primarios, secundarios y enzimáticos calculados sobre diferentes procesos catalizados por enzimas en el marco de la Teoría del Estado de Transición y haciendo uso de potenciales híbridos QM/MM. Nos centraremos en aspectos como el controvertido debate sobre si los movimientos de las proteínas están vinculados a la etapa de la reacción química paso, los efectos cuánticos, la estabilización del estado de transición por efectos electrostáticos, o el impacto de efectos de compresión en reacciones enzimáticas de transferencia de metilo.

Mots-Clés: QM/MM, Free Energies, KIEs, dynamic effects, electrostatic effects, HIV1, PR, GNMT

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Communications

Comm_01 - Explications chimiques et représentations de la matière en chimie

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Quelques réflexion générales inspirées par une longue pratique de la Chimie Quantique.

Mots-Clés: interpréter, représenter, expliquer

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Comm_02 - Formación espontánea de radicales y generación de esponjas de aniones a través de enlaces de Berilio

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La formación de radicales, por la fisión homolítica del enlace Y-R en una amplia serie de compuestos (Y = F, OH, NH_2, R = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, NO), se favorece dramáticamente por la asociación de la molécula con derivados BeX2 (X = H y Cl), como demuestran cálculos *ab initio* de alto nivel. Este comportamiento es consecuencia de dos efectos concomitantes, el gran debilitamiento del enlace Y-R después de la formación del enlace de berilio Be···Y y la enorme estabilización del radical $F^\bullet$ ($OH^\bullet$, $NH_2^\bullet$) tras su asociación con la molécula de BeX_2. En aquellos casos en que R es un grupo electronegativo, la formación de los radicales no sólo es exergónica, sino además espontánea.[1]
Cálculos similares muestran igualmente que los derivados de 1,8-diBeX-naftaleno (X = H, F, Cl, CN, CF_3, $C(CF_3)_3$) se comportan como esponjas aniónicas, de análoga forma a la que los derivados 1,8-bis(dimetilamino)naftaleno se comportan como esponjas de protones. El hecho de que los sustituyentes BeX sean grupos típicamente deficientes de electrones favorece una fuerte transferencia de carga desde el anión hacia dicho grupo, lo que da lugar a afinidades de aniones que están entre las más grandes publicadas en la literatura para moléculas neutras. [2]
Análogamente, estos derivados de berilio exhiben una gran afinidad electrónica, al ser capaces de formar enlaces Be-Be de un electrón muy fuertes. [3]

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Mots-Clés: Beryllium bonds, Radicals, Anion sponges, one electron bonds

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Comm_03 - De glaciēbus or Deductive Molecular Mechanics of Crystalline Water

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Yet in 1960' s Del Re with coworkers considered electronic structure of organic molecules using hybrid orbitals. They studied simplest molecules: CH_4, NH_3, H_2O, and more complex ones: cyclopropnae, cyclobutane, cubane, using either the optimal overlap or maximal localization principles to determine the hybrids. Malrieu with coworkers used hybrid orbitals in the PCILO method. Later, we determined either the form and orientation of the hybrid orbitals or two-electron functions of the two-center bonds constructed in the basis of these hybrids from the minimum condition for total electronic energy as implemented in the SLG method. This produces significant efficiency improvement: the dependence of the required computational resources on the molecule size reduces to *O(N)*. The paradigm based on the usage of the variation principle for determination of either the hybrid orbitals or the elements of the reduced density matrices in their basis, allows one to formulate and prove exact statements about the electronic structure. We start from establishing the energy expression for highly symmetric non-molecular ice X and prove mathematically the stability of this polymorph above critical external pressure. Below the critical one we derive the pressure dependence of the interaction energy of the effective dipoles emerging in the system when the symmetric lay-out of the hydrogen atoms between the oxygen atoms, characteristic for ice X, breaks down. This reproduces semiquantitatively the characteristic and unusual form of the boundary between the areas of the ordered and disordered ices VIII and VII. We also discuss the possibility of describing the differences between the ices phases existing at lower pressures (down to normal) of account of including the long-range electrostatic contributions: charge-charge (Madelung) and dipole-dipole (orientational) into the crystal energy.

Mots-Clés: water, ice, Deductive Molecular mechanics, phase diagram

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Comm_04 - Fully Internally Contracted Multi-reference Perturbation Theory using Density Matrix Renormalization Group

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Modern electronic structure theory has a crucial role to play in various domains of active research, for example in understanding biological processes involving transition metals, or in helping the design of efficient energy storage and energy conversion materials. These systems are challenging for the state-of-the-art models of electronic structure, but promising leads are developed by the community. Among those leads one can find implementatons of Multi-Reference Perturbation Theory (MRPT).
The latest interests in MRPT include the use of Density Matrix Renormalization Group (DMRG) techniques as a zero-th order solver. This amounts to a treatment of the systems using for the multi-reference theory an active space of considerable size. The application of this DMRG/PT scheme to the large molecules that are of interest for biological processes and for energy storage materials requires some efforts toward the efficient implementation of approximations.
Lately, our group have implemented a fully internally contracted version of several multi-reference perturbation theory versions (NEVPT, MRLCC, ...) up to third-order, coupled with density fitting and cumulant approximation for the higher reduced density matrices involved in the derivation. These steps are but a starting point towards the treatment of large molecules and clusters.

Mots-Clés: multi reference, perturbation theory, density matrix renormalization group

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Comm_05 - A QM/MM Approach to Chiroptical Properties and Spectroscopies of Aqueous Solutions

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Modeling chiroptical properties, i.e. the response of a chiral system to the left- and right- circularly polarized light, is a challenging topic in modern quantum chemistry [1]. In particular, it has been demonstrated that it is only by including solvent effects that chiroptical spectra directly comparable with experiments can be obtained [2]. Currently, the standard procedure to include the effects of the environment on such properties is limited to continuum solvation models [3]. However, such approaches can completely fail at describing strongly interacting solute-solvent couples [4].
In this contribution, a QM/MM/continuum model based on fluctuating charges (FQ), that can greatly improve the description of chiroptical properties when an aqueous solution is considered, is presented [5-8]. For some particular examples it will be shown how our mixed explicit-implicit strategy substantially improves the agreement between calculations and spectroscopic measurements compared to continuum solvation approaches [9-11].

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Mots-Clés: QM/MM, Spectroscopy, Solvent Effects

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Comm_06 - Excited states deactivation in model proteins chains: Nonadiabatic dynamics simulations and ab initio methods

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Following UV absorption, many **biomolecular systems** are endowed with mechanisms of **excited-states deactivation** that ensure their **photochemical stability**. One of the major goals of our research is to investigate conformer-selective dynamics of biologically relevant molecular systems by an original innovative computational strategy in order to document the **basic physical phenomena** controlling the **lifetime** of excited states, highlighting the **link between electronic dynamics and structure**. This **innovative multi-step computational strategy** allows to both characterize the first excited states of bio-relevant systems and model efficiently their potential energy surfaces, using, first, **non-adiabatic dynamic simulations** based on TDDFT (NA-TDDFT) to provide hints about the critical motions that drive the deactivation, which will then be **investigated at a better level** with two families of methods: i) the **standard approximate coupled cluster** singles and doubles method (CC2) and ii) and **multireference** (MRCI) methods. **Developed** on small capped peptide models and always backed up by **key conformation-selective gas phase experiments** carried out in our team at several timescales,[1,2] this innovative strategy is now applied to monohydrated capped peptides as well as capped dipeptides. We will present here the last results obtained on these systems. In addition, **benchmark of the CC2 method** on a set of model peptide chains [3,4] as well as **assessment of the CC2 method validity** from comparison with **MRCI methods** [5] will be also reported.

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Mots-Clés: Excited states computations, Photochemistry of biomolecules, Nonadiabatic dynamics, Size extensive CC and MRCI linear scaling methods, TDDFT

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Comm_07 - Reactive molecular dynamics with ReaxFF: Complex chemical engineering processes simulated at the atomistic level.

Ole Carstensen *† [1]

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Reactive molecular dynamics techniques such as ReaxFF afford valuable insight in highly complex chemical processes such as combustion, heterogeneous catalysis, battery discharge and material degradation.
The talk will highlight recent developments in the ADF/ReaxFF code.
New ReaxFF force fields can be parametrized with the help of a Monte Carlo based global optimization procedure put forward by E. Iype and coworkers.
Automated detection tools give both qualitative and quantitative insight in chemical reaction networks. Even highly complicated reactions can be mapped out and interactively browsed and reaction rates automatically determined.
The recently developed eReaxFF-method put forward by A. van Duin and coworkers allows for a pseudo-classical treatment of explicit electrons. First eReaxFF simulations of reductive decomposition reactions in Li-ion batteries indicate an adequate description of redox reactions in complex interfacial reactions.
Accelerated dynamics techniques such as force-bias Monte Carlo give access to even longer time scales at the molecular level, enabling better integration with mesoscale tools for multi-scale methods used for modeling chemical engineering problems.

Mots-Clés: Reactive Force Fields, Molecular Dynamics, Batteries, Combustion, Reaction Networks, Kinetics, Reparametrization, ReaxFF, Atomistic

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Comm_08 - Vibrational computations beyond the harmonic approximation: from molecules to periodic systems

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The talk deals with time independent (static) vibrational computations beyond the harmonic approximation as implemented in the CRYSTAL code [1]. The Vibrational Configuration Interaction procedures from Harmonic Oscillators (VCI-HO) [2] or Vibrational Size Consistent Field (VCI-VSCF) basis sets are detailed. The Anharmonic treatment of Infrared (IR) and RAMAN activities which provides information about intensities of overtones and combination bands is also presented. The construction of anharmonic force fields and its improvement from the concept of Adaptative Generation of Potential Energy Surfaces [3], particularly for a better description of soft modes and double well problems, is discussed. These implementations which might be necessary to correctly analyse experimental IR or RAMAN spectra of molecules (0D), polymers (1D), surfaces (2D) and crystals (3D) are illustrated by several examples.

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Mots-Clés: code crystal, anharmonicité, systèmes périodiques

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Comm_09 - Some Remarks on Activation and Relaxation Processes in Chemical Reactions : la Merveilleuse Équation de Marcus

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Activation and relaxation processes have been studied in many different contexts, mainly with the aim of getting insights on the physical nature of the forces that triggers these processes. The Marcus equation [1] is one of the most famous and successful analytic forms that provides nice ways to rationalize the activation energy and to characterize the transition state through the Hammond postulate [2] and the Br'onsted coefficient [3]. The Marcus' equation involves the reaction energy and the so-called Marcus' intrinsic activation energy that describes the structural distorsion of reactants at the transition state. On the other hand, activation and relaxation processes can bestudied from the perspective of the reaction force analysis (RFA) [4,5,6], in this context rational partitions of direct and reverse activation energies emerges naturally. Within the RFA's framework the activation and relaxation energies are characterized in terms of reaction works defined at different regions along the reaction coordinate, thus producing interesting insights on energy barriers and rate and equilibrium constants. In this presentation, Marcus equation and RFA approaches to activation and relaxation processes are compared and discussed, few examples of different kind of chemical reactions are used to illustrate the discussion on the physical nature of activation energies.

Acknowledgements: Financial support from ICM, Milenio Grant N° 120082, Nucleus Millennium CPC is acknowledged.

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Mots-Clés: Marcus Equation, Activation Energy, Transition State, Reaction Force Analysis

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Comm_10 - The Virtual Multifrequency Spectrometer: status and perspectives of an undergoing project

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The impressive advances of computer power, effective and user friendly software and graphical interfaces are leading to the development of a new generation of virtual tools able to deal effectively with the complex systems and phenomena of current interest in the study of molecular systems. Going from collections of numbers for oversimplified models toward vis-a-vis comparison between in silico and in vitro outcomes for real systems together with 3D renderings and natural interfaces should finally overcome the diffidence of experimentalists versus theoreticians mentioned in the title. Among those virtual instruments, we will be concerned here with the multifrequency spectrometer (VMS) our group is developing in the last few years [1], which allows vis-a-vis comparison of experimental spectra with their simulated counterparts and interpretation of the results in terms of the interplay among different well defined effects [2,3]. The main building blocks of this tool are, apart from powerful 3D pre- and post-processing tools, first-principle and semiempirical models based on the density functional theory for the proper treatment of stereo-electronic effects, polarizable atomistic and continuum models to deal with environmental effects, and perturbative treatments for describing nuclear motions either beyond the harmonic level, or involving more than one electronic state [8]. In this presentation I will sketch the present status of the multifrequency spectrometer and the ongoing efforts toward increasing its range of application with special reference to excited electronic states of molecular systems both in the gas phase and in more complex environments. Some case studies will be selected to better illustrate the above concepts.

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Mots-Clés: Computational Spectroscopy, Software, Graphical User Interface

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Comm_11 - Simulation of electron dynamics in polarizable environments

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In this communication, an original methodology for simulating attosecond electron dynamics in large molecular systems will be introduced [1]. Our approach is an original combination of Real-Time Time-Dependent-Density-Functional-Theory (RT-TDDFT) [2] and polarizable Molecular Mechanics (MMpol) with the point-charge-dipole model of electrostatic induction [3]. This methodology has been implemented in the software deMon2k [4] and relies heavily on auxiliary fitted densities. In the context of RT-TDDFT/MMpol simulations, fitted densities allow the cost of the calculations to be reduced drastically the cost of the Kohn-Sham potential calculation and of the polarizable QM/MM interaction. Tests of the using of fitted densities gave encouraging results both for computational efficiency and accuracy. The methodology will be applied to the determination of absorption spectra. I will analyze the distance-dependent responses of the environment of a peptide perturbed by an electric field. Different response mechanisms are identified. It is shown that the induction on MM sites allows excess energy to dissipate from the QM region to the environment. In this regard, the first hydration shell plays an essential role in absorbing energy.

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Mots-Clés: Real time TDDFT, polarizable QM/MM, attosecond dyamics, solvent

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Comm_12 - Ozone and other 1,3-dipoles: toward a quantitative measure of diradical character

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Ozone and its sulfur-substituted isomers are studied by means of the Breathing Orbital Valence Bond (VB) ab initio method, with the aim of estimating their controversial diradical characters. The calculated weights of the various VB structures and their individual diabatic energies are found to be consistent with each others. All 1,3-dipoles can be described in terms of three major VB structures, one diradical and two zwitterionic ones, out of the six structures forming a complete basis. It will be shown that the VB-calculated weight of the diradical structure of a molecule qualifies itself as a quantitative measure of diradical character, and not only an indicator of tendencies. Moreover, the description of 1,3-dipoles in terms of the three major VB structures yields VB weights in full agreement with simple chemical wisdom.

Mots-Clés: Valence Bond, Lewis structures, diradical character, 1_3 dipoles.

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Comm_13 - An effective quantum dynamics approach to charge transfer in molecular wires: the hole transfer in DNA

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A new methodology to study the dynamics of hole (or electron) transfer processes in bridged systems which relies on the partitioning of the Hilbert space of the time independent vibronic states in subspaces of increasing dimensionality is presented. In that method, DNA is described as a supramolecular assembly formed by interacting sites, the nucleobases, in which a hole has been injected. Since each nucleobase can be found either in its neutral or charged state, a set of orthogonal diabatic electronic states is adopted, corresponding to the hole fully localized on one molecular site, so that only one uncoupled hole energy per type of nucleobase and only one electronic coupling per base-base dimeric stack are the needed parameters. Hole energies and electronic couplings have been obtained by analyzing the ionization energies of specific DNA sequences in terms of a generalized two state model. Ionization energies of oligonucleotides including the sugar-phosphate backbone and solvation have been computed at the DFT level. The reliability of the model Hamiltonian and the quality of the parameters is demonstrated by the excellent agreement between predicted and observed hole-trapping efficiencies of adenine/guanine tracts. Furthermore, kinetic constants computed by solving the time dependent Schroedinger equation with a specifically tailored strategy for pruning the basis set of vibronic states reproduce in a quantitative way the observed distance dependence of hole transfer rates, shedding light on the role played by delocalized domains in the hole transfer process in DNA.

Mots-Clés: Quantum dynamics, Hole transport, DNA oxidation

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Comm_14 - Range separated double hybrid approximations: inclusion of wavefunction theory at the short range part

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Over the past two decades, Kohn-Sham DFT (KS-DFT) [1] has been a method of choice to study ground state properties of large systems. KS-DFT is formally exact, but it involves a functional called the exchange-correlation functional. Nevertheless, the exact form of the exchange-correlation functional is still unknown, hence semilocal density functional approximations (DFAs) has been developed in order to improve the accuracy of KS-DFT. Semilocal DFAs are able to describe properties that depend on short-range exchange-correlation effects, molecular geometries and bond enthalpies for instance. However, there are still some problems to be addressed. One problem concerns the issue of self-interaction error (SIE): in one electron systems, the Hartree and exchange functional do not cancel each other exactly. Another problem associated to the current DFAs is related to the fact that the correlation functional does not take into account dispersion interactions. Perhaps the most appealing approach to deal with the problem mentioned above consists in developing range separated double hybrid functionals, which mix exact exchange and non local correlation effects. These methods are able to deal with the SIE and to take into account the dispersion interactions.
In standard range separated hybrid methods [2], the short range part of the Coulomb interaction is usually handled by a functional of the density while the long range electron interaction is treated by wavefunction theory. Here, we propose to include a fraction of wavefunction theory in the short range part in order to improve the accuracy of short range properties.

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Mots-Clés: range separated double hybrid, DFT

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Comm_15 - Analysing the Density-Based Index Behaviour in Photochemical Reactions within Post-HF and DFT Methods

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The DCT density-based index allows in a simple and intuitive way to quantify the spatial extend of a charge transfer excitation within a molecule. The construction of the index only requires access to the ground and excited states total electron densities. Hence, any quantum method supplying these electron densities is suited to compute the DCT index. Although this index has proven to be a powerful tool in the analysis of different photochemical reactions within the density functional theory, to the best of our knowledge, no work in the literature has ever reported an application of this index using wave-function theory methods. The main goal of this project is to show that the DCT index is a good descriptor of the excited states not only in density functional theory (DFT) but also in wave-function theory (WFT). To this end, the DCT results obtained for an organic photochemical reaction using both DFT and WFT approaches are analysed and compared in this study. The reaction studied concerns the photoinduced enol-keto tautomerization of the 2-(2'-hydroxyphenyl)benzothiazole (HBT) which is a very well-known example of an excited state intramolecular proton transfer (ESIPT). A reduced model of the HBT molecule is used in this project. Upon photoabsorption, redistribution of electronic density across the molecule increases the acidity/basicity of the donor/acceptor groups involved resulting in a fast proton transfer in the excite state. Phototriggered molecular rearrangements like this ESIPT have gained an ever-growing interest among the scientific community, over the last few decades. This interest arises from the wide scope of technological applications ranging from optical high capacity storage devices to miniaturized photomechanical gadgets. Funding: This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 648558, STRIGES CoG grant).

Mots-Clés: Excited States, Charge Transfer, DCT Density Based Index, Excited State Intramolecular Proton Transfer (ESIPT), enol keto tautomerism, Photochemistry

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Comm_16 - Exploration des processus de fragmentation des HAP par dynamique moléculaire/DFTB

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L'étude de l'évolution physicochimique (formation, destruction, réactivité) des hydrocarbures aromatiques polycycliques (HAP) interstellaires fait actuellement l'objet de recherches intensives. Dans les régions de photodissociation du milieu interstellaire, les HAP sont soumis à des photons UV. Suite à cette absorption, l'énergie peut être dissipée par ionisation, relaxation radiative dans l'infrarouge, transitions électroniques, ou éjections de petits fragments neutres comme H, H_2, C_2H_2 [1]. Dans des environnements plus violents, les HAP peuvent être détruits par les vents stellaires, ondes de choc et collisions avec des atomes de gaz ionisé. Avancer dans la compréhension de ces phénomènes requiert la synergie entre études astrophysiques et de laboratoire, expérimentales et théoriques. Ce travail entre dans ce contexte.
Nous présentons des études de dynamique moléculaire sur la dissociation des cations HAP de taille croissante du naphtalène $C_{10}H_8$ au coronène $C_{24}H_{12}$. Elles sont menées dans l'état fondamental électronique, la structure électronique étant déterminée en vol avec l'approche SCC-DFTB (Self-Consistent Charge Density Functional based Tight Binding) [2]. La dépendance des voies et de la cinétique de fragmentation avec la taille et l'énergie interne a été étudiée [3]. Les résultats seront discutés à la lumière des approximations effectuées.
La dissociation est précédée de réactions d'isomérisation, impliquant des migrations de H et des ouvertures de cycle C-C, ces dernières conduisant à la formation de cycles à 5 et à des fonctions éthynyles. Des études DFT statiques ont été effectuée afin d'extraire les barrières énergétiques typiques pour ces processus élémentaires [4]. La compétition entre les processus de déshydrogénation et d'isomérisation sera discutée.

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Mots-Clés: dynamique moléculaire, DFTB, dissociation, HAP

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Comm_17 - Ibuprofen and its analogs as COX-1 inhibitors: Discrimination of their enantiomers' binding modes using molecular dynamics

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Ibuprofen is the first drug of Propionic acid derivatives introduced in 1969 as a better alternative to Aspirin. Its effects are due to the inhibition of cyclo-oxygenases (COX-1 and COX-2), involved in the synthesis of prostaglandins. In this work, ibuprofen and some of its analogs, selected from the literature with their relative activity on COX-1 enzyme [1, 2], are chiral compounds but one of them can be toxic. In order to assess the anti-inflammatory activity of each of the pure enantiomers, it would be useful to first predict *in silico* the enantiomer that is responsible for the activity. Therefore, we investigated them using theoretical modeling aimed to discriminate between the two enantiomers of the same compound. Firstly, a molecular docking study was performed in the active site of cyclooxygenase-1(COX-1). Thereafter, molecular dynamic (MD) simulations were carried out, in the physiological environmental conditions.
The structural and energetic information obtained from the MD simulations results, allowed to understand the difference in binding modes between the two enantiomers of each compound.
MD Simulations study highlighted the major role of water molecules in ligand-protein interactions. This combined computational approach reveals, without any ambiguity, that the binding mode of the ibuprofen's S-enantiomer and that of its analogs, within COX-1 active site, is more favorable than that of R-enantiomer.

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Mots-Clés: COX 1, Chiral NSAIDs, Ibuprofen analogs, MD simulations, Binding modes

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Comm_18 - Dipolar effects in magnetic nanoparticle assemblies from Monte Carlo simulations in the framework of effective macro spin models.

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The field of nanoscale magnetic materials is still very active for both the potential applications (nanomedicine, high density recording) and the fundamental aspects which are all the more important that magnetic nanoparticles can be synthetized in a wide range of size and shapes and assembled in a large diversity of organizations.

Under a critical size of typically few tenth of nanometer in diameter, corresponding to the minimal size for the material to accomodate domain walls, magnetic nanoparticles are single domain objects. Then for sufficiently hard materials, i.e. when vortex formation can be avoided, the local magnetization structure at the atomic scale does not play a central role and one can model the macroscopic properties of magnetic nanoparticles assemblies via dipolar hard sphere like models widely studied in the more general field of dipolar fluids.

In this presentation we limit ourselves to the case of well coated nanoparticles, free of super-exchange interactions, and thus interacting only through the dipole-dipole interaction (DDI) to which we add the magnetocrystalline energy (MAE). The latter is to understood as an effective anosotropy energy and in general present a uniaxial symmetry. We present mainly some peculiarities of the ordered magnetic phase which can occur at low temperature and discuss the conditions under which supra crystals made of nanoparticles can present a dipolar ferromagnetic phase (super- ferromagnetic, SFM, phase).

Mots-Clés: Magnetic nanoparticles, Monte Carlo simulations, Nanoscale magnetism.

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Comm_19 - Computational insights on the molecular basis of the inhibition of Prostaglandin Endoperoxide H Synthase 2 (PGHS-2 or COX-2) activity by nitroarachidonate

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Prostaglandin Endoperoxide H Synthases (PGHSs) are heme enzymes that catalyze arachidonate (AA) oxidation to prostaglandin H2 (PGH2). PGHSs are homodimers that function as conformational heterodimers composed of an allosteric subunit and a catalytic one, each containing both cyclooxygenase (COX) and peroxidase (POX) sites. The COX activity of PGHSs converts AA and O2 to prostaglandin G2 (PGG2), which is reduced to PGH2 by thePOX activity. PGHSs have pharmacological importance as targets for anti-inflammatory drugs. Nitro-fatty acids are novel endogenous signaling mediators, exerting pluripotent anti-inflammatory actions in cells and tissues. Among them, nitro-arachidonic acid (NO2AA) inhibits PGHS-1/-2, both *in vitro* and in biologically relevant cellular models, through a mechanism involving heme cofactor displacement from binding in the POX site, leading to loss in POX and COX activities. Using PGHS-2 variants with mutations at the COX or POX sites we showed that NO2AA inhibition would not involve residues at the former site, while H207 and H388 at the POX site appeared as directly implied. Here we apply a computational approach to gain further insight into a detailed mechanism consistent with such observations. The use of the single catalytic subunit as a reduced model for assessing inhibition was firstly validated by 500 ns of classical MD simulations on the PGHS-2 dimer and the catalytic subunit alone with bound AA. The interaction of NO2AA was thus examined in detail by combining MD simulations and QM/MM calculations using the monomer with bound AA. Our results show that NO2AA binds into the POX site disrupting the normal disposition of residues required for a proper positioning of the heme cofactor and to maintain iron with the adequate reduction potential. NO2AA interaction also affects the structure of the COX site, altering residues that are important for a productive binding of the AA substrate.

Mots-Clés: PGHS_2, nitroarachidonate, MD simulations, QM/MM

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Comm_20 - Cs^+/π interactions and the capture of environmental radiocesium

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A recent database analysis of crystallographically determined cesium complexes revealed that the macrocyclic receptors bearing aromatic substituents have the ability to establish multiple Cs^+/π interactions with this ion [1]. To unravel the nature of Cs^+/π interactions in the above complexes, we have computationally investigated two simple models, the first one where a single Cs^+ ion interacts with the arene C6R6 (R=H,F,Cl,Br) and a second one containing a counteranion interacting with the arene and placed on the opposite side of Cs^+. The electronic charge densities of these two models have been subject to topological analyses based on the quantum theory of atoms in molecules (QTAIM).
We intend to exploit the present QTAIM results in the design of artificial receptors for the recognition of Cs^+ ions which represent an environmental hazard when released from nuclear power plants as radioactive Cs-137 [2,3]. In particular, we aim to functionalize different macrocycles with one or more phenyl groups so as to enhance their selectivity toward the complexation of Cs^+ which can be coordinated using the oxygen atoms of the carbonyl or carboxyl groups that are already present on the receptor.

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Mots-Clés: Ion recognition, noncovalent interactions, radioactive nuclides, computational environmental chemistry, DFT, QTAIM

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Comm_21 - Assessing Density Functional Theory Approaches for Predicting the Structure and Relative Energy of Salicylideneaniline Molecular Switches in the Solid State

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Molecular switches, such as photochromic and thermochromic compounds, are widely studied because of their potential applications in sensing devices. The focus (design and characterizations) was mainly on the liquid state, in both experimental and theoretical studies. However, in order to move toward real applications, the liquid phase is replaced by the more practical solid phase, i.e. by crystallization. Using various density functional theory exchange-correlation (XC) functionals (of which several have been tuned for the solid state), the geometrical structures and relative energies of salicylideneaniline (anil) molecular switches in the crystalline state have been determined using periodic structure calculations. The first target was on predicting the unit cell and intramolecular geometrical parameters for three anil derivatives. Of which, two are in majority in the enol (E) form ((E)-2-methoxy-6-(pyridine-3-yliminomethyl)phenol, PYV3 and N-(5-chloro-2-hydrox-ybenzylidene)-aniline, HC) while the last one in the keto (K) form (N-(5-chloro-2-hydrox-ybenzylidene)-hydroxyaniline, POC). The best performance for the unit cell parameters, in comparison with single-crystal X-ray diffraction (XRD) data, is achieved with XC functionals developed for the solid state (PBEsol and PBEsol0) as well as with ωB97X. The second target was the characterization of the variations of energy and structural parameters when switching between the enol and keto forms. Only hybrid functionals correctly predict which form is the most stable in the crystalline state. Then, the bond length changes in the O-C=C-C=N-C (or O=C-C=C-N-C) π-conjugated segment that occur upon enol to keto transformation are similarly predicted by all functionals and are consistent with the reversal of the single/double bonds pattern.

Mots-Clés: organic crystal, DFT, switch

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Comm_22 - Frozen-density embedding calculation of second-order magnetic properties in the relativistic framework

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Magnetic properties are widely used to gain detailed information on the electronic and geometrical structure of molecules in the condensed phase, the most striking example being that of nuclear magnetic resonance (NMR) spectroscopy. Electronic structure calculations can be valuable tools to help interpret such experimental spectra provided they properly describe, apart from electron correlation, the interaction between the molecule of interest and its environment and, in the case of species containing heavy elements, relativistic effects.
Embedding approaches [1] are efficient alternatives to standard quantum chemical calculations for describing environment effects. Among these, frozen density embedding (FDE) is particularly well-suited to such cases as it can accurately describe specific interactions such as hydrogen bonding, and can be combined to different relativistic Hamiltonians in a straightforward manner.
In this contribution we outline the implementation of the nuclear magnetic resonance (NMR) shielding (σ), isotope-independent indirect spin-spin coupling (K) and the magnetizability (ξ) tensors for FDE using the four-component (4c) relativistic Dirac–Coulomb (DC) Hamiltonian and the non-collinear spin density functional theory (SDFT). [2] The formalism takes into account the magnetic balance between the large and the small components of molecular spinors and assures the gauge-origin independence of NMR shielding and magnetizability results.
We discuss the method's performance compared to supermolecular calculations for hydrogen-bonded $HXH\cdots OH_2$ (X = Se, Te, Po) model systems. Furthermore, we address the differences between 4c results for σ and K and those obtained with the approximate Zeroth-Order Regular Approximation (ZORA) Hamiltonian, in order to assess the latter's accuracy with increased atomic number for the heavy center.

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Mots-Clés: Frozen density embedding, molecular properties, relativistic effects

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Comm_23 - Correlation consistent versus polarization consistent optimized basis sets in density functional calculations of halogen oxide species

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Electronic structure calculations are performed nowadays using molecular orbital (MO) methods or, alternatively, density functional theory (DFT). Simple MO calculations can be improved through a series of well-defined steps. Dynamical electron correlation can be included, at the simplest level, using low-order perturbation theory, like MP2. More exact results are obtained using coupled-cluster theory, most usually CCSD(T), but also CCSDT or even CCSDTQ in certain cases. Non-dynamical correlation energy (i.e. the need of a multideterminantal wavefunction) is usually included employing CASSCF and MRCI calculations. The basis set effect is usually removed considering the complete basis set (CBS) limit.
There is not such a clear cut path for DFT methods. An approximate analogue is the Jacob's ladder hierarchy of DFT methods, as proposed by Perdew. However, it has been suggested that more elaborate approaches are leading us away from expected accuracy. Much discussion is going on in the literature about the precision and accuracy of DFT methods with respect to some molecular sets. More work is needed anyway, especially concerning challenging bonds like those present between atoms with siilar, strong electronegativity, like those present in halogen oxides.
In this presentation, I will talk about the basis set effect (using Dunning's correlation consistent (cc) and Jensen's polarization consistent (pC) basis sets) on some halogen oxides (XO, XOX, XXO, etc) and peroxides (XOO) for X = F, Cl and Br. Dynamic and non-dynamic correlation energy effects, convergence toward the CBS limit and Jacob's ladder effects on the structure and enthalpies of reaction of formation of a few chosen molecules. The main conclusion is that a semiempirical well-balanced approach can be proposed for reasonably accurate calculations (i.e. with errors of about 2 kcal/mol) of these challenging species.

Mots-Clés: Halogen oxides, DFT, M06, CBS, CCSD(T)

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Comm_24 - Low-lying Electronic States of Diatomic Molecules AB (A = Sc – Ni, B = Cu/Ag/Au)

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Diatomic molecules formed by atoms of d-block elements are building blocks for catalytically and photochemically active systems, for nanostructured materials, and for electronic devices that receive considerable attention in both fundamental and applied research, see e. g. **[1]**. Therefore, the detailed study of their electronic structure, in both ground and low-lying excited states, is of great importance. We present a systematic study of low-lying electronic terms of heteronuclear diatomic molecules AB (A = Sc – Ni, B = Cu/Ag/Au). Our approach is based on a scalar relativistic description using the Douglas-Kroll-Hess (DKH) Hamiltonian **[2]**. Subsequently, the Breit-Pauli Hamiltonian **[3]** is used to include spin-orbit coupling perturbatively. In Russell-Saunders coupling, the molecular electronic terms included in our study result from the lowest asymptote(s) $A(^{2S+1}L) + B(^2S)$, where the integer 2S+1 ranges from 2 to 7 and L is either S, or D, or F. Complete potential energy curves (PEC) for several low-lying electronic terms of these molecules (both Lambda–S and Ω terms) have been obtained at the complete active space self-consistent field (CASSCF) and the multi-reference configuration interaction (MRCI) levels of theory. Standard sets of spectroscopic constants as well as dipole moment curves are also available. A group theoretical method **[4]** has been used to determine all relevant molecular Lambda–S or Ω terms, respectively, in each case.
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Mots-Clés: Molécules diatomiques, éléments de transition, chimie quantique relativiste, couplage spin/orbite, opérateur hamiltonien Douglas/Kroll/Hess, opérateur hamiltonien Breit/Pauli

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Comm_25 - Theoretical Study of Porous Surfaces Derived from Graphene and Boron Nitride

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The interest in carbon-like systems had increased considerably due to their great scientific and technological interest in material science and their possible applications in nanoelectronics and nanodevices. There is a particular interest devoted to two-dimensional (2D) graphene-like materials (honeycomb network) which extends it to inorganic materials, such as hexagonal Boron nitride (hBN). The null band gap of graphene leads to a restricted application in electronic devices. Therefore, several ways to modify or replace materials with such limitations attracted the attention of many research groups. Based on this, porous graphene (PG) and the structure called biphenylene carbon (BPC) known as graphenylene and, the inorganic analogous pBN and IGP, respectively, have also called attention as a promising material with non null band gap. Aiming to study, understand and elucidate important properties of porous surfaces with an accurate prediction, is carried out the computational simulations with periodic DFT theory applied to study the structural, electronic, elastic and vibrational properties of such porous surfaces.

Mots-Clés: graphene, Boron nitride, surfaces, porous

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Comm_26 - 8-hydroxyquinoline as a 'green' corrosion inhibitor of Al: a DFT study

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Because of the high toxicity and carcinogenic risks associated with chromates, restrictions are imposed on their use against corrosion of metals. Some potential corrosion inhibitors are environmental friendly organic molecules: the 8-hydroxyquinoline (8HQ) is an efficient corrosion inhibitor of aluminum. In order to elucidate the origin of the inhibition mechanism at the atomic level, we performed Density Functional Theory computations. We investigated the adsorption mode of the 8HQ molecule and its derivative, tautomer and dehydrogenated molecules, on ultrathin aluminum oxide layer supported on the parent Al metal. The chemisorbed mode is the most stable mode for the dehydrogenated 8HQ and the tautomer, while the native 8HQ can only physisorb on the surface. At half and full ML, dehydrogenated species have the largest adsorption energy (-2.73 and -3.18 eV/molecule, see Figure 1) followed by tautomer (-1.54 and -2.00 eV/molecule) and 8HQ molecules (-1.06 and -1.29 eV/molecule). The stability of the organic layer on the surface increases at full coverage (ΔE = -0.45 eV for the dehydrogenated and tautomeric form, ΔE = -0.23 eV for the native 8HQ). All chemisorbed molecules form covalent bonds with the Al atoms of the oxide and electronic transfer occur from the aluminum oxide to the molecule and to the aluminum metal. The electronic features (Density of States, charge variation...) and the inhibition of the reduction of O2 in presence of the molecules bring information about the protection mechanism.

Mots-Clés: adsorption, aluminum, corrosion inhibition, surface, 8HQ

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Comm_27 - Ab initio study of the Solvent-Electrode Interface under electrochemical conditions

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The electrochemical interface is fundamental to understand electrochemical reactions either for electrocatalysis applications (fuel cells), corrosion, electroplating or for energy storage such as Li-ion batteries. Nevertheless, it is extremely complex to model not only because of the occurring electrochemical effects but also because of the complexity of the electrode-solvent interface. Classical models fairly well reproduce the behavior of such an interface by introducing more or less complex description of the electric double layer (Helmholtz plane, diffuse layer etc.), but are oblivious to the quantum phenomena occurring at the interface. Ab initio approaches can describe this quantum behavior with good accuracy, nevertheless most of these approaches are not accounting the full complexity of the electrochemical interface as it would necessitate including the solvent (at least hundreds/thousands of molecules) and electrolyte (with their interaction with the solvent and the surface) in their structural and time-dependent dimension leading to costly calculations. We will present a mixed implicit/explicit solvent approach (exemplified by a Li/Ethylene carbonate interface) that allows recovering the proper electrochemical properties (surface capacitance...) at a limited cost. We will highlight the effect of the model parameters on the quality of the calculation. We will discuss how implicit/explicit model should be used in order to recover the potential stability for Li-electrodes in carbonate solvents and how the electrode growth or consumption are linked with the local chemical/electrochemical parameters. We will also focus on the interface electrification and how part of the electrode charge can partially delocalized on the closest solvent layer. This effect has a strong impact on surface electrochemical reactivity and can be investigated by mean of the Fukui function descriptor. Finally, the impact of the electrochemical dimension on the reactivity can also be rationalized by including the solvent approach and can gives quantitative insights into an interface electrochemical reactivity.

Mots-Clés: electrochemistry, interface, solvent, Fukui

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Comm_28 - Theoretical design of new metal hydrides $NiMg_3AlH^-_{2n}$, n = 1-6.

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Recently we have reported a theoretical design of new metal hydrides clusters based on the high stability of the $Al_4H^-_7$ system [1]. Our results showed that the systems with the higher stability and a high percentage of hydrogen, by weight, correspond to systems where three aluminum atoms have been substituted by three Mg-H and Be-H units, $Be_3AlH^-_{10}$ and $Mg_3AlH^-_{10}$ systems. Interestingly, these tetrahedral conformations persist after being doped with Na^+ as contraion. Investigations in the area of hydrogen storage reveal that the combination of elements such as nickel and magnesium generates high-efficiency materials. In this work we report a theoretically study about of which is the effect on the hydrogenation process when a nickel atom is added in a Mg-Al cluster, with a ratio of 3:1 (Mg_3AlNi^- cluster); this cluster is stable: a closed shell system within a Jellium model. The explorations on the potential energy surfaces (PES), for the hydrogenation process with H_2, showed that this cluster allows stabilizing, covalently, up to twelve hydrogen atoms ($Mg_3AlNiH^-_{2n}$, n = 1-6). The global minima conformations show that the Ni atom is being located in the center of the system as n increases, obtaining a maximum coordination number of 8: four Ni-H, and four Ni-Mg and Ni-Al bonds. Finally, the calculations on the dehydrogenation energies showed that the energy required removing a hydrogen molecule increase as n raise, from 13 to 30 kcal.mol-1. The results obtained in this work shows that the cluster $NaMg_3AlNi$ should be used as assembly blocks for the formation a larger system.

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Mots-Clés: Metal Hydrides, Atomic clusters, hydrogenated atomic clusters.

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Comm_29 - Diabatic Strategies for Molecular Photodynamics

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Quantum dynamics simulations applied to ultrafast photoinduced processes often require an adiabatic-to-diabatic transformation (diabatisation) of the data produced from quantum chemistry calculations. The vibronic coupling Hamiltonian (VCH) quasidiabatic model developed by K'oppel and coworkers is a fruitful strategy that has been used for calculating photoabsorption and photoelectron spectra with the multiconfiguration time-dependent Hartree (MCTDH) method. We present here an example of strategy whereby a generalised VCH approach was applied to the description of the excited-state intramolecular proton-transfer (ESIPT) process in 3-hydroxychromone simulated with the multilayer formulation of MCTDH termed ML-MCTDH [1].
Alternatively, the direct dynamics variational multiconfiguration Gaussian (DD-vMCG) wavepacket method frees simulations from this preliminary step by calculating the potential energy and its derivatives on the fly. Various diabatisation procedures for generating quasidiabatic Hamiltonians on-the-fly have been implemented in the current code and are being tested at the moment. This is illustrated with simulations of internal conversion in fulvene [2,3].

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Mots-Clés: Photochimie, photophysique, états excités, intersections coniques, diabatisation, dynamique quantique non adiabatique

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Comm_30 - Nanoscale mixing favourability of Titanium and Silicon Oxide materials

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Oxides based on mixing titania and silica represent an important class of materials widely studied and used for many technologically and environmentally friendly applications such as solar cells, self cleaning systems, gas sensors, selective molecular sieves, material for removing water pollutants and photocatalysts for many reactions. In many applications titanosilicates not only take advantage of the properties of pure titania (semiconductor) and silica (high thermal stability and high mechanical strength) but from the symbiotic properties which emerge from the TiO_2-SiO_2 interaction. As an example, one of the most industrially important mixed TiO_2-SiO_2 materials, known from early 80s, is the synthetic titanosilicate-1 (TS-1). It is used as industrial redox catalyst for oxidizing organic molecules in mild conditions with the presence of hydrogen peroxide. The active site is an isolated 4-foulded titanium uniformly dispersed in a porous silica structure with 1.0-2.5% of TiO_2 molar inclusion. In such systems, it is relatively difficult to increasing the amount of active Ti-centers due to their tendency to aggregate and separate into two phases. This suggest that titania and silica mixing at bulk level is unfavourable. At nanoscale (_~ 1 nm nanoparticle diameter), however, the mixing between TiO_2 and SiO_2 is favourable for a wide range of mixing compositions. Here, we want to achieve a better understanding of the driving force behind the mixing of titania with silica at a fundamental microscopic level. For doing so, we use a range of computational modelling methods such as Monte Carlo Basin Hopping global optimization approach and Density Functional Theory. Our primary goal is to understand why and how these materials mix together at the nanoscale. The secondary objective is to design new titanosilicate materials based on the acquired knowledge, (theoretically) characterize them from chemical-physical point of view, and provide useful information in order to experimentally synthetize them.

Mots-Clés: Global optimization, Monte Carlo Basin Hopping, mixed oxides, nanoscale, nanoparticles, titanosilicates

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Comm_31 - Etude mécanistique de la photoaquation d'un complexe polypyridylique de ruthénium

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Photoluminescence and photoreactivity processes in polypyridyl Ruthenium(II) complexes have attracted a considerable attention over the last four decades. Among all these processes, ligand substitution is one of the elementary reaction of photoexcited complexes and a large number of experimental studies have focused on photosubstitution reactions in polypyridyl Ruthenium(II) complexes. Indeed, there are obvious interests for these complexes in biological applications (light-activable anticancer compounds, light controlled molecular machine) or in technological application. However, theoretical mechanistic studies of photosubstitution reaction are still scarce. Following the work of Roberts&Stavros (PCCP **2014**), Morokuma (JCTC **2014**), Schlegel (Inorg. Chem. 2015), we will show what we believe contribute to understand the underlying mechanism of the photocleavage process. From this combined experimental and DFT study, we propose, by determining an adiabatic pathway, an explanation of the influence of four different polypyridyl spectator ligands on the quantum efficiency of the photosubstitution of a thioether ligand by a water solvent molecule. This work reveals that the different behavior of ruthenium complexes in term of quantum yield of photosubstitution can be rationalized by the existence of a particular photoreactive ligand-field state (3MC) and by the different topology of the corresponding triplet excited-state potential energy surfaces.

A.G'otlle, F.Alary, M. Boggio-Pasqua, I.Dixon, J-L. Heully, A. Bahreman, S. Askes, S.Bonnet, Inorg Chem, 10.1021/acs.inorgchem.6b00268

Mots-Clés: Photochemistry, Ruthenium, triplet states, DFT

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Comm_32 - The adsorption of dopamine on nitrogen-doped graphene: a DFT study

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The DA (dopamine) molecule is an important neurotransmitter that plays a significant role in the function of the mammalian central nervous, renal and hormonal systems. The detection of dopamine performed by voltammetric techniques with graphene electrodes was a subject of increasing interest, taking into account that dopamine is an electrochemically active compound through the oxidation of DA phenolic hydroxyls. Recently the dopíng of graphene with nitrogen in these electrodes has been proposed as a way to achieve a better resolution in oxidation peaks. In the present work, the neutral DA adsorption on the G (graphene) surface and three different G-N (defected graphene with nitrogen as dopant) systems was studied in the framework of DFT (Density Functional Theory) formalism as implemented in VASP (Vienna Ab-initio Simulation Program) code. The surface was modeled with a slab where G is replicated in the normal direction with a vacuum gap of 25 Å. In the calculations, the vdW-like dispersive interactions were taken into account by using the vdW-DF2 method due to Langreth y Lundquist. The G supercell has 50 carbon atoms. Several adsorption modes for the DA/G and DA/G-N systems were considered. In general, the adsorption modes where the molecule is parallel or quasi-parallel to the surface are the most favored. The substitutional doping with nitrogen in graphene lattice regular sites increases the magnitude of adsorption energy, making these sites more appropriate for the anchoring of molecules that undergo the oxidative electrochemical process. In all cases considered the adsorbate-substrate interaction is in agreement with the presence of a fisisortive adsorption. Nevertheless, an important electronic charge redistribution occurs due to adsorption. The attractive non-covalent interactions of the different DA/G-N systems were analyzed with the non covalent index (NCI) and the electronic structure by means of the projected density of states concept.

Mots-Clés: Dopamine, Graphene, N doping, Adsorption, VASP

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Comm_33 - Phase transition and dynamics of a confined colloidal mixture in an external field : a simulation study

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The effective interactions between colloidal particles can be tuned to some extent, with the help of a chemical treatment of their surface for example. Colloidal suspensions are also responsive to external fields and spatial confinement. These aspects can thus be combined to obtain the behavior required for specific applications. In this vein, we show how an external field can reversibly control the adsorption of a binary colloidal mixture confined in a slit pore. In particular, an external field applied only in the pore can produce an inverted population with respect to the bulk reservoir.
We illustrate this population inversion by Monte Carlo simulations of the minimal model of non-additive dipolar hard-sphere mixtures. We emphasize the robustness of this behavior and its relation to the demixing transition of the bulk fluid [1].
We next use Langevin dynamics simulations to discuss the physical time of cyclic filling and emptying of a finite-length channel by the dipolar minority species. We examine how this time scales with the size of the particles. We also explore how reproducible irreversible cycles may be observed [2].

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Mots-Clés: Monte Carlo, Colloids, Dipolar particles

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Comm_34 - Caractérisation d'interactions 3-centres/2-électrons pour le stockage de l'hydrogène

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Notre société fait face à un défi important : les ressources de combustibles fossiles naturels sont limitées et leur utilisation conduit à l'émission de gaz à effet de serre. Un changement majeur vers l'utilisation d'énergies renouvelables et non polluantes est nécessaire. Le dihydrogène pourrait constituer un vecteur d'énergie idéal dans le secteur des transports et la production d'électricité.[1,2] Sa génération par voie chimique pourrait se faire par déhydrogénation d'amine boranes catalysées par des complexes organométalliques.[3]
Les complexes agostiques intramoléculaires ainsi que les complexes σ intermoléculaires ont été identifiés comme constituant des intermédiaires clés dans ces processus de déhydrogénation. Cependant, l'ensemble du mécanisme réactionnel aboutissant à la libération du dihydrogène est encore mal compris au niveau moléculaire.
Pour mieux décrire ces interactions de type 3-centres/2-électrons (3c/2e), nous avons effectué des études systématiques sur des prototypes : $Cp_2M(H)$-NR_2BH_3 et Cp_2M-η^2-H_2BR_2 avec M est un centre métallique (Ti, Zr, Hf, V, Nb) et R un substituant.

Les approches topologiques QTAIM (Quantum Theory of Atoms in Molecules)[4] et ELF (Electron Localization Function)[5] permettent l'identification et la caractérisation des interactions 3c/2e. Deux critères topologiques ont permis de quantifier l'interaction par l'approche QTAIM. Cette étude montre que la nature de centre métallique, du substituant ainsi que du ligand, joue un rôle important sur la force de l'interaction 3c/2e.

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Mots-Clés: Economie Hydrogène, Analyses topologiques QTAIM et ELF, descripteurs topologiques, interactions 3C/2e

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Comm_35 - Breaking bonds from an intracule perspective.

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The intracule density is a function obtained upon integration of the pair density [1] and it is defined as

$$I(\mathbf{u}) = \Gamma(\mathbf{r}_1, \mathbf{r}_2)\delta[(\mathbf{r}_1 + \mathbf{r}_2) - \mathbf{u}]d\mathbf{r}_1 d\mathbf{r}_2 \tag{1}$$

where $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$ and $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the pair density function[2] which can be also obtained from experimental X-Ray Scattering Cross-Sections.[3] Given the central role of the electron pair in chemical binding theory, the I(u) should contain information to understand chemical reactions that is averaged out when we only use the electronic density ρ(r). However, it retains the simplicity of the density because it depends only on the interelectronic distance vector and, therefore, it can be plotted in the usual manner. From intracule plots, we unveil information that is complementary to that of the topological analysis of the density as it was shown previously.[4,5] The purpose of the present contribution is to present some information that we might address by using the spherically averaged I(u) along the dissociation process. Namely, the information from the difference

$$\Delta I(u) = I(R, u) - I(R', u) \qquad : R' < R \tag{2}$$

where R and R' are the interatomic distances, will be studied for H_2, H_eH^+, BH, LiH, F_2, CO and BH at accurate levels of theory (FCI and Full-Valence CASSCF). Plots at different distances of the $\Delta I(u)$ will reveal the electronic rearrangements during the molecular dissociation and will be used to characterize the bonding interaction.

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Mots-Clés: Intracule, Electronic rearrangements, Dissociation, Diatomics

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Comm_36 - A new model for reference densities

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Constructing reference densities has always been a central topic to understanding interactions. Within crystallorgraphic analysis, it has been quite common to compare the final electron density to the sum of spherically averaged atomic densities. However, it is well known, that this density (also known as promolecular density) already contains a lot of interaction information. For example, the promolecular density already shows critical points which are similar in nature and properties to the ones of the final system.
We will show a new reference model, the independent gradient model (IGM), where electron densities are summed up, just like in the promolecular approach, but the gradients are not allowed to interfere thanks to the used of absolute values within non interacting regions/atoms.
This new model provides a better reference for analyses based on density gradients, such as Atoms in Molecules or the Non-Covalent Interaction index. Due to the special suitability of promolecular approaches for the latter, this new model provides an extremely good reference for obtaining intermolecular properties and defining in an objective manner interacting fragments, which always becomes a hassle in energetic partitions.

Mots-Clés: densidad electrónica, modelo, interacción

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Comm_37 - Curly Arrows, Electron Flow and Reaction Mechanisms from the Perspective of the Bonding Evolution Theory

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Despite its relevance in chemistry, a direct connection of curly arrows with a quantum chemical description is still controversial. While the paradigmatic description – from first principles - of the mechanistic aspects of a given chemical process is mainly based on the geometrical rearrangements of relevant intermediates or transition states, it is not sufficient to describe chemical systems in terms of bonding aspects. Herein, we present the bonding evolution theory (BET) interpreted as the joint use of the electron localization function (ELF) and Thom's catastrophe theory (CT) as a powerful tool to analyze the electron density flow in chemical reactions. In turn, this present approach retrieves the classical curly arrows used to describe the rearrangements of chemical bonds for a given reaction mechanism, providing a detailed physical grounds for this type of representation.

Mots-Clés: Electron localization function, Catastrophe theory, Electronic Flux, Curly Arrows

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Comm_38 - Décrire la structure électronique de radicaux obtenus après réduction; un challenge pour la DFT

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De très nombreux processus chimiques passent par une étape de réduction électronique d'un composé à couche fermée, conduisant à la formation d'un intermédiaire à couche ouverte. La structure électronique de ces intermédiaires est souvent mal connue car l'électron ajouté peut être situé sur différents sites de la molécule. L'estimation de cette délocalisation électronique est une question encore non résolue par les méthodes de modélisation actuelles.
Nous avons étudié deux familles d'intermédiaires réduits, les peptides protonés et les complexes organométalliques possédant des ligands redox-actifs. Nous avons montré, par comparaison avec des méthodes de référence post-HF, que les méthodes DFT non-corrigées de l'erreur de self-interaction ne peuvent décrire convenablement la structure électronique de peptides réduits en phase gazeuse.[1-3]

La même question de la localisation de l'électron a été abordée pour le cas des complexes organométalliques réduits qui sont utilisés comme catalyseurs. Pour ces systèmes, outre nos modélisations à l'aide de fonctionnelles DFT conventionnelles et corrigées à longue portée, des données expérimentales en phase gazeuse ont été obtenues.[4] Celles-ci permettent non seulement d'estimer la fiabilité des différentes méthodes de modélisation utilisées pour décrire la structure électronique de ces espèces, mais aussi de montrer que lors du calcul d'un spectre infrarouge, une correction affine des fréquences de vibration donne des résultats plus proches de l'expérience qu'une correction avec un facteur multiplicatif.[5]

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Mots-Clés: Théorie de la fonctionnelle de la densité (DFT), erreur de selfinteraction, structure électronique, peptides, complexes organométalliques

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Comm_39 - A Combined Computational-Experimental Study of the Intramolecular Oxa-Michael Reaction on α,β-dehydroamino Acid Esters

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A mechanistic, combined computational-experimental study on highly diastereoselective intramolecular oxa-Michael reaction on α,β-dehydroamino acid esters is presented. In the last two decades, this process has emerged as a very powerful tool to synthesize *syn* 1,3-diols and relative natural products. However, very few examples exist in literature where α substitutions to the Michael acceptor are described. A plausible explanation is that the use of a hetero substitution in that position would change the reactivity on the β carbon of the Michael system. Nevertheless, groups such as nitrogen α to the Michael acceptor can be useful to obtain bioactive compounds. Thus, the detailed reactivity of α substituted substrates under an operative and mechanistic point of view remains unclear. Motivated by this lack of information and by the possibility to employ this transformation in the synthesis of more complex systems, we carried out a combined computational-experimental study of an addition/intramolecular oxa-Michael sequence using α,β-dehydroamino acid esters as Michael acceptors. Delightfully, the computations (DFT and semi-empirical molecular dynamics) turned out to be in excellent agreement with the experimental evidences and allowed us to fully unveil the reaction mechanism and shed light on unexpected factors, which determine the reaction yield and stereochemical outcome. In particular, the computational results indicate that: 1) strong electrophilic reagents such as trifluoroacetophenone are needed in the first stage of the process, although EWG on benzene ring have a dampening effect; 2) electronic features of substituents of the nitrogen α to the Michael acceptor strongly influence the reaction yields; 3) different elements such as the counter-ion identity and nitrogen substituents are key in modulating the *syn:anti* selectivity.

Mots-Clés: DFT calculations, reaction mechanism, oxa Michael reaction, diastereoselective synthesis, semi empirical molecular dynamics

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Comm_40 - DFT Based Studies on Bio/Biological Materials

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Hydroxyapatite as the main compound of human bones and calcium oxalate as main compound of kidney stones. In this broad study around chemistry of life, materials chemistry and computational chemistry we focus on two materials in particular: Calcium Oxalate and Hydroxyapatite. We have performed DFT studies on different interfaces and investigated the interaction with a series of bio-organic molecules. From the bulk crystal structures of calcium oxalate polymorphs obtained through DFT methods [2] one can build for example the low index surfaces. The calculation of the interaction of the calcium oxalate surface with water, urea, and other small molecules will give us the possibility to understand the change in crystal morphology of the final oxalate crystal in its natural medium. The final aim is the prediction of the shape of the kidney stone in its natural medium. Another biomineral studied is hydroxyapatite, being the major mineral component of tooth enamel, dentin and bone in which it is currently associated to biomolecules and various biopolymers. Organic nanosized particles are described as comprising a heart surrounded by a crystalline hydrated amorphous layer. In this study the characterization of the surface of hydroxyapatite nanoparticles is essential to better understand their formation, and dissolution mechanisms and interactions existing at the interface between the crystalline and amorphous phases. The purpose of this study is to model a surface(s) of hydroxyapatite and analyze the physicochemical properties using the methods of quantum chemistry (periodic DFT) in particular with the software VASP and CP2K.

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Mots-Clés: DFT, Biomateriaux

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Comm_41 - Isostructural second-order phase transition of beta-Bi2O3 at high pressures

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We report an experimental and theoretical study of the structural and vibrational properties of synthetic tetragonal bismuth oxide (b-Bi_2O_3) at high pressures, where room temperature angle-dispersive x-ray diffraction, Raman scattering and optical absorption measurements have been complemented with *first principles* total-energy, lattice dynamics and electronic band structure calculations.
Striking changes in Raman spectra were observed around 2 GPa while x-ray diffraction measurements evidence no change in the tetragonal symmetry of the compound, a significant change exists in the compressibility when increasing pressure above 2 GPa. Our results show the presence of a second-order isostructural phase transition in Bi_2O_3 (from b-to-b') around 2 GPa and of a phase transition above 15 GPa combined with a pressure-induced amorphization above 17-20 GPa.

In order to further understand the pressure-induced phase transitions and amorphization occurring in b-Bi2O3, we have theoretically studied the mechanical and dynamical stability of the tetragonal structures of b- and b'-Bi2O3 at high pressure through calculations of their elastic constants, elastic stiffness coefficients and phonon dispersion curves calculated with the stress-strain theorem as implemented in VASP program1. The pressure dependence of the elastic stiffness coefficients and phonon dispersion curves confirm that the isostructural phase transition near 2 GPa is of ferroelastic nature.

Furthermore, we have calculated the topology of the electron density from the charge density obtained with VASP coupled to the CRITIC2 program2. The topological study of the electron density shows that the ferroelastic transition is not caused by a change in number of critical points (cusp catastrophe) but by the equalization of the electron densities of both independent O atoms in the unit cell due to a local rise in symmetry.

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Mots-Clés: High pressure, phase transition, betaBi2O3, DFT calculations

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Comm_42 - Séparabilité, non-additivité et anisotropie des potentiels de mécanique/dynamique moléculaires polarisables.

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Nous présentons des résultats de validations récentes, à l'aide de la chimie quantique ab initio, du potentiel de mécanique/dynamique moléculaire anisotrope et polarisable SIBFA [1]. Nous soulignons la nécessité de la séparabilité de DE en cinq contributions distinctes, comme pour l'énergie d'interaction intermoléculaire en chimie quantique DE(QC). Deux applications en sont illustrées: le profil d'énergie pour le passage de quatre cations monovalents à travers des tétramères empilés de guanine [2]; et les interactions intermoléculaires de trois dérivés d'un ligand anionique et conjugué dans le site de complexation du Zn(II) d'un métalloenzyme binucléaire à zinc, la métallo-b-lactamase de VIM2, responsable de maladies nosocomiales [3]. Les comportements souvent contrastés des contributions individuelles de DE(QC) en fonction du type de complexe ou de leurs structures sont reproduits de manière fiable par DE(SIBFA). Des applications à de très gros complexes macromoléculaires, sur de très longues échelles de temps pourront être ainsi envisagées de manière fiable dans ce cadre à l'aide du logiciel massivement parallèle, Tinker-HP, dans lequel ce potentiel et ses gradients ont été très récemment codés.

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Mots-Clés: Mecanique/dynamique moleculaire polarisables, separabilite, tetrameres empiles de guanines, metalloenzymes a zinc.

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Comm_43 - Local Environments Modulating Cysteine pKa and Reactivity towards Oxidation by Hydrogen Peroxide

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Checking **Mots-Clés:** cysteine oxidation, pKa & reactivity modulation by environment, hydrogen bonding networks, post transition state proton transfer

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Comm_44 - Synthesis, Characterization and Theoretical Study of a New Ruthenium(II) - 1, 2, 4-Triazepine Complex

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Like all metal drugs, the activity of the ruthenium compounds depends on both the oxidation state and the ligands. In addition, ruthenium has unique properties which make it particularly useful in drug design. For these reasons, and because of triazepine derivatives are well known for their anti-convulsant and anti-anxiety medicinal properties, we will discuss in this work not only the synthesis, but also the structural and energetic aspects of ruthenium (II) complex incorporating 2,7-dimethyl-3-thio-5-oxo-3, 4, 5, 6-tetrahydro-2H-1, 2, 4 - triazepine chelating ligand H2TAZO. Characterization by NMR spectroscopy (1H, 13C and 31P) is in agreement with crystallographic molecular structure. Theoretical calculations are performed to understand the electronic structures as well as the most stable isomer of RuL2 (HTAZX)2 (X=O, S and L=PPh3) which is in good agreement with the experimental observations.

Mots-Clés: Ru(II), triazepines, complexation, regioselectivity, structures.

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Poster Session 1

Mardi 4 Juillet (17h30 / 20h00)

P1_01 - Evaluation of disulfide bonds thermostability and their correlation with classical and quantum electrostatic potentials of cyclotides from Rubiacea family.

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Cyclotides are circular polypeptides without terminal residues. They were used in traditional medicine by Congo tribes, in the form of infusions and ointments from native plants of the region. The best-known species was Kalata-kalata from the Rubiacea family. The main feature of the structure of these polypeptides is the presence of a cysteine cyclic knot. We used molecular mechanic techniques with force field OPLS-AA in GROMACS v.5.0.5 software. We used 78 cyclotides of the Rubiaceae family that were reported. At the beginning, structures were minimized using "steep" method. Then, a molecular dynamics simulation was done in an NVT ensemble with physiological temperature. An annealing within 300k – 400k with 10 degrees intervals was made in average selected structures (zone of equilibrium). Quantum mechanics analysis was made in five cyclotides in deMon2k v.4.x software. In this research work we present comparative results regarding thermostability (classical mechanics) and global properties (quantum mechanics).

Mots-Clés: cyclotides, thermostability, molecular mechanics

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P1_02 - Molecular Mechanics of Caffeic Acid in food profilins allergens

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Allergies are a worldwide health problem. An import group of this are caused by food. Profilins are structural proteins found in eukaryotic cells. Some profilins have been identified as allergen from vegetables and fruits. Some studies have shown that caffeic acid may have a certain inhibitory effect on some allergens. Using computational techniques based on molecular mechanics we aim to evaluate interactions properties between seven profilins and caffeic acid. Profilins selected was: Api g 4 (celery), Ara h 5 (peanut), Cit s 2 (orange), Gly m 3 (soybean), Mus xp 1 (banana), Lyc e 1 (tomato) and Zea m 12 (maize). Three-dimensional structures were obtained from crystal form or by modeling from their primary structure. Then, the structures were geometrically optimized by using molecular mechanics techniques. The molecular interaction between profilins and caffeic acid was carried out and, finally, molecular dynamics simulation was made in all complex (protein-ligand). Caffeic acid has more affinity and interaction capability with profilins from peanut and tomato.

Mots-Clés: profilin, allergy, molecular mechanics, caffeic acid

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P1_03 - Substituent effect study on 3-amino-1-hydroxy-3, 4-dihydroquinolin-2 (1h) –one based on the Density Functional Theory of Chemical Reactivity

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Schizophrenia is one type of psychotic disorder. It progressively deteriorates patient quality of life. Understanding the pathophysiology, like dopaminergic and glutamatergic routes, and the search for new treatments is an important field that involves organic chemistry and pharmaceutical science. 3-amino-1-hydroxy-3,4-dihydroquinoline-2 (1h) -one drug has been taken as base for the present study, it acts as an inhibitor on the enzyme KAT-II. We design structures derived by substitution from donors and acceptors of electrons. CAM-B3LYP, wB87XD and LC-wPBE functionals and TZVP base set was used for geometric optimization. Global and local reactivity indices were calculated for all structures using Koopman approximation. For a systematization of its electronic properties we present the frontier orbital profiles (HOMO and LUMO) and electron localization function (ELF).

Mots-Clés: quantum mechanics, schizophrenia, Density Functional Theory, KAT II

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P1_04 - Obtención e interpretación de las características estructurales de los dúplex de Watson y Crick vía cálculos de mecánica molecular de fragmentos simples de ADN

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La doble hélice de Watson y Crick posee características distintivas muy particulares, una de las cuales es la dependencia de traslape de las bases apiladas respecto a la secuencia. Anteriormente, usando el método DFT se mostró que estas características ya están predeterminadas en la estructura molecular de los fragmentos mínimos del ADN: desoxy-dinucleósidomonofosfatos complementarios (cdDMP)[1]. En este trabajo utilizamos el programa AMBER16 y sus tres campos de fuerza (CF): FF99, OL15 y BSC1[2] para optimizar los cdDMPs de las conformaciones B1, neutralizando las cargas negativas de los grupos fosfato con iones de sodio. Al comparar las características principales de las estructuras optimizadas con los resultados de DFT y los datos experimentales para cristales de fragmentos de dúplex de ADN, se observa la misma dependencia de éstas sobre las secuencias de los nucleótidos en los cdDMP. Para el estudio de fragmentos más grandes, es necesario quitar las contribuciones de las interacciones sodio-sodio, y se proponen tres esquemas de modificación de las cargas en el esqueleto azúcar-fosfato para neutralizan su carga. Estas modificaciones producen cambios mínimos en las características estructurales de los cdDMP. Se realizaron los cálculos para tres, cuatro, cinco y seis pares de nucleósidos complementarios A:T o G:C utilizando las cargas modificadas. Para el CF FF99 se obtienen las estructuras con todos los parámetros pertenecientes a la familia B1, mientras que las conformaciones optimizadas con los CF OL15 y BSC1 algunos cdDMP cambian a la conformación B2.

Los autores agradecen al Laboratorio Nacional de Supercómputo del Sureste de México perteneciente a la red de laboratorios nacionales CONACYT, por los recursos computacionales, el apoyo y la asistencia técnica. Trabajo apoyado por el proyecto VIEP-BUAP POV-EXC17-G.

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Mots-Clés: Dúplex ADN, Mecánica Molecular, Dependencia de secuencia

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P1_05 - On the q-deformed Potentials with Hypergeometric Wavefunctions

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Almost three decades ago, Arai[1] proposed the so-called q-deformed hyperbolic potentials which does not have symmetry in their solutions. Along the time, several methods have been used to solve the Schr'odinger equation for different models of q-deformed potentials that have been proposed with the aim to improve the theoretical calculations of vibrational spectra of diatomic molecules. In this work, the canonical transformation method applied to the Schr'odinger equation to transform it into a second order differential equation(DE) of hypergeometric-type is presented[2]. As an important result, we find an exactly solvable multiparameter exponential-type potential with hypergeometric wavefunctions from which non deformed and q-deformed potentials can be obtained as particular cases. At this regard, the non deformed potentials are those which parameters are independent of q while the q-deformed potentials have parameters that are depending on q. Specifically, in this work our interest is in q-deformed potentials and as useful application we derive many already known q-deformed potentials which indicates that our method can be viewed as an unified treatment to the study of q-deformed exponential-type potential models, with the advantage that it is not necessary to use a special method to solve the Schr'odinger equation for each potential because solutions are obtained here by the simple selection of the involved parameters. Furthermore, it becomes possible to derive new q-deformed potentials, some of them as interesting alternatives in quantum chemical applications.
Acknowledgments: This work was partially supported by the projects UAM-A-CBI-2232004 and 009. One of us(JGR) thanks the Instituto Politécnico Nacional for the financial support given through the COFAA-IPN project SIP-20170810. We are grateful with the SNI-Conacyt-México for the stipend received,

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Mots-Clés: Canonical transformation, Schr'odinger like equation, Hypergeometric, DE, q deformed exponential type potentials, diatomic molecules.

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P1_06 - H2 dissociation and surface oxygen vacancy formation on (111)-CeO2 surface: a periodic DFT approach

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Most of the applications of ceria are linked to its redox properties associated to the easy formation of oxygen vacancies and the simple change in oxidation states of cerium: CeIV ↔ CeIII. Moreover, ceria is important in heterogeneous catalysis, especially in the alkyne semi-hydrogenation where it has been shown to be able to split H2 in the absence of noble metal[1]. Interestingly, the hydrogenation of ceria is found to take place through a hydride specie that plays a key role[1-3].
In the present study, we investigate the detailed mechanism for the formation of surface oxygen vacancy via H2 dissociation following by H2O desorption on (111)-CeO2 using PBE+U method and periodic approach as implemented in VASP software.

It was found that molecular hydrogen adsorbs very weakly to the surface. Then, the strong ionic nature between cerium and oxygen in ceria induces the polarization of the H – H bond and favor an heterolytic dissociation of H2 with the formation of an ion pair Hδ+ – Hδ- [2]. However, the product of the heterolytic dissociation being metastable [2,3], the hydride can easily move on to a hydroxyl group to form water molecule. Finally, water desorption leads to the formation of one surface oxygen vacancy along with the reduction of two cerium atoms. Several hydrogen species – like hydride, radical hydrogen and proton – are involved during the different steps of the reaction.

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Mots-Clés: ceria, CeO2, H2 dissociation, DFT, hydride, oxygen vacancy

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P1_07 - Hydrogenation of Carbon Dioxide over Magnesium and Copper Alkoxide-Functionalized Metal-Organic Framework

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In recent years, many approaches have been proposed and developed to reduce emissions. Immobilization of CO2 via hydrogenation to form formic acid (HCOOH) is considered one of the most promising strategies, catalytic hydrogenation provides a variety of useful compounds.
In this work, we have studied the reaction mechanism of hydrogenation of carbon dioxide catalyzed by magnesium and copper alkoxide-functionalized metal-organic framework (Mg-MOF-5 and Cu-MOF-5). The aim of this study is to compare the mechanism involved between the reaction with and without catalyst, and between both alkoxide, to understand how these influence the reaction. Both reactions, with and without catalyst, proceed via stepwise mechanism; however, a more detailed analysis of the electronic activity during the reaction shows that they are different. Transition states and energy barriers are discussed in terms of the reaction force analysis (RFA) and Marcus equation. Equilibrium and rate constants are determined and their physical nature is unveiled.
All the systems are characterized computationally using Density Functional Theory (DFT) with the methodology M06-L and the basis set 6-31G(d,p) for H, C and O, while the Mg and Zn atoms were described with the LANL2ZD pseudopotentials basis set. All calculations were performed with Gaussian 09.

Mots-Clés: Hydrogenation, Carbon Dioxide, Metal, organic Framework, Magnesium, Copper.

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P1_08 Modeling the Modulation of Emission Behavior in E/Z Isomers of Diphenyldipyrroethene

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Phenomena that induce change in the expression of emission properties of organic chromophores is of major interest nowadays with potential applications in optoelectronic devices such as fluorescent sensors in cell imaging.[1] Those phenomena are known as Aggregation Caused Quenching (ACQ) and Aggregation Induced Emission (AIE) or Crystallization Induced Emission (CIE). Depending on whether ACQ or AIE (CIE) is considered, properties in a given phase (dilute or concentrated solution, solid films, ...) will be radically different, resulting in a quenching or enhancement of the emission behavior for the molecule. Here we attempt to describe and rationalize, thanks to theoretical tools, the different behavior of isomer E and Z of DPYDPE[2] in terms of emission properties in three different phases, namely the solution, crystal and aggregate. Both isomers will be studied with the help of (TD-)DFT in solution (PCM model), crystalline phase (QM/QM') and in aggregated phase (Molecular Dynamics combined with QM/QM'). To get a deeper comprehension of the AIE and CIE effects, Huang Rhys[3](HR) factors and reorganization energies (that strongly influence the non radiative decay rate) were calculated to explain the emission behavior of an isomer in the three different phases but also the observed difference between isomers E and Z.

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Mots-Clés: DFT, TDDFT, UV Vis, Fluorescence, CIE, AIE

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P1_09 QTAIM and ELF topological analyses of zinc-amido or tin-amido oligomers formed during the synthesis of zinc or tin oxide nanoparticles

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Metal oxides may be prepared in the form of nanoparticles of controlled sizes and shapes via an organometallic route, involving the hydrolysis of an organometallic precursor in the presence of additional ligands such as fatty amines or fatty acids [1]. Starting from a zinc-dicyclohexyl complex or from a bis(m2-dimethylamido)-bis(dimethylamido)-di-Tin complex, an organometallic gel may be obtained. Nuclear magnetic resonance (NMR) and Wide-Angle X-ray Scattering (WAXS) spectra suggest the formation of oligomeric structures through the deprotonation of the amine to an amido ligand, which is able to bridge two metallic centres. Entanglement and cross-linkage between chains of these oligomeric structures further lead to the gelification and solidification processes [2].

The structure of small size oligomers, containing up to 12 metal atoms, has been investigated by DFT computational studies and a possible polymerization pathway is proposed on the basis of energy stabilization calculations. The comparison of experimental and calculated WAXS spectra allows to discriminate among the various possible structures or size of Zinc-amido and Tin-amido oligomers. The various metal-nitrogen and metal-alkyl bonds (M = Zn or Sn) have been finely characterized using Quantum Theory of Atoms in Molecules (QTAIM) and Electron Localization Function (ELF) topological analyses. Fukui indices condensed on the QTAIM or ELF basins allow for the comparison of the chemical reactivity of the oligomers of increasing size. The original nature and reactivity of the terminal metal-amino bonds with respect to the bridging metal-amido bonds or to the terminal metal –alkyl bonds is evidenced.

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Mots-Clés: metal oxide nanoparticles, zinc, amido or tin, amido oligomers, Wide, Angle X, ray Scattering (WAXS) spectra, QTAIM and ELF topological analyses

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P1_10 - Molecular switching properties of octaphyrins

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Recently, expanded porphyrins emerged to be a promising class of p-conjugated molecules with exceptional electronic, optical and conformational properties. Interestingly, several expanded porphyrins can switch between planar and twisted topologies encoding for distinct photophysical properties. Therefore, expanded porphyrins represent a promising platform for development of a novel type of molecular switches based on topology and/or aromaticity changes for nanoelectronics applications. Despite a tremendous amount of experimental studies on expanded porphyrins, the design of molecular switches based on these unique macrocycles has only been scarcely investigated.1 In our research, we have assessed computationally the feasibility of optical switches based on octaphyrins for the first time.2,3 Octaphyrins correspond to macrocycles consisting of 8 pyrroles separated by a methylene bridge and they adopt different p-conjugation topologies upon protonation and redox reactions. In order to determine the optimum conditions for efficient molecular switches, we have carried out a comprehensive quantum chemical study focused on the conformational preferences and interconversion pathways of [36]octaphyrins. Furthermore, we have identified effective stimuli for triggering the topological switch and scrutinized how the photophysical and nonlinear optical properties changes as a function of the molecular topology. Aromaticity emerges as the key concept determining the photophysical properties of those macrocycles. Accordingly, we proposed a set of different methods (structural, magnetic, energetic and reactivity indices) to quantify the H'uckel and M'obius aromaticity of these macrocycles taking into account the multidimensional character of aromaticity.2 By using these descriptors, a triangular relationship between the p-conjugation topology, the oxidation state and the aromaticity of octaphyrins has emerged.

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Mots-Clés: molecular switches, octaphyrins, aromaticity

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P1_11 - Treatment of intermolecular interactions in polarizable force fields.

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Intermolecular interactions play an important role in a wide range of systems, from gases phase to condensed matter. In biological systems, the interactions between entities are mainly due to weak forces. Over the past year, polarizable force fields, such as SIBFA [1], have been developed to study this type of systems. SIBFA computes the intermolecular energy in a physically meaningful way, as a sum of electrostatic, exchange-repulsion, polarization, charge-transfer and dispersion interactions. The calibration of these five classical components is done as to follow their quantum counterparts. Therefore, we have studied two types of energy decomposition methods as reference and we have applied them on cations (K+, Na+, Mg2+ , Ca2+ , Zn2+) – H2O dimers.
On one hand, variational methods (RVS [2], ALMO [3] and CSOV [4]) decompose the total interaction energy as a sum of electrostatic, exchange-repulsion, polarization and charge-transfer energies. On the other hand, perturbational methods (SAPT and SAPT-DFT [5]) decompose the total interaction energy as a sum of electrostatic, exchange-repulsion, induction, charge-transfer and dispersion energy.

The aim of this work is to identify the main differences, similarities and shortcomings of these five methods in order to choose the most accurate energy decomposition method to parametrize a polarizable force field. Comparing these methods will give us a better understanding on how to treat short and long range intermolecular interactions.

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Mots-Clés: intermolecular interactions, SIBFA, SAPT, EDA

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P1_12 - Interacciones de apilamiento en los dímeros de cafeína. Comparación de diferentes métodos computacionales y datos experimentales.

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Las interacciones de apilamiento constituyen un desafío para los métodos de cálculo de mecánica cuántica. Diferentes funcionales de DFT se han elaborado para poder reproducir este tipo de interacción. La molécula de cafeína (1,3,7-trimetilxantina) es un modelo idóneo para el estudio de las interacciones de apilamiento, debido a su estructura aromática, presencia de tres grupos metilo y ausencia de donadores de enlaces de hidrógeno. Esto hace que el dímero de cafeína forme únicamente cinco diferentes estructuras de apilamiento, que se encontraron primeramente por método de mecánica molecular[1], y posteriormente confirmadas en las estructuras cristalinas de la cafeína anhidra[2-4]. En este trabajo optimizamos estas cinco estructuras utilizando diferentes funcionales DFT (M062X, MPWPW91, PWB95, PWB6K, MPWB1K, B97-1, B3LYP) y el método MP2/6-31G(d,p) con corrección de BSSE. Las estructuras resultantes se comparan con las estructuras experimentales [2-4] tomando como principales criterios: las distancias y paralelismo entre planos de las moléculas en el dímero, y los traslapes de los anillos de las moléculas. Con MP2/6-31G(d,p)/BSSEcorr los resultados muestran la menor diferencia con los datos experimentales, las distancias promedio que proporciona(3.39Å) son muy cercanos al valor promedio experimental (3.4Å). Los funcionales B97-1 y B3LYP muestran distancias más grandes: 3.63 y 3.65Å respectivamente, M062X muy pequeñas(3.1Å), los funcionales MPWPW91, PWB95, PWB6K, MPWB1K muestran el mismo comportamiento entre ellos con distancias de 3.55Å.
Los autores agradecen al Laboratorio Nacional de Supercómputo del Sureste de México perteneciente a la red de laboratorios nacionales CONACYT, por los recursos computacionales, el apoyo y la asistencia técnica. Trabajo apoyado por el proyecto VIEP-BUAP DEAL-EXE17-G.

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Mots-Clés: Cafeína, stacking, DFT, MP2

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P1_13 - Orbital localization and electron correlation in [n]acenes and [n]phenacenes

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The [n]acenes (benzene, naphthalene, anthracene, tetracene, pentacene, ...) and the [n]phenacenes (phenanthrene, chrysene, picene, ...) are two homologous series of polycyclic aromatic hydrocarbons (PAH). They are finite-sized precursors of carbon nanoribbons of minimal width, derived from zig-zag or armchair single-wall carbon nanotubes (SWCNT). Our work addresses the problem of generation of localized orbitals in these PAHs (especially for the pi-system), and their subsequent use for correlation energy calculations. The [n]acenes and [n]phenacenes up to $n = 30$ were considered and a closed-shell electronic ground state was assumed, in order to allow for the application of different methods of orbital localization and local correlation treatment **[1, 2, 3]**. It is shown that different methods for orbital localization and electron correlation calculation, if correctly and properly applied, yield practically the same results for the correlation energy. The issue of extrapolation to the limit of the infinite chain (n to infinity) is also addressed.

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Mots-Clés: Hydrocarbures aromatiques polycycliques (HAP), localisation d'orbitales, corrélation électronique

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P1_14 - On the nature of electron delocalisation in pericyclic transition state structures.

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The nature of the electron delocalisation at the cyclic center of reaction associated to six-membered TSs of representative examples of the so-called *pericyclic* reactions is re-examined. Results based on the topological analysis of both the electron localisation function (ELF) and the electron density (QTAIM), as well as magnetic-dependent responses (NICS, ACID), challenges classical interpretations based on the *aromaticity* concept within such a framework.

Mots-Clés: cyclic electron conjugation, aromaticity, pericyclic transition structures, electron localization function (ELF), Atoms in Molecules (AIM), Anisotropy of the Induced Current Density (ACID)

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P1_15 - Optical Vibrational modes of GaSb nanowires from first principles calculations

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In recent years there has been an increasing interest on the development of materials for optoelectronic devices, binary semiconductors, gallium antimonide (GaSb) is especially attractive due to its direct electronic band gap and high hole mobility. On the other hand semiconductor nanowires have shown promise for applications on optoelectronics due to quantum confinement effects that allow for an engineering of the electronic, vibrational and optical properties of these materials compared to their bulk counterparts. Although GaSb nanowires (GaSbNWs) were difficult to synthetize, recent experiments have proven that these nanowires show impressive electrical properties, however their vibrational properties have not been studied theoretically at the best of our knowledge. In this work the optical vibrational modes of GaSb nanowires are studied using a first principles density functional theory scheme within the generalized gradient approximation. The nanowires are modelled by removing atoms outside a circumference on the [111] direction of an otherwise perfect GaSb crystal according to the supercell scheme [1,2]. The surface dangling bonds are passivated with H atoms. The results show that hydrogen introduces some vibrational modes in highest frequencies due to stretching and bending modes with respect to the bulk crystalline GaSb. Besides, the RBM for these nanostructures could be fitted by an inverse power law, thus decreasing as the nanowire diameter increases which could be useful for vibrational characterizations such as Raman.
Acknowledgments: this work was partially supported by Multidisciplinary projects SIP-IPN 2016-1770 and 2016-1771

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Mots-Clés: GaSb Nanowires, DFT, phonons

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P1_16 - Growth of TiO_2 aligned nanorods: a surface science DFT study

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Synthesis of aligned single-crystalline semiconductor nanorods is a challenge nowadays because of their potential applications in photovoltaic devices, for example in dye-sensitized solar cells (DSSCs). A facile, hydrothermal method was developed to grow oriented, single-crystalline rutile nanorod films on transparent conductive fluorine-doped tin oxide (FTO) substrates.1 After that, a growth model of rutile nanorod was proposed, but still many points in the mechanism are unclear.2
In this study, surface science and Density Functional Theory (DFT) was used to combine with previous studies data, in particular make the mechanism of rutile nanorod more clear and complete as regards the role of the solvent (water) and the precursor, TiCl4. The Vienna Ab initio Simulation Package (VASP) was employed to model the surface structure and simulate the growth mechanism. In a first step we focus on the interaction of water with selected terminations of rutile i.e. (001), (110), (111), (110) and (100). The MAPS code was used to construct the slab models. In a second step we plan to study the adsorption energy between each termination and . The computational characterization of the coadsorption between precursor and water on the rutile nanorod will provide important data about the growth mechanism.

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Mots-Clés: titanium, titanium dioxide, DFT, surfaces, nanorods

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P1_17 - Towards the modelling of the plasmonic response of silver nanoclusters embedded in a matrix from TDDFT calculations

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The absorption spectra of silver nanoparticles are characterized by a strong response in the UV-visible range, usually interpreted in the framework of (semi-)classical optics in terms of plasmon excitations due to the s electrons (Mie's Theory)[1]. Recently, Time-Dependent Density-Functional Theory (TDDFT) calculations have been shown to well reproduce the experimental spectra of metal nanoclusters when using range-separated hybrid (RSH) functionals[2]. This approach gives a new description of the plasmon phenomenon from a quantum point of view. It also gives a framework to investigate the optical properties of small-sized metal clusters for which the classical approaches are no longer valid.
We will present new TDDFT simulations of the optical properties of Agn (n=20-147) clusters using RSH-type functionals. Our results are compared to very recent experimental data measured on clusters embedded in a rare gas matrix[3,4] or in an oxide matrix, or in contact to a oxide surface[5]. The effects of those matrices over the cluster's optical response are described and evaluated. Particularly, we have developed a method allowing us to reproduce the main features caused by Ne matrices on clusters spectra. We will also present our simulations on Agn clusters embedded inside a SiO2 amorphous matrix. We were able to reproduce experimental results with unprecedented accuracy, and using appropriate descriptors and tools we can give a new picture of the plasmon phenomenon.

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Mots-Clés: metal clusters, silver clusters, TDDFT, plasmon

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P1_18 - Théorie de la Fonctionnelle de la Densité Relativiste à Séparation de Portée

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L'utilisation de la séparation de portée pour l'interaction Coulombienne a pour but de tirer le meilleur partie des méthodes de DFT et de fonction d'onde, à travers une fonctionnelle de la densité (semi-)locale pour la courte portée et l'utilisation d'une méthode de calcul explicite à plusieurs corps pour la longue portée. Au cours de ces travaux nous avons étendu le formalisme du terme d'échange Coulombien à courte portée à un cadre relativiste à 4 composantes à travers des calculs sur le gaz d'électron homogène, soit une approximation locale de type LDA. L'utilisation d'une expression du terme d'échange en fonction du trou de Fermi relativiste s'est avérée nécessaire, celui-ci permettant de mieux comprendre le changement de comportement du gaz relativiste en fonction de la densité.

Afin de pouvoir construire une fonctionnelle d'échange-corrélation à courte portée il faudra par la suite prendre en compte le terme de corrélation Coulombien relativiste, puis les termes d'échange et de corrélation lié à l'interaction de Breit.

Mots-Clés: DFT, Séparation de portée, Relativité

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P1_19 - Conformational study of fluorescent oligopeptides: the repairing of Tyrosine by adjacent Tryptophan

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7-aminocoumarins studied by density function theory (DFT), with *non*-restricted rotation of amine, showed a highly emissive intramolecular charge transfer band (ICT) strongly dependent of solvent polarity, and a *non*-fluorescent twisted ICT (TICT) by rotation of amino group. Conversely, 7-aminocoumarins, with restricted rotation of amine group, showed besides radical formation detected by laser flash photolysis (LFP), taking advantage from this, we have used coumarin derivatives to label proteins and lipids in order to study the effect of distance of aminoacid residues tyrosine (Tyr) and tryptophan (Trp) on the repairing mechanism of oligopeptides containing coumarin as source of radicals (e.g. **Coumarin**-Linker-**Tyr**-Pro-**Trp**-Arg-Arg). Our results indicate that photoinduced electron transfer is promoted from coumarin upon two photon process ejecting an electron, which is able to damage Tyr residue. The capability of Trp to repair the damaged Tyr depends strongly of pH, redox potential and distance between Trp and Tyr. At the same time, results by UHPC-MS/MS of these oligopeptides, strongly suggest presence of dimeric species, whose could be responsible of any deactivation process. To evaluate those effects, conformational studies of several peptides were carried out using molecular dynamics pointing out the acting of linker residue between Tyr and Trp, plays a key role over the folding of peptide, determining the critical distance and the preferential orientation adopted of each aromatic aminoacid residue.

Mots-Clés: coumarin, peptides, photophysics, photo electron transfer, repairing mechanism

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P1_20 - Efficient calculation of the Hamiltonian for RT-TDDFT in parallel architectures

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Recent advances in the creation of intense laser pulses with femtosecond durations have risen interest in the analysis of electron dynamics processes. As these pulse durations have reached the limit in which electron motion takes place, new mechanistic insights are needed. When molecules are exposed to short, intense laser pulses they can undergo strong field ionization that cannot be described by perturbative models. Methods which solve the time-dependent Schr'odinger equation (TDSE) for electronic wavefunctions need to be employed.

A practical methodology to simulate electron dynamics is Real Time-Time Dependent Density functional theory (RT-TDDFT). RT-TDDFT proceeds by the construction of an effective Hamiltonian, followed by the direct propagation of the electronic density using this Hamiltonian. Since this procedure requires repeated calculations of the electron repulsion integrals (ERIs) to perform the density matrix propagation, the computational chemistry program deMon2k is suitable to achieve the task. The mixed SCF scheme implemented in deMon2k reduces the ERIs computation time up to 90% using a combination of ERI storage in RAM and the double asymptotic expansion. This methodology is parallelized, thus providing an excellent ground for simulations in the framework of RT-TDDFT. The mixed SCF has been tested in the deMon2k implementation of Born-Oppenheimer Molecular Dynamics, allowing calculations of thermodynamic properties in medium-size metallic clusters.

Benchmarks on a variety of systems are presented to show the performance of the mixed SCF implementation in the RT-TDDFT module of deMon2k. The results show that the mixed SCF will be a key feature to reach RT-TDDFT calculations of biological systems subject to laser pulses. Moreover, the recent Quantum Mechanics/polarizable Molecular Mechanics (QM/MMpol) implementation in deMon2k will allow to include explicit solvents with polarization effects due to the changes in the electrostatic potential of the perturbed molecule.

Mots-Clés: Density functional theory, Real time time dependant DFT, electron repulsion integrals, parallel computing, electron dynamics, ionization

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P1_21 - Computational study of mbandakamine A – a dimeric naphthylisoquinoline alkaloid with antimalarial activity

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Mbandakamine A is one of the naphthylisoquinoline alkaloids isolated from the leaves of Congolese *Ancistrocladus* species and showing good antimalarial activity. It is also one of the first dimeric naphthylisoquinoline with an unsymmetrically coupled central biaryl axis to be discovered [1]. The molecule consists of two units, with each unit containing one naphthalene moiety and one isoquinoline moiety. The substituents on the rings comprise four OH groups and four OCH_3 groups. The OH groups can be H-bond donors, either to the methoxy group in the same moiety or to other OHs from another moiety. Conformers can have up to three O-H$\cdots$O intramolecular hydrogen bonds (IHBs) simultaneously, and also other H-bond type interactions (O-H$\cdots$p and C-H$\cdots$O). A detailed conformational study was performed *in vacuo* and in three solvents with different polarities and different H-bonding abilities (chloroform, acetonitrile and water), using two levels of theory, HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p). Because IHBs have a relevant role in determining conformational preferences, all combinations of IHBs and IHB-type interactions were considered, for a total of 52 conformers. The four moieties tend to be mutually perpendicular, which results in the naphthalene moiety of one unit being parallel to the isoquinoline moiety of the other unit. Because of this particular orientation, a benzene ring of the naphthalene moiety of one unit and a benzene ring of the isoquinoline moiety of the other unit come sufficiently close to each other to interact (stacking interaction).

Mots-Clés: Antimalarials, intramolecular hydrogen bonding, mbandakamine A, naphthylisoquinoline alkaloids, stacking interaction

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P1_22 - Complexes of 1-[3-geranyl-2,4,6-trihydroxyphenyl]-2-methylpropan-1-one with a Cu2+ ion. A DFT study

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1-[3-geranyl-2,4,6-trihydroxyphenyl]-2-methylpropan-1-one is an acylphloroglucinol present in various plants. Together with hyperjovinol A, is one of the major responsible of the antioxidant activity of *Hypericum Jovis*[1].
Complexes of this molecule with a Cu2+ ion were calculated considering all the sites to which the Cu2+ ion may bind (the four O atoms in the acylphloroglucinol moiety and the two C=C p bonds in the geranyl chain) and including also simultaneous coordination to two sites, when geometrically possible. Calculations were performed at the DFT level with the B3LYP functional, the 6-31+G(d,p) basis set for the C,O and H atoms and the LANL2DZ pseudopotential for the Cu2+ ion. The results show that Cu2+ is reduced to Cu+ in all the calculated complexes, which is consistent with the antioxidant activity of the molecule.

Comparisons with analogous complexes of three related molecular structures are utilised to evaluate the influence of specific structural features on the molecule's reducing ability. Comparisons with the complexes of hyperjovinol A[2]–having a similar molecular structure, with an additional OH in place of the first p bond in the geranyl chain–enable an evaluation of the relative effects of an OH group or a p bond on the molecule's reducing ability. Comparisons with the complexes of a structure in which the first p bond in the geranyl chain is removed enable an evaluation of the relevance of this p bond. Comparisons with the complexes of a structure in which the geranyl chain is replaced by a prenyl chain enable an evaluation of the relevance of the second p bond in the geranyl chain.

- [1] K. Athanasas, P. Magiatis, N. Fokialakis, A. L. Skaltsounis, H. Pratsinis and D. Kletsas, *J.Nat.Prod.*, 2004, 67, 973.
- [2] L. Mammino, *J.Molec.Model.,* 2013, 19, 2127–2142.

Mots-Clés: acylphloroglucinols, antioxidants, complexes of organic molecules with metal ions, intramolecular hydrogen bonding, molecule ion interaction energy

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P1_23 - Estimating Local Bonding/Antibonding Character of MO based on the Dynamic Orbital Force

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The derivative of a MO energy with respect to a given bond length reveals the nature and the degree of the bonding/antibonding character of this MO with respect to this bond. This derivative is called the Dynamical Orbital Force (DOF)**[1]**. The bonding or antibonding "lone pairs" of various small molecules will be presented. For example, the comparison of the isoelectronic species CO and N2 is of special interest because N2 is also able to act as a ligand in a variety of metal complexes: the HOMO "lone pairs" of CO is found to be antibonding (DOF $<$ 0) whereas the HOMO of N2 is found to be bonding (DOF $>$ 0). Furthermore, t*he DOF of selected MOs as a function of the reaction coordinate (RC) of representative reactions mechanisms will be exposed. The results highlight the nature of the main MO reorganization, and at what stage of the RC they occur.*

- [1] P. Chaquin, Y. Canac, C. Lepetit, D. Zargarian and R. Chauvin, IJQC, **2016**, 116, 1285-1295.

Mots-Clés: molecular orbital, Dynamical Orbital Force, lone pairs, reaction coordinate

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P1_24 - Etude de mode de coordination et de la structure électronique à des complexes de métaux de transtion des ligands carbéniques.

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La chimie organométallique des ligands polycycliques aromatiques est très connue, ainsi que, l'impact de l'insertion d'un hétéro-atome (N, O, S et P) a pour conséquence l'augmentation de l'aromaticité dans le polycycle. La chimie organométallique des ligands hétéropolycycliques est moins étudiée comparativement à celle polycycliques, en particulier sur le plan théorique. Notre étude s'inscrit dans un objectif de développement de cet axe de afin de pallier ce déficit. Nos travaux récents ont montré des résultats très satisfaisants qui nous ont encouragé à poursuivre nos recherches, afin de bien rationaliser les propriétés physico-chimiques de ce genre de composés, de mieux comprendre le mode de liaison et de la coordination qui les régit. Il est maintenant relativement facile d'accéder à la structure électronique de nombreuses molécules quelles que soient leurs tailles par l'intermédiaire de calculs théoriques utilisant la fonctionnelle de densité (DFT). Une des applications importante des méthodes théoriques concerne la prédiction de la réactivité des complexes de métaux de transition et la proposition de nouveaux modèles moléculaires susceptibles de posséder de propriétés électroniques intéressantes. Le sujet traite d'un point de vue théorique le mode de coordination et la structure électronique des complexes de métaux de transition des ligands carbéniques en fonction de la nature du métal (M = Mn, Co et Cu, X = et Cl), du nombre d'électrons de valence et de l'état de spin en utilisant la méthode DFT. Plusieurs sites de coordination sont possibles donnant lieu à plusieurs isomères classés entre eux en fonction de leurs énergies relatives.

Mots-Clés: Coordination, hapticité, DFT, fonctionnelle hybride, fonctionnelle non hybride, métaux de transition, ligand, fragment métallique, site de coordination, état de spin.

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P1_25 - Simulation of Natural Dyes Adsorbed on TiO_2 for Photovoltaic Applications

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The study of the electronic structure and optical properties of natural pigments using state of the art time-dependent first-principles calculations is presented to highlight their usefulness for photo electrochemical devices. Ground state geometries, UV–vis spectra and photovoltaic properties are reported. In the family of chosen anthocyanidins, it is observed that the frontier molecular orbitals (FMOs) are mainly localized over the whole molecule with exceptions noted for Delphinidin and Petunidin, while in the anthocyanins all the FMOs are localized over the three rings of the molecule, without any contribution of the glycoside motifs. Conversely, the interaction between Cyanidin and Cyanidin 3,5 diglucoside with TiO_2 as the semiconductor in its cluster and surface form was also studied using periodic density functional calculations for suitable supercell models representing the systems of interest. For the Cyanidin 3,5-diglucoside/TiO_2 system the results showed that its highest occupied molecular orbital (HOMO) is located in the TiO_2 bandgap and its lowest unoccupied molecular orbital (LUMO) is close to the TiO_2 conduction band minimum (CB) leading to greatly enhanced visible light absorption.

Mots-Clés: DSSC, TD DFT

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P1_26 - Theoretical Study of Anatase TiO_2 Nanotube

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Titanium dioxide, TiO_2, is a multifunctional semiconductor, which has been used in several areas. We have reported the study of anatase TiO_2 nanotubes (TiO_2NT) with different thickness and diameters. First-principles calculations based on periodic density functional theory associated with B3LYP hybrid functional have been performed to study the single-walled and three monolayers (3 ML) anatase TiO_2NT. Theses nanotubes with different diameters were formed from anatase (001) surface that has a squared unit cell.

The results were analyzed calculating the strain and formation energies and compared to the surface and bulk energies in order to verify from it structure (surface or bulk) the nanotubes are formed more easily. The electronic properties were also studied.
This work was supported by FAPESP (process number 2017/07240-8).

Mots-Clés: TiO_2, Nanotube, DFT

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P1_27 - High pressure, structural and electronic properties first principle study of wurtzite, zincblende and rocksalt Al_(1-x)In_xN alloy

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A DFT based study of three different phases of Al_(1-x)In_xN alloy is carried out. Wurtzite (WZ) to Rocksalt (RS) as well as Zincblende (ZB) to Rocksalt transition phase pressures (TPP) are determined and related phase stabilities are analyzed. Calculated TPP are found in good agreement with data of AlN and InN whereas they are also predicted for ternaries for different values of In composition.
Then structural and electronic properties such as lattice parameter, bulk modulus energy band gap Eg and electron effective mass of the alloy are investigated throughout the whole range of indium contents at ambient pressure. Comparison between different phases and with available data is presented. An engineering of band gap is reviewed through variation of Eg with pressure.
Alloy randomness is taken into account using a special quasi-random structure (sqs), while alloy stability is considered through variation of the mixing enthalpy. Density functional calculations are performed by using Perdew -Burke-Ernzerhof gradient corrected functional for solids (PBEsol) as well the modified Becke -Johnson (TB-mBJ) potential exchange to ensure a better accuracy of the gap.

Mots-Clés: AlInN alloy, DFT, High pressure, Transition phase

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P1_28 - Study of monoamine oxidase by molecular modeling

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Monoamine oxidase (MAO) is an important drug target for the treatment of neurological disorders .MAO-B is an enzyme which decomposes naturally chemicals in the brain. MAO-B inhibitors, are considered useful in the therapy of Parkinson's disease since oxidation by MAO-B represents a major catabolic pathway of dopamine in the central nervous system. A series of indole derivatives were synthesised and evaluated as inhibitors of MAO-B, In general, the derivatives were found to be selective MAO-B inhibitors with IC50 values [1]. In our work, the interaction between bioactive structures will be studied by methods of molecular modeling (MM, DM, Docking).We conclude that these indole derivatives are promising reversible MAO-B inhibitors with a possible role in the treatment of neurodegenerative diseases such as Parkinson's disease (PD).
In this study, we used of indole derivatives which are synthesized [1]. As shown in figure 1.The found structures were optimized by DFT level using hybrid functional density B3LYP with 631G basis (Gaussview 2.1).

- [1] Louis H.A. Prins, Jacobus P. Petzer, Sarel F. Malan. Inhibition of monoamine oxidase by indole and benzofuran derivatives.European Journal of Medicinal Chemistry 2010,45, 4458-4466.

Mots-Clés: Parkinson's disease (PD), Monoamine oxidase (MAO), indole derivatives, molecular modeling, DM, Docking, Molegro

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P1_29 - Metallic Nanoparticles Growth on Semiconductor Surfaces upon Electron Irradiation from Theoretical Calculations

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Our society demands the development of new materials increasingly sophisticated with innovative properties. The structural study of a-Ag2WO4 at atomistic level using electron microscopy pointed out the discovery of a novel phenomenon that was not reported in the literature before. Hence, the electron irradiation on this material in the electron microscopy leads to the formation of metallic silver nanostructures. This system is an excellent ozone sensor and also exhibits significant bactericide behavior. However, along with the applications already characterized, there is major interest on the understanding of the electron-semiconductor interactions leading to the formation of metallic Ag from a fundamental level. We have examined, from computational methods based on the density functional theory and *ab initio* molecular dynamic simulations, the structural and thermodynamical aspects of the nucleation and growth of Ag filaments from a-Ag2WO4 crystals upon electron irradiation. Our calculations supply an atomistic approach to the local geometry and the electronic structure of the surfaces exposed to the electron beam irradiation and gain insight into the initial stages of the metallic Ag growth on the a-Ag2WO4 surfaces. We also show results on other different systems BiOX (X=F,Cl, Br) with similar striking behavior.

Mots-Clés: electron irradiation, semiconductors, DFT

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P1_30 - Double Gold Activation of 1-Ethynyl-2-(Phenylethynyl)Benzene Toward 5-exo-dig and 6-endo-dig Cyclization Reactions

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In this work, a detailed characterization of the ring closure mechanism of EPB (1-ethynyl-2-(phenylethynyl) benzene) toward the 5-exo-dig and 6-endo-dig cyclization reactions catalyzed by two Au-NHC moieties was carried out. It was found that the 5-exo-dig cyclization takes place with a slightly lower activation barrier and larger exothermicity compared to that of the 6-endo-dig cyclization, in agreement with the available experimental data. A phenomenological partition (structural and electronic) for rate constants computed using transition state theory and the reaction force analysis was used to shed light into the nature of the activation rate constant. It was found that rate constants are influenced by an strong structural component being for the 5-exo-dig cyclization larger due to the strain to form the five-membered ring. On the other hand, the gold activation mechanism is evidenced by a $\sigma-$ and $\pi-$coordination of the Au-NHC moieties to the EPB substrate. It was found that differences in the $\sigma-$coordination arise on the reaction path for the 5-exo-dig and 6-endo-dig cyclizations. Thus, in the 6-endo-dig cyclization the σ gold-EPB interaction is weakened as a consequence of the formation of the cationic aryl intermediate while for the 5-exo-dig cyclization this interaction was found to be favored. Furthermore, although minor changes in the Au-EPB coordination occur on the reaction path, these bonds are formally established in the TS vicinity. It supports the concerted nature of the dual gold activation mechanism.

Mots-Clés: Double Gold Activation, Gold Catalysis, Reaction Mechanism, Reaction Force, Reaction Electronic FLux

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P1_31 - The regioselective reaction of the substituted maleimides and the diaminopyridine : A theoretical approach.

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In our study, the reaction mechanism in the synthesis of isomers imidazopyridinyl-acetamide by the action of 2, 3 diaminopyridine on the maleimide, presents very important pharmacological properties. The two carbons, seats of the nucleophilic attack of nitrogen pyridinic and the nitrogen atom outside the cycle (NH2), are the C=O and the C=C of the substituted maleimide . Our aim is to conclude if the nitrogen pyridinic attacks the C3=C and thus the nitrogen atom (NH2) on the C2=O (way 1) or the opposite (way 2). Our goal is to conclude the preference from one or the other of the two isomers. Calculations were carried out in gas phase using semi-empirical method PM3 and the density functional theory (DFT) with the B3LYP functional and the 6-311+G* basis set. Various reactivity descriptors and appropriate local quantities have been calculated from Mulliken Population analysis (MPA) and the population analysis has also been performed by the natural bond orbital (NBO). To determine the various states (intermediate, transitions and final states) in this reaction, we used the following techniques of calculations: Scan and QSTN.We also used NBO analysis to search and confirm the stability of the theoretically produced isomers. The reaction of obtaining the imidazo pyridin-yl acetamide is done according to two ways of synthesis. The results are in favor of way 1 of synthesis. The value of activation energy for way 1 is 37.4 Kcal/mol and the value of activation energy for the way 2 is 55.8 Kcal/mol (R=H). We studied various substitutions (R=H, CH3, C2H5, C6H5) and we noticed that the product given with R=C6H5 is the most stable. The obtained results are compared with available experimental data.

Mots-Clés: DFT, AM1, NBO, maleimide, diaminopyridine, reactivity .

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P1_33 - Dopamine species adsorbed on Ag: a DFT study of the degree of protonation and the effect of electric field

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Dopamine (DA) is a catecholamine that binds and activates cell surface receptors in humans and mammalians. This neurotransmitter plays an important physiological role in the central nervous, renal and hormonal systems. It is of great medical and pharmacological interest to study chemical interactions in which this molecule is involved. According to the pH value of the solvent medium, different forms of catecholamine molecules have been reported, including neutral, zwitterionic, cationic and anionic species. Recently, several proposals for DA detection have published based on cyclic voltammetry and surface-enhanced Raman spectroscopy where the use of colloidal Ag nanoparticles as substrate for DA adsorption allows a better detection of this molecule. In this work, the adsorption of the zwitterionic (Z-DA), protonated (P-DA) and deprotonated (DP-DA) species on the surface of Ag(111) and Ag (110) was studied using the Vienna Ab Initio Simulation Package (VASP) in the context of the Density Functional Theory (DFT) formalism. The repeated slabs representing the Ag(110) and Ag(111) surfaces contain five and four layers of atoms, respectively, and a vacuum gap in the normal direction. The adsorbed species and at the same time the first and second atomic layers for Ag(110) were allowed to relax. In the case of the Ag(111) surface only the first atomic layers was relaxed. For the adsorption of DA species a horizontal orientation was considered, with the aromatic ring parallel to each Ag surface. The adsorbate-substrate interaction was evaluated by computing the electronic charge-density difference and the DEEC6 atomic-charge analysis, showing an important reorganization of electronic charge. The effect of an homogeneous electric field on the adsorption of Z-DA on Ag systems was also studied.

Mots-Clés: Zwitterionic Dopamine, Protonated/Deprotonated Dopamine, Ag, Electric Field, VASP

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Poster Session 2

Jeudi 6 Juillet (17h30 / 20h00)

P2_01 - Tetra- and penta-coordinated geometry in Zn sal(ph)en complexes

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The preferences of coordination geometry related to Zn(II) metal in sal(ph)en complexes have attracted much attention because of the large structural diversity hence induced. Furthermore, Zn-sal(ph)en complexes are known from their ability to accept one axially coordinated species, when the usual tetrahedral geometry of Zinc metal center is inaccessible, allows easy formation of stable penta-coordinated, (distorted) square pyramidal, make them suitable candidates for supramolecular synthesis1. The purpose of this work is to understand, using conceptual density descriptors, how all Zn2+complexes can fit into tetrahedral and penta-coordinated geometries.
In a first approach the properties of the [ZnCl4]2- cluster have been studied, and some general rules extracted. To generalize the behavior of coordination of Zinc in sal(ph)en complexes, few complexes adopting tetrahedral2 and penta-coordinating geometry3 based on salen ligand are selected, and their properties are analyzed and rationalized.

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Mots-Clés: coordination chemistry, zinc complexes, structure

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P2_02 - Influence of the Spin-Orbit Coupling on many uranyl species in a solvated medium

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It is acknowledged that the relativistic quantum treatments are mandatory when molecular species involve a heavy-element (Z> 54). Among these species, the uranyl isoelectronic cations, especially $UO_2^{(2+)}$ and UON^+, have been widely studied in the scientific litterature. Indeed, these species play a key role in the nuclear combustible cycle and a better knowledge of their chemical properties remains of crucial importance. However, most of quantum calculations, aimed at describe the molecular structure and spectroscopic properties, are performed in a non-relativistic frame, or sometimes in taking into account only the scalar relativistic effects. Relativistic spin-dependent effects are usually forgotten. In this contribution, the spin-orbit coupling (SOC) effects on the spectroscopic parameters have been investigated for solvated uranyl cations species $UO_2^{(2+)}(H_2O)_n$ and $UON^+(H_2O)_n$ (n=0,1,2,3,4,5) at the quasirelativistic 2c-DFT level (2-component). Recently, the topological analysis of the electron density (atoms in molecules theory QTAIM), well established in the non-relativistic field for long time ago, has been extended to quasirelativistic quantum calculations (Pilme et al, 2014). In this context, it has been shown that the density analysis provides a straightforward way to highlight the SOC effects on the classical chemical paradigms. Using the QTAIM approach in this quasirelativic framework, we will present in this contribution an original strategy to analyze together solvation effects and relativistic effects (scalar and SOC) on the bonding schemes.

Mots-Clés: uranyl, relativity, spin, orbit, topology, solvation

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P2_03 - Modelling the electronic states of polyphenylene-ethynylene

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Hydrocarbon dendrimers are macromolecules experimentally well-known for their interesting optoelectronic properties[1]. Phenylene-ethynylene (PE) dendrimers behave as light-harvesting antennae in which unidirectional exciton transfer occurs along a series of linear, conjugated building blocks connected *via* the *meta*-substitution of phenylene rings. Thus, PE dendrimers have received much interest as artificial photosynthetic systems. Recent theoretical investigations based on semi-classical dynamics simulations[2] have indicated that the unidirectional energy transfer involves a cascade of conical intersections between excited states localized on different linear fragments. Yet, the calculations of potential energy surfaces (PES) remains out of reach for any level higher than semi-empirical, due to the size of the systems.
Previous investigations using TD-DFT calculations showed that the electronic states involved in the energy transfer are almost pure single excitations localised on linear fragments, which allows a first-order description in terms of near-frontier π-orbitals. Calculations based on the extended H$'$uckel approach confirmed that the frontier molecular orbitals (FMOs) of linear PEs (i) are dominated by the interaction between the FMOs of the fragments of benzene and acetylene (ii) bear some similarity with polyene chains when the number of units increases. In addition, we analysed the dependence of the FMOs on the main geometrical deformations occurring during electronic transitions. This work is the basis for a semi-empirical-type model to be used ultimately in quantum dynamics simulations of energy transfer processes.

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Mots-Clés: phenylene, ethynylene dendrimers, light, harvesting antennae, excitation energy transfer, effective Hamiltonian, semiempirical model, H$'$uckel description

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P2_04 - On the applicability of MP2.5 method in atmospheric reactivity

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Quantum chemical study has been performed on the reaction energies of the reactions of methyl iodide CH3I, di-iodomethane CH2I2 and tri-iodomethane CHI3 with hydroxyl radical. All series of reactions were treated using the following methods: MP2, MP3, CCSD, CCSD(T) and with the so-called MP2.5 approximation which is expected to be computationally efficient approximation to CCSD(T) within either chemical (± 4kJ/mol) or sub-chemical accuracy (± 10kJ/mol). We have used the correlation consistent cc-pVTZ basis set for light elements and cc-pVTZ-PP basis set for iodine in all calculations. In these atmospheric reactions, we considered various types of products (closed- and open-shell species). The reactions represent either isogyric processes or processes leading to atomic species. The differences between MP2.5 and CCSD(T) were evaluated. When comparing the MP2.5 and CCSD(T) data for reaction energies, the results indicate that majority of MP2.5 reaction energies are in good agreement with the CCSD(T) ones, differences ranging from "chemical" (+-4kJ/mol) to "sub-chemical" (+-10 kJ/mol) accuracy. However, all the reactions including IO species do not fit into these error bars, most probably due to considerable multireference character of IO moelcule. Possible extension and optimization of this method for similar difficult cases will be discussed.

Acknowledgement

We thank Slovak Grant Agencies VEGA (Grant 1/0092/14) and APVV (Project APVV-15-0105) for support.

Mots-Clés: atmospheric chemistry, reaction energy, perturbation theory, coupled cluster, iodine, MP2.5

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P2_05 - Tautomerism of Uracil: Revisited

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The one-step tautomerization processes of uracil and its radical cation and radical anion have been investigated in the light of the reaction force and reaction electronic flux (REF) formalisms. The relative energies of the different tautomers as well as the corresponding tautomerization barriers have been obtained through the use of the G4 high-level ab initio method and by means of B3LYP/6-3111G(3df,2p)//B3LYP/6-3111G(d, p) calculations. Systematically, the enol radical cations are more stable in relative terms than the neutral, due to the higher ionization energy of the diketo forms with respect to the enolic ones. Conversely, the enol radical anions, with the only exception of the 2-keto-N1 anion, are found to be less stable than the neutral. The effects of the ionization are also sizable on the tautomerization barriers although this effect also depends on the particular tautomerization process. The reaction force analysis shows that all reactions are mainly activated through structural rearrangements that initiate the electronic activity. This electronic activity is monitored along the reaction coordinate through the REF that obeys a delicate balance between the acid and basic character of the atoms involved in the hydrogen transfer.

Mots-Clés: Uracil, DFT, Tautomerism, Reaction Electronic flux

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P2_06 - Statistical vs non-statistical effects and the importance of the activation method in unimolecular fragmentation of peptides via chemical dynamics simulations

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Often a reliable description of the potential energy surface (PES) leads to a good knowledge and prevision of a reaction mechanism and the associated rate constants. However, non-statistical and non-equilibrium effects are often observed in reaction dynamics in both molecular dynamic simulations (MD) and experiments. Those influence the reactions in a way that their mechanisms and rate constants are not predictable by means of statistical theories as transition state theory, Rice-Ramsperger-Kassel-Marcus (RRKM).
Unimolecular dissociations should undergo into rapid and complete internal vibrational relaxation to be modelled through RRKM. However, this is not always observed, especially in gas phase where the system is not fast thermalized by the bath and fast processes are often favoured. The way in which the system is thermalized (or not) could, indeed, induce a statistical (or not) dissociation of the system. MD, where the electronic structure problem is solved *on-the-fly* and many trajectories are propagated provide useful information. Here we have studied gas phase reactivity using MD with semi-empirical Hamiltonians, which are compulsory when studying large systems.
We have recently studied the fragmentation different behaviour as obtained by direct dynamics simulations in which the system is vibrationally activated by explicit collisions and by a microcanonical energy activation for the deprotonated di-proline and doubly protonated peptides [1], TIK(H+)2 and TLK(H+)2[2,3]. Different pathways and mechanisms are observed depending on the activation way.
Finally, we will explain in details the L-cysteine fragmentation, which appears experimentally different as function of the activation mode. The combination of collision simulations and PES study provided an explanation of such experimental observation.

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Mots-Clés: Molecular dynamics, Unimolecular fragmentation, Peptides

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P2_08 - Electron Localization Function From Density Components

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In this contribution, the decomposition of the Electron Localization Function (ELF) into partial density contributions using an appealing split of kinetic energy densities is presented. Regarding the degree of the electron localization, the relationship between ELF and its usual spin-polarized formula will be discussed. A new localization function, quantifying the measure of electron localization for only a subpart of the total system, will be also introuduced. The methodology appears tailored to describe the electron localization in bonding patterns of subsystems, such as the local nucleophilic character. Beyond these striking examples, this work opens up opportunities to describe any electronic properties that depend only on subparts of the density in atoms, molecules or solids.

Mots-Clés: ELF, decomposition, spin, density, Nucleophilic, Fukui

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P2_09 - Microsolvated Electron in Water

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Electron-solvation and charge-transfer processes are relevant in physics, chemistry and biology. Hydrated electrons are systems of broad interest of themselves and useful to understand many chemical processes. These species have some distinctive features, such as: a broad absorption spectrum with a maximum around 720 nm, a vertical detachment energy (VDE) around 3.3 eV for electrons in the bulk, and a life time of a few picoseconds before recombining completely with the environment. However, attempts to explain these phenomena are still inconclusive and it is necessary to conduct additional studies.

Taking into account that many physicochemical properties are not exclusively dependent on the global energy minimum of a chemical species, we carried out exhaustive explorations of the potential energy surfaces (PESs) for clusters-like models of the micro-hydrated electron by using a stochastic search program (ASCEC [1,2]). We report the geometries and properties of 85 structural motifs located on the CCSD(T)/Aug-cc-pVTZ//MP2/6-311++g** PESs of anionic water clusters, for different sizes (n=2-6), distributed as: 2 for the dimer, 3 for the trimer, 17 for the tetramer, 22 for the pentamer, and 41 for the hexamer.

Most motifs are within 0.20 eV of the lowest energy structure. Binding energies per water molecule (BE/n) increase in going from the dimer to the hexamer and reach values of up to 0.29eV. VDE is negative only in the case of the dimer. For the hexamer, VDE is close to the value reported for pre-hydrated electrons.[3] Our results show that all structural motifs can be classified into two classes, depending on whether the excess electron is located peripheral to a water dimer in the structure or inside a cavity formed by 2 opposing water molecules with hydrogen atoms facing each other. These two motifs are the building units for larger clusters.

Mots-Clés: Microsolvation, Hydrated electron, Stochastic exploration

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P2_10 - Force fields and vibrational assignments of alkaloid cocaine as free base, cationic and hydrochloride forms by using the SQM methodology

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The pharmacological and medicinal properties that have the tropyl alkaloids as cocaine are attributed to the tertiary nitrogen atom belonging to the > N-CH3 group. The identification of this drug is of interest for the human health because high doses of cocaine cause your brain cells to kill themselves [1]. The vibrational spectroscopy is the technique most used to quantify mixed of cocaine or simply to identify it using a fast screening method but, so far, the complete assignments of their vibrational spectra were not reported. Hence, in this work the structural and vibrational properties of the free base, cationic and hydrochloride species of cocaine in gas and aqueous solution phases have been studied by using DFT calculations. The experimental available ATR, FTIR, FTRaman and Terahertz spectra, the corresponding normal internal coordinates together with the SQMFF approach were employed in order to perform the complete vibrational assignments. The force constants and the complete assignments of the 123, 126 and 129 vibration normal modes expected for the free base, cationic and hydrochloride species respectively are reported for first time. In addition, the predicted IR spectrum for cocaine hydrochloride reveals that in the solid state this species is in their cationic form, as observed by the experimental IR spectrum. The cation cocaine in both media is most electrophilic and reactive than the cation tropane increasing notably their reactivity. However, the nucheophilicity indexes for the tropane alkaloid in both media are comparable to those observed for toxics substances as saxitoxin and cation pyridonium. Probably these results for tropane, different from cocaine species, suggest that the modifications in the stereochemistry of tropane generate a loss in their potency, as was reported in the literature [2].

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Mots-Clés: Cocaine, vibrational spectra, molecular structure, descriptor properties, DFT calculations

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P2_11 - Chemical reactivity of uncatalyzed and Lewis acid-catalyzed Mukaiyama reaction between C,O,O-tris(trimethylsilyl)ketene acetal and aldehydes using density functional theory

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Mukaiyama aldol1 reaction is an efficient reaction for forming carbon-carbon bonds. This reaction is an addition of silyl enol ether (enolsilane) or ketene silyl acetal on carbonyl compounds. In 2001, Bellassoued and co-workers2 studied Mukaiyama aldol reaction between C,O,O-tris(trimethylsilyl)ketene acetal and a variety of aldehydes (aliphatic, vinylic, and aromatic), catalyzed by HgI2 at room temperature and in toluene solutions. This aldol reaction affords to prepare *syn* and *anti* β-trimethylsiloxy-α-trimethylsilyl alkanoic acid silyl esters in low diastereoselectivity.
This Mukaiyama condensation in absence of catalyst and in the presence of MX3-Lewis acid catalyst has been studied theoretically using density functional theory with the M06-2X exchange-correlation functional.3 These DFT calculations mostly demonstrate that (i) all reactions are exothermic and exergonic, (ii) the *syn* product is both kinetically and thermodynamically favored, (iii) the diastereoselectivity decrease strongly from uncatalyzed to Lewis acid-catalyzed reaction. Analyzing the concerted mechanism unravels four types of cyclic transition states for uncatalyzed reaction, with two pro-*anti* and two pro-*syn* whereas six types of open transition states for MX3-catalyzed reaction have been obtained, with three pro-*anti* and three pro-*syn* transition states.

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Mots-Clés: DFT, catalyzed and uncatalyzed Mukaiyama aldol reaction, reaction mechanism, diastereoselectivity

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P2_12 - Metal clusters as hydrogen storage: Transformation of Isoelectronic [EnAl4-nH7+n]- (E = Be, Mg, Ca, Sr, Ba; n = 1- 4) systems

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One of the forms of chemical hydrogen storage materials is the covalently bound hydrogen in either solid or liquid phase. Among them, metal hydrides, such as BeH2, MgH2, CaH2, SrH2, BaH2 and AlH3 have been interesting due to they can store high percentages in weight of hydrogen. An experimental and theoretical study about closo-alanes series revealed that the Al4H7- composition possesses an exceptional stability and low reactivity; properties that make possible its potential use as building blocks for assembled nanomaterials. It is well know that the enhancing of the chemical and physical properties of atomic clusters can be acquired by doping these structures rationally with chemical species that are isoelectronic to the ones that they replace, i.e., which have the same number of valence electrons. Based on this strategy, we present here the design of some systems analog to Al4H7-, but with a higher hydrogen content. For this purpose we carried out explorations on the Potential Energy Surfaces (PESs) of EAl3H8-, E2Al2H9-, E3AlH10- and E4H11- (where E = Be, Mg, Ca, Sr and Ba) systems, through of the Gradient Embedded Genetic Algorithm (GEGA) program. Vertical Electron Affinity (VEA), Vertical Ionization Potential (VIP) and HOMO-LUMO gap descriptors indicate that the most stable systems correspond to clusters doped with beryllium and magnesium atoms. The chemical bonding analysis of the most stable clusters, through the Adaptive Natural Density Partitioning (AdNDP) analysis, showed that the increment in the 3c-2e E-H-Al bridge-like chemical bonds is the way of incorporation and stabilization of the extra hydrogen atoms. Finally, explorations on the PESs of the neutral species (using Na+ as counterion) indicate that the NaBe3AlH10 and NaMg3AlH10 minimum-energy structures retain the original geometrical shapes of the anionic systems. This result supports the potential use of these species as building blocks for cluster-assembled hydrides.

Mots-Clés: hydrogen storage, chemical bonds, metal hydrides, AdNDP, GEGA

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P2_13 - Vibrational assignments of cationic, neutral and hydrochloride species of alkaloid tropane by using their normal internal coordinates and the SQM procedure

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The vibrational studies of molecules with heterocyclic rings with pharmacological activities are very important to our investigations [1]. In this work, the complete vibrational assignments of cationic, neutral and hydrochloride species of alkaloid tropane and their force fields were studied in gas and aqueous solution phases by using the experimental available FT-IR spectrum of tropane hydrochloride in the solid state and hybrid calculations derived from the density functional theory (DFT). The normal internal coordinates for all species were employed to compute the corresponding force fields by using the scaled quantum mechanical force field (SQMFF) methodology [2] at the B3LYP/6-31G* level of theory. The theoretical structures studied can be seen in Figure 1.
All structures were optimized in both media with the Gaussian 09 program by using the same level of theory [3]. As the bicyclic (N-methyl-8-a-zabicyclo[3.2.10]octane) group is constituted by two fused piperidine and pyrrolidine rings, as shown in Figure 2, we have performed the vibrational analysis by using the normal internal coordinates corresponding to rings of six and five members and taking into account the redundant internal coordinates due to that the C-N-C group is common to both rings. This way, the force fields were obtained by using the SQMFF procedure with the Molvib program [4].

The force constants and the complete assignments of the 66, 69 and 72 vibration normal modes expected for the neutral, cationic and hydrochloride tropane species, respectively are reported for first time.

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Mots-Clés: Tropane, vibrational spectra, molecular structure, DFT calculations

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P2_14 - Influence of water, hydrogen and dioxygen on the Stability of the Cr2O3 surface

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The understanding of surface nature of chromium oxide is an important scientific and industrial problem. The determination of the actual outer layer of such a surface is of critical importance in the case of nuclear plant accident as various products will react with partially oxidized surface witch may reduce or increase the effect on the environment.
This work has been motivated by the lack of information in the literature concerning the reduction of chromia surfaces by H2 (the formation of di-hydrogen being expected in case of nuclear accident) and the confusion about the nature of these surfaces in presence of H2O.
In this theoretical work, the stability of α-Cr2O3 surfaces in various oxidizing and reducing environments has been investigated. The electronic structure calculations, the magnetic properties of the bulk and surfaces have been explored within the DFT+U framework. Investigating a large number of possible terminations we show that the oxidation promotes the formation of a chromyl surface in agreement with the existing literature. We show that the hydrogenation of bare chromia surface is not thermodynamically favoured, however, adding hydrogen to the chromyl surface leads to a very stable hydroxide termination. Regarding water adsorption, we discuss the differences between the experiments results: the ones published in (M. A. Henderson, S. A. Chambers, Surf. Sci. 449 (2000) 135), leading to a fully hydrated surface, and the others published in (V. Maurice, S. Cadot, P. Marcus, Surf. Sci. 458 (2000) 195), leading to a fully hydroxylated surface. Finally we present a new hydrated surface (fully hydroxylated surface) noted [-Cr2-(OH)3], which is consistent with experimental observations.

Mots-Clés: Surface stability Chromium oxide, Chemical potential, Magnetism

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P2_15 - From Au or Ag clusters to nanoparticles : an ab initio and atomistic study

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Noble metal nanoparticles are valuable because of their relevant and intriguing physic/chemical properties at the interface with chemical or biological species, conferring them a decisive role in many application fields such as new technologies and medicine [1]. Nonetheless the physico-chemical phenomena inducing those properties are not well understood yet. A lot of simulation models have been implemented in order to reproduce their properties but these models are still considered insufficient.
We intend to carry out reliable simulations of both gold and silver nanoparticles in interaction with alkane thiolates as ligand molecules in order to understand differences between these two metals, as evidenced by experimental results.
First, we will study the metal/thiolate interactions from small clusters ($<$ 3 nm) to periodic surfaces ($>$ 10 nm) using calculations based on " Density Functional theory" (DFT) followed by a topological analysis of chemical bonding using the Quantum Theory of Atoms In Molecules (QTAIM) method.
In the second part, obtained results will be adapted to a new approach of molecular dynamics using polarizable force field or reactive force field (ReaxFF). Thanks to LAMMPS software, this approach will able us to investigate gold/silver nanoparticles coated with thiolates in vacuum and then in solvents for which a large amount of experimental data exists [2]. The method should reproduce both M-M and M-S bond breaking, the well known "staple" motif [3], as well as atomic diffusion on the surface of the nanoparticle.

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Mots-Clés: metallic clusters, metallic nanoparticles, thiolates, ligands, multiscale simulations

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P2_16 - Theoretical extension and computational implementation of CCSD and CCSD(T) under APMO framework

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Equations of Coupled Cluster Singles and Doubles (CCSD) under the Any Particle Molecular Orbital (APMO) framework, have been derived by using an extended version of SymPy package which is able to manipulate second-quantized operators for multiple quantum species. Additionally, APMO/CCSD equations have been extended to perturbative triples excitations under Many-Body Perturbation Theory (APMO/CCSD(T)).

Both APMO/CCSD and APMO/CCSD(T) extensions have been implemented in the LOWDIN quantum chemistry package [1]. In order to test our implementation, we have benchmarked it against Gaussian and Gamess obtaining linear correlation.

Finally, we have calculated several properties on molecular systems including the calculation of the positron binding energy for the Positronium Hydride (PsH) recovering 49,37% of correlation energy with respect to the APMO/HF result.

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Mots-Clés: Coupled Cluster Theory, APMO method, SymPy package, Many Body Perturbation Theory, LOWDIN software package, Positron Binding Energy

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P2_17 - Electrochemical behaviours and relativistic DFT calculations to understand the terminal ligand influence on the [Re6(μ3-Q8)X6]4- Clusters

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A Born-Haber thermodynamic cycle was used to determine the redox potential in a series of rhenium (III) clusters of the form [Re6(μ3-Q8)X6]4- where Q = S2-, Se2- and X = F-, Cl-, Br-, I-, CN-, NC-, SCN-, NCS-, OCN-, NCO-. Frequency analysis, relativistic and solvent effects were taken into account to estimate the free energy of the reversible process ReIII6/ReIII5ReIV at DFT level of theory. All the redox potential were reported with respect to the SHE and are in good agreement with the available experimental results. For example for [Re6(μ3-Se8)CN6]3- /4, [Re6(μ3-S8)CN6]3- /4-, [Re6(μ3-S8)Br6]3- /4- and [Re6(μ3-S8)Cl6]3- /4- clusters, reported values of 0,57 V 0,79 V, 0,55 V and 0,51 V respectively, close to calculated values 0,60 V, 0,78 V, 0,50 V and 0,53 V, for the same clusters. This means that the DFT method with the Born-Haber cycle used to obtain values of potential redox is a good approximation for the prediction in this type of clusters.In general, the molecular orbitals involved in the redox process are located in the core of the cluster and therefore the peripheral ligands acting only as a crystal field influencing the energy splitting of the molecular orbitals. Additionally, the theoretical approach was validated by an experimental protocol to study the electrochemical behavior of [Re6(μ3-Se8)I6]3- cluster. An important first reversible reduction process was found at E1/2 = +0.47 V (SHE), which is in good agreement with the value predicted theoretically.

Mots-Clés: Rhenium (III) clusters, relativistic DFT, cyclic voltammetry

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P2_18 - On Hydrogenation Reactions of Precursor of Amino Acids in the Interstellar Medium: Theoretical Study Based Upon the Reaction Force Analysis

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Based on the experimentally determined network of hydrogenation processes of hydrogen cyanide **HCN** into methylamine **CH3NH2** [1], in this research we studied the mechanisms of hydrogenation of precursors needed in the amino acids formation reactions that takes place in the interstellar medium. Using high level ab-initio calculations and theoretical descriptors of the electronic and structural activity taking place during a chemical reaction, a detailed characterization of the mechanisms involved in the different steps of the hydrogenation are provided.
The study is based upon the reaction force analysis [2,3] and takes advantage of the partition of the reaction coordinate into reaction regions where different mechanisms might be taking place. The reaction mechanisms are elucidated through the characterization of the evolution along the intrinsic reaction coordinate of various structural and electronic properties. Transition states structures, the physical nature of activation energies and the specific interactions driving the reaction mechanisms are analyzed and discussed.

Acknowledgments: This work was supported by FONDECYT through project No 1141098
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Mots-Clés: Hydrogenation reactions, reaction force, reaction electronic flux, isomerisation reactions

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P2_19 - Analysing the DCT Behaviour in Photo-induced Charge Transfer Processes

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Phototriggered molecular rearrangements as Twisted Intramolecular Charge Transfer (TICT) and Excited State Intramolecular Proton Transfer (ESIPT) have gained an ever-growing interest among the scientific community, over the last few decades. Indeed, through-space charge transfer (CT) excitations play a key role in many technological applications from solar-to-electricity conversion devices to natural and artificial photosynthetic architectures.Here we present a TD-DFT study, intended to provide a simple understanding and characterization of excited-state CT processes. We rely on the DCT index, which recovers the effective charge/hole distance associated to a given transition, based on the computed ground state and excited state relaxed or unrelaxed densities.Aside a standard Excited States PES analysis we introduce an alternative, yet equally valid method for the characterization of the CT phenomena at the excited state, relying on the idea that at the excited state, the DCT minimum lies very close to the energy one. To this end, the DCT results obtained for two different organic photochemical reactions are analyzed and compared in this study. The first reaction studied concerns the TICT Excited-State Processes in 4-(N,N-Dimethylamino)benzonitrile (DMABN), in which the torsion of the dimethylamino group around the CN bond to the phenyl ring induces a charge transfer in which the former group acts as electron donor and the benzonitrile moiety as the electron acceptor. Secondly we study the DCT change in a well-known example of an ESIPT, that is the photoinduced enol-keto tautomerization of the 2-(2'-hydroxyphenyl) benzothiazole (HBT). Based on these two studies we design a new computational protocol, which allows the following of excited-state electron transfer processes based on the minimization of the DCT index. **Funding:** This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 648558, STRIGES CoG grant).

Mots-Clés: Charge Transfer, Excited State, ESIPT, TICT, DCT, Dual Emission

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P2_20 - Different mutual positions of double bonds in open chains and information from magnetically-induced current densities

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Magnetically-induced current densities have been utilised extensively to investigate aromaticity. On the other hand, an applied external magnetic field induces a current in all chemical bonds. The present work investigates the values and patterns of magnetically-induced current densities in the pi bonds of dienes and polyenes (open chains containing two or more double bonds). The three possibilities for the mutual positions of the double bonds (conjugated, isolated and consecutive) are considered with an adequate number of molecules for each category. More than one molecule with the same pi-system is often considered, to highlight the effect of the molecular context. Both *cis* and *trans* isomers are considered for each case, to verify whether current densities differ for different isomers.

In the case of conjugated double bonds, the current circulates through all the double bonds thanks to electron delocalization. Comparisons with the calculated molecules of the other two categories - involving double bonds without electron delocalisation - highlight the effect of the delocalization associated with conjugation. For isolated double bonds, the current pattern in each individual bond resembles that of ethylene (used as reference, as the smallest system with a pi bond). In the case of consecutive double bonds, there is no electron delocalization because the planes of any two consecutive pi bonds are perpendicular to each other; this requires separate calculations for each plane, with the magnetic field perpendicular to one or the other of the planes.

The presentation includes three-dimensional streamline plots as well as three-dimensional plots of the magnitude of the current density, to better highlight the typical features of each category. Comparisons of the current patterns in open chains containing three conjugated double bonds with those in benzene highlight the effect of aromaticity with respect to the effect of the sole electron delocalization of the open chain.

Mots-Clés: current density, electron delocalization, aromaticity

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P2_22 - Reactivity of CH3I and CH2I2 with H: (H, I)-abstraction and I-substitution reaction pathways

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Organic compounds CH3I and CH2I2 have been detected in marine boundary layer in the coastal water or in the open ocean. They participate in the generation of aerosols in coastal zones.The reactions of CH3I with O, H, and OH have been the subject of several theoretical studies [1,2,3]. The reactivity of CH2I2 with OH radicals have been also investigated recently [3]. However, the kinetic parameters and thermochemical properties of H+CH2I2 reactions are unavailable experimentally. In this work, we provide reliable kinetic and thermodynamic data for the gas phase reactions using DFT and high-level ab initio methods.
To characterize the different reaction channels, optimized structures and vibrational frequencies were computed at the MP2/aug-cc-pVTZ level of theory. More accurate potential energies were computed for geometries previously optimised using coupled cluster theory and the aug-cc-pVnZ (n=T,Q) basis sets for C and H and Peterson's pseudo potential basis set for Iodine including the core valence and the scalar relativistic corrections (ECP28MDF). The spin-orbit coupling for the iodine specieswas evaluated at the MRCI/aug-cc-pVTZ level of theory taking the CASSCF wave function as a reference.Transition state theory is employed to provide rate constants as a function of temperature. The I-abstraction is predicted to be the major pathway for both reactions as it was not the case for the OH+ CH3I, CH2I2 reactions. The same methodology will be extended to investigate the thermochemical properties and reactivity of halogenated peroxy radicals on their atmospheric degradation pathways.

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Mots-Clés: Iodine, spin orbit coupling, thermochemical properties, rate constants, transition state theory

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P2_23 - Point defect calculations to rationalize the opto-electronic behavior of the CdIn2S4 material: quantum chemistry meets experiments

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In the last decade, the development of new materials designed for embedded photovoltaic devices has considerably increased to answer to the growth of energy demands of consumers. Among all these researches, the Institut des Matériaux Jean Rouxel (IMN) has found that the treatment by KF in CIGS based thin-films creates a CdIn2S4 inter-layer. Upon creation of this interlayer, the performance of the system is ∼15 % and is also perfectly reproducible.
CdIn2S4 is a material which crystalizes in a direct spinel in which the Cd2+ and the In3+ are respectively in tetrahedral and octahedral sites. Most of the properties of a material are coming from its defects, intrinsic or extrinsic ones. Furthermore, the spinel structure possesses a large capability to form point defects. Among them, one may cite: vacancies, substitutions, antisites. Therefore, a theoretical investigation on the impact of defects on the CdIn2S4 spinel material has been performed.
In this presentation, it will be demonstrated that the study of defects using quantum calculations is a powerful technique to obtain new insights in materials. Furthermore, it will be showed that the calculations provide a full explanation of the electrical behavior on the CdIn2S4 target. Finally, a rationalization of the synthesis atmosphere will be furnished.

Mots-Clés: DFT, First principles calculations, defects, semiconductors

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P2_25 - CaSnO3 perovskite applied in the catalytic reduction of NO

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In the present work, the orthorhombic calcium stannate (CaSnO3) (001) surface was studied, due to the low cost of raw materials. Besides that, the well known use of SnO2 as sensor for different gases, indicating that stannates with perovskite structure may be used in catalytic reactions for different gases, in particular, NO with CO or NH3. Simulations under Density Functional Theory and PBE and PBE0 functional was carried out with CRYSTAL program in order to give an insight into the catalytic results. The experimental results indicate that the NO to N2 conversion catalyzed by CaSnO3 was favored for the NO + NH3 reaction. Carbon monoxide, CO, and ammonia, NH3, gases were adsorbed onto SnO2-terminated surface. The surface and adsorptions were evaluated using Density of States (DOS), Raman intensities (through the Coupled-Perturbed-Hartree-Fock/Kohn-Sham algorithm) and QTAIM. The CO adsorption was weaker than the adsorption of NH3. Both of them presented large shifts on the Raman spectra, however only NH3 presented a new intense Raman peak at about 3098 cm-1.

Mots-Clés: calcium stannate, perovskite, catalytic, DFT, CRYSTAL

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P2_26 - Theoretical analysis of ZnO/GaN nanotubes via DFT

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The wurtzite phase of Zinc oxide (ZnO) presents an intrinsic n-type semiconducting due the defects such as oxygen vacancies and zinc interstitials. However, from the electronic point of view, pn-type junction materials are promising due to applications in semiconductors devices such as solar cells, light-emitting diodes, photodetectors, rectifier diodes, and bipolar transistors. Based on that, the p-type Gallium nitride (GaN) it is the ideal material to do a heterojunction with ZnO due to its natural p-type, similar semiconductor behavior and slight lattice mismatch.

The ZnO/GaN interface have attracted much attention and they are promising candidates for optoelectronic devices. However, despite the several works about these heterostructures, there are a few about nanotubes and, as far as we know, there are no reports about the ZnO/GaN nanotubes. Therefore, the aim of this work was to analyze the stability of double-walled ZnO/GaN armchair and zigzag nanotubes, performed by Density Functional Theory (DFT), and also for calculations of structural, electronic, elastic and piezoelectric properties.

DFT simulations were conducted using CRYSTAL14 program, with B3LYP hybrid functional and all-electron basis set. From the optimized ZnO/GaN armchair and zigzag nanotubes it was possible to conclude that the outer walls are determinant for nanotube stability and also for electronic properties. If ZnO is the outer wall, the nanotubes have small strain energy and greater energy band gap, in comparison to nanotubes with GaN outer walls. The Density of States shows that the electron transition always occurs between the outer walls atoms, due to the higher contribution of these atoms. The coloration of ZnO/GaN nanotube in the electromagnetic emission spectra also depends of the material that constitutes the outer wall. Thus, the observed coloration for the ZnO/GaN nanotube with ZnO constituting the outer wall was the same coloration observed for the pure ZnO.

Mots-Clés: ZnO/GaN, nanotube, DFT

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P2_27 - Truncated Conjugate Gradient : a non-iterative method for computing polarization in molecular dynamics

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In classical Molecular Dynamics, taking polarization into account is still a non-trivial problem: it is computationally very costly, and usual algorithms introduce a drift, an error on the dynamics that accumulates with time and threatens the simulation's stability. We introduce a new class of methods, the Truncated Conjugate Gradient, in order to tackle both these issues. TCG methods are based on the truncation of the conjugate gradient algorithm, an iterative solver insuring convergence typically used in this context. Our methods allow the user to drastically reduce and control the computational costs, as well as providing, thanks to its non-iterative nature, analytically exact expression for the forces, effectively solving any issue on the stability of the simulation. We also present an implementation scheme for this method and in particular the evaluation of the gradients, which is not as straightforward as one could think, in order to exploit TCG to its full potential. This new polarizable force field scheme will be part of TinkerHP v.1.1, a Molecular Dynamic simulation package designed for High Performance computation on supercomputers. We will present a quick overview of this package's features and interests.

Mots-Clés: classical MD, polarization, solver, method

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P2_28 - Nitriles/Isonotriles : looking for missing isomers

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The nitriles/isonitriles family is the most represented one among the two hundred or so molecules which have been detected in the interstellar medium (ISM). This family involves the largest molecule ever found in the ISM, composed by a linkage of thirteen atoms, HC11N. However, in spite of this wealth of molecules, little is known about the interstellar chemistry of nitrogen. One of the remaining questions is the identification of isomers to be searched for in the ISM in order to build a chemical model of nitrogen species. It has been recently verified that, in most cases, the most abundant isomer of a given chemical formula corresponds to the most stable one, and that the abundance of isomers decreases as their relative energies increase: this "minimum energy principle" (MEP) can thus be viewed as a guide for the detection of new species.[1]
In this work, we have been interested in isomers with formula C2H3N. The geometries of all nine isomers have been optimized at the MP2/Aug-ccpVT level; single-point calculations at the CCSD(T)/Aug-cc-pVTZ (respectively CCSD/Aug-cc-pVTZ) have been performed to obtain reliable values of electronic energies and rotational constants (respectively dipole moments). The results are in agreement with the MEP: indeed the most stable isomer, acetonitrile, is the most abundant in the ISM, whereas the abundance of isoacetonitrile is lower than the one of etheneimine, in agreement with their relative stabilities (+24.2 and 27.2 kcal.mol-1respectively). The following isomer to be searched for would be ethynamine, but its high energy relative to acetonitrile (+41.3 kcal.mol-1) makes its detection by rotational spectroscopy unlikely. Successive elimination of hydrogen atoms consecutive to attacks by hydroxyle radicals has also been considered, and the exothermicities of the reactions will be presented.

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Mots-Clés: Astrochemistry, isomers, molecular complexification, reactivity, MP2, CCSD

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P2_29 - Theoretical exploration of the reaction between sulfenyl and thiol radicals

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Hydrosulfenyl ($HSO^{\bullet}$) and thiol ($HS^{\bullet}$) radicals are small sulfur species that participate in atmospheic mechanisms of ozone destruction. Furthermore, they can be viewed as the smallest species exhibiting the coupling between sulfur atoms with different oxidation states, as observed in enzymes like peroxiredoxin, sulfiredoxin and sulfurtransferases. In this work, we have applied CCSD(T), composite methods (CBS-QB3, G4 and W1BD) as well as dispersion corrected density functional theory (DFT), PBE0-GD3 and M06-GD3, to the study of the reactions paths of those species. Dunning correlation consistent basis sets, cc-pVnZ (n=3,4,5), were used for the DFT and CCSD(T) calculations. All reaction paths starting from the most stable initial complex HS-S(=O)H as well as from the least stable one, HS-O-SH, were explored. Free energies of reaction obtained with the ab initio methods behaved as CBS-QB3 $<\sim$ G4 $<\sim$ W1BD$\sim$ CCSD(T). Results obtained with DFT methods were in general of similar quality to CCSD(T), although important deviations were observed in some points of the PES. Whenever that happened, it was observed that the M06-GD3 results were much more similar to CCSD(T) than those obtained with PBE0-GD3. The most stable reaction products obtained were H2O and 3S2. The free energy of reaction in this case was obtained as -55.1(CCSD(T)/cc-pV5Z), -55.6(W1BD), -53.4(G4), -54.2(CBS-QB3), -54.8(M06-GD3/cc-pV5Z) and -53.2 kcal/mol (PBE0-GD3/cc-pV5Z). Other products, like SSO+H2 and H2S+3SO, were thermodinamically less stable (-36.4 and -32.5 kcal/mol at the CCSD(T)/cc-pV5Z level).
To explore further the eventual meaning in relation to the reactions in proteins, the interaction between HSOX and HSY (X,Y=$^{\bullet}$,–,H) was investigated. Eight specific reactions were explored
(1)$HS^{\bullet}$+$HSO^{\bullet}$ →HSS(=O)H (2)HS–+$HSO^{\bullet}$ →HSS(=O)$H^{\bullet}$– (3)$HS^{\bullet}$+HSO–→HSS(=O)$H^{\bullet}$–
(4)HS–+$HSO^{\bullet}$ →HSSH+HO– (5)HSH+HSO–→HSSH+HO– (6)HS+HSOH →HSSH+H2O
(7)$HS^{\bullet}$+HSOH→HSSH+$HO^{\bullet}$ (8)HSH+$HSO^{\bullet}$ →HSSH+$HO^{\bullet}$
Only reactions (1),(2),(3)and(6) presented negative free energies, with reaction(3) the more favorable. Further studies are been performed on these species.

Mots-Clés: sulfenyl radical, thiol radical, DFT calculations, atmospheric chemistry, disulfide bonds

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P2_30 - DFT and TDDFT study of Avobenzone in Different environments

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Organic ultraviolet filters (UV) such as Avobenzone which have effectiveness of filtering UV radiations, is used in the cosmetic or pharmaceutical products to minimize the damages caused by the exposure of the skin to the sun.
In this work, a detailed study of the photostability, structural and electronic properties of the three tautomers of Avobenzone, were carried out by using DFT method and its approach dependent on time called TDDFT. We have selected some solvents employed in cosmetic and differ in polarity and proticity such as a fatty acid (hexanoic acid), a fatty alcohol (1-hexanol) and cyclohexane.
The objective of this study is to examine theoretically the effect and influence of these solvents on the stability of the Avobenzone. Spectral profile UV of Avobenzone was also simulated, and the results showed a good agreement with the experimental data.

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Mots-Clés: Avobenzone, keto, enolic equilibrium, photostability, DFT, TDDFT

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P2_31 - Novel Carbone/Germanium cages structure: Theoretical Study with MP2 and Density Functional Theory.

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Carbone and Germanium are members of the same group in the periodic table, suggesting a great probability to form similar and combined structures. Furthermore, due to the importance of germanium that is a promising material in some physical process; substantial efforts have focused on theoretical investigating novel Carbon-Germanium (CGe) structures. However, it is difficult to form cages like carbon fullerenes purely with Ge atoms, due to the fact that germanium does not favor the sp2 hybridization that carbon does. Carbon normally forms strong π bonds trough sp2 hybridization, which can facilitate the formation of two-dimensional spherical cages (or planar structures such as benzene and graphene). Germanium however, usually forms covalent σ bonds with sp3 hybridization, which favors a three dimensional structure. CGe structures as the candidates to replace organic molecules for their structural similarity have opened considerable research interest. The aim of the present work is to discuss the results of MP2 and density functional calculations on the geometric and electronic properties of the news CnGen structure and C2nGe2n nano-cage with n= 3, 4, 5, 6, 7 and 8. We investigated the dipole moment, molecular orbital energy analysis, energy with zero point energy correction (ZPEC) and quantum molecular descriptors including chemical potential μ, global hardness η, index of electrophilicity ω and energy gap [EHOMO - ELUMO] of the news CnGen molecule and C2nGe2n nano-cage.

Mots-Clés: MP2, DFT, Novel Carbone/Germanium structures.

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