12TH CONGRESS ON ELECTRONIC STRUCTURE: PRINCIPLES AND APPLICATIONS

ESPA 2022

21-24 JUNE 2022

VIGO

BOOK OF ABSTRACTS

CONTENT

WELCOME

Dear Colleagues,

On behalf of the organizing committee, it is our pleasure to welcome you to Vigo to the 12th Congress on Electronic Structure Principles and Applications (ESPA2022). ESPA is a series of international conferences organized by the Spanish Community of Quantum Chemists. The ESPA conferences, initiated in 1998, have a two-year periodicity and cover all major fields of Theoretical and Computational Chemistry from method development to state-of-the-art applications across computational molecular science.

The previous ESPA editions were organized in Madrid (1998), San Sebastián (2000), Sevilla (2002), Valladolid (2004), Santiago de Compostela (2006), Palma de Mallorca (2008), Oviedo (2010), Barcelona (2012), Badajoz (2014), Castellón (2016) and Toledo (2018).

These conferences were initially intended to bring together the Spanish Theoretical and Computational Chemistry community, however, they grew over time (both in national and international participation), thereby evolving into a key event with international reputation in the field.

The organizers of this conference are delighted and honored to host this edition of ESPA, the 2nd Biannual Meeting of the Group of Chemistry and Computers of the Spanish Royal Society of Chemistry and the 9th Young Scientists Workshop on Theoretical Chemistry and Computational Modelling (Workshop on TCCM).

This book collects the abstracts for the plenary and invited lectures, oral communications and poster presentations of ESPA2022, as well as the abstracts for the oral communications and poster presentations of the Workshop on TCCM.

We would like to thank our sponsors, specially the Xunta de Galicia, the Vigo Convention Bureau, the University of Vigo and the Chemistry and Computation Division of the Spanish Royal Society of Chemistry, for their financial support to organize the conference.

We wish you a successful congress both scientifically and personally in the magnificent natural environment that the city of Vigo offers its visitors.

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WORKSHOP ON TCCM

June 20 – Monday

8:30-9:00 **Registration**

9:00-11:00 **Session 1.** Chairman: Enrique Sánchez-Marcos (Universidad de Sevilla)

9:00-9:15 **WOC1: Toraya Fernández Ruiz** – Universidad de Cantabria, ES

"Second principles time dependent simulations of electric transport in graphene"

9:15-9:30 **WOC2: Genis Lleopart Motis** – Universitat de Barcelona, ES

"Evidence for low-lying correlated gapped states in strained graphene and α-graphyne"

9:30-9:45 **WOC3: Asier Urriolabeitia Rodrigo** – Universidad de Zaragoza, ES

"The role of pyridone assistance in the selective Rh catalyzed dimerization of terminal alkynes"

9:45-10:00 **WOC4: Silvia Escayola Gordils** – Universitat de Girona, ES

"The intriguing aromaticity of (sub)phthalocyanines"

10:00-10:15 **WOC5: Oksana Azpitarte** – Euskal Herriko Unibertsitatea, ES

"Physicochemical, structural and conformational study of FMN-containing miniSOG"

10:15-10:30 **WOC6: Raquel Yanes Rodríguez** – IFF-CSIC, ES

"Exploring guest-host (lattice) interactions in noble gas clathrate hydrates through first-principles computations"

10:30-10:45 **WOC7: Raquel Rubert Albiol** – Universitat de València, ES

"Theoretical study of dicyanomethylene-based π-conjugated compounds with diradical character"

10:30-10:45 **WOC8: Marti Gimferrer** – Universitat de Girona, ES

"Assignment of oxidation states from optimally fragment-localized orbitals"

11:00-11:30 **Coffee Break**

11:30-13:30 **Session 2**. Chairman: Victor Polo (Universidad de Zaragoza)

11:30-11:45 **WOC9: Gustavo A. Cárdenas** – Universidad Autónoma de Madrid, ES

"MoBioTools: A toolkit to automatically set up QM/MM calculations from an ensemble of geometries"

11:45-12:00 **WOC10: Daniel Gonzalo Palao** – Universitat de Barcelona, ES

"Environment effects change FRET distributions in a fluorophore-tagged disordered protein"

12:00-12:15 **WOC11: Fernando Romeo Gella** – Universidad Autónoma de Madrid, ES

"Rationalizing the photophysical properties of BODIPY derivatives"

12:15-12:30 **WOC12: Miriam Navarrete Miguel** – Universitat de València, ES

"Photoinduced repair mechanism of various oxetane models of (6-4) photo-product DNA lesions"

12:30-12:45 **WOC13: Santiago Movilla Núñez** – Universitat Jaume I, ES

"Dual allosteric activation of the Prp2 ATPase/helicase by RNA. A computational mechanistic study on the ATP hydrolysis"

12:45-13:00 **WOC14: Luca Nicoli** – Politecnico di Milano, IT

"In search of the best polarizable embedding approach to calculate electronic excitations in aqueous solutions"

13:00-13:15 **WOC15: María Zubiria Ulacia** – DIPC, ES

"Triplet excimers of small aromatic molecules"

13:15-13:30 **WOC16: Sergio Boneta Martínez** – Universidad de Zaragoza, ES

"Computational approach to the hydride transfer in the human Apoptosis Inducing Factor enzyme (hAIF)"

13:30-15:00 **Lunch**

15:00-17:00 **Session 3**. Chairman: Raquel Castillo (Universitat Jaume I)

15:00-15:15 **WOC17: Adriana Cabrera Ramírez** – IFF-CSIC, ES

"A quantum chemistry study on CO_2 clathrates: Exploring the formation, energetics and the stability"

15:15-15:30 **WOC18: Andoni Ugartemendia** – Euskal Herriko Unibertsitatea, ES

"Ge as a promoter for the catalytic oxidation of CO by Pt clusters"

15:30-15:45 **WOC19: Raúl M. Alvarado de la Torre** – Universidade de Vigo, ES

"Simulating detection of dioxine-like pollutants with 2D surface enhanced Raman spectroscopy using h-BNC substrates"

15:45-16:00 **WOC20: Waqas Amber Gill** – Universitat de València, ES

"Analytical interaction potentials for carbon dioxide"

16:00-16:15 **WOC21: Sergi Danés Pibernat** – Universitat de Girona, ES

"How to safely assess the oxidation state? Pros and cons from the EDA-NOCV scheme"

16:15-16:30 **WOC22: Xiang Xu** – DIPC, ES

"Natural-orbital based multireference diagnostic for wavefunction methods"

16:30-16:45 **WOC23: Anna Piras** – Heidelberg Institute for Theoretical Studies, GE

"Nitroaromatic pollutants on graphene: from physisorption to redox properties"

16:45-17:00 **WOC24: Marta Queizán Cores** – Universidade de Vigo, ES

"Novel computational techniques within the multiconfigurational approach applied to metal cyanin complexes"

17:00-17:30 **Coffee Break**

17:30-18:30 **Session 4**. Chairman: Mokhtar Lamsabhi (Universidad Autónoma de Madrid)

17:30-17:45 **WOC25: Josep Borràs de Llano** – Universidad Autónoma de Madrid, ES

"The effect of Feschbach resonances on the different vibrational states of N_2 in a RABBIT experiment"

17:45-18:00 **WOC26: Kilian Arteaga Gutiérrez** – Universidad Autónoma Madrid, ES

"Multiphoton double ionization of H_2 induced by attosecond pulses"

18:00-18:15 **WOC27: Amel Derradji** – Universidad de Alicante, ES

"Computational design of conjugated molecules with lower (or isoenergetic) S1 than T1 excited-state energies"

18:15-18:30 **WOC28: Joel Fallaque** – Universidad Autónoma de Madrid, ES

"A simple model to engineer single-molecule conductance of acenes by chemical disubstitution"

ESPA2022 CONFERENCE

June 21 – Tuesday

8:30-9:15 **Registration**

9:15-9:35 **Opening Ceremony**

9:35-11:00 **Session 1.** Chairman: Antonio Fernández (Universidade de Santiago de Compostela)

9:35-10:20 **PL1: Donald G. Truhlar** – University of Minnesota, US
"New methods for quantum mechanical photochemistry"

10:20-10:40 **IL1: Juan J. Nogueira** – Universidad Autónoma de Madrid, ES
"Modeling membrane transport and protein binding"

10:40-11:00 **OC1: Marta E. Alberto** – University of Calabria, IT
"Ru(II)- and Os(II)-polipyridil photosensitizers with highly photocytotoxic 3ILCT states in both normoxia and hypoxia: theoretical insight"

11:00-11:30 **Coffee Break**

11:30-13:35 **Session 2**. Chairman: Ramón Sayós (Universitat de Barcelona)

11:30-12:15 **PL2: Maria J. Ramos** – Universidade de Porto, PO
"Mechanisms of enzymatic reactions"

12:15-12:35 **IL2: David Ferro** – Universidade de Santiago de Compostela, ES
"New computational tools for chemical kinetics: The cathedral package"

12:35-12:55 **IL3: Mar Reguero** – Universitat Rovira i Virgili, ES
"Determining the mechanism of the catalytic reduction of CO_2 by Zn molecular complexes. Difficulties and options"

12:55-13:15 **OC2: Ferran Feixas** – Universitat de Girona, ES
"Navigating the conformational landscape of interacting biomolecules: Millisecond time scale activation of allosterically regulated enzymes"

13:15-13:35 **OC3: Natacha Gillet** – CNRS École normale supérieure de Lyon, FR
"Mapping guanine oxidation in nucleosomal DNA using multiscale simulations"

13:35-15:30 **Lunch**

15:30-17:35 **Session 3**. Chairman: Andrea Lombardi (Università degli Studi di Perugia)

15:30-16:15 **PL3: Jesús M. Ugalde** – Euskal Herriko Unibertsitatea, ES
"Chirality transmission, over distant achiral molecules, aided by plasmonic nanoparticles tagged with chiral molecules"

16:15-16:35 **IL4: Chérif F. Matta** – Mount Saint Vincent University, CA
"ATP Synthase: A moonlighting enzyme with unique functions"

16:35-16:55 **IL5: Maria N. D. S. Cordeiro** – Universidade de Porto, PO
"Fine-tuning deep eutectic solvents for CO_2 capture using machine learning tools"

16:55-17:15 **OC4: Roberto A. Boto** – DIPC, ES

"Identifying electromagnetic and chemical contributions to SERS"

17:15-17:35 **OC5: Henar Martínez** – Universidad de Valladolid, ES

"Computational study on the affinity of potential drugs to SARS-CoV-2 main protease"

17:35-19:00 Poster Session I + Coffee Break

PO1-PO63 + WPO1-WPO35

19:00-20:00 Meeting of the RSEQ group in Chemistry and Computation – Conference Room

June 22 – Wednesday

9:00-11:05 Session 4. Chairman: Saulo Vázquez (Universidade de Santiago de Compostela)

9:00-9:45 **PL4: Krishnan Raghavachari** – Indiana University, US

"Beyond chemical accuracy at DFT cost: Models combining connectivity-based fragmentation and graph-based machine learning"

9:45-10:05 **IL6: Noelia Faginas** – Università degli Studi di Perugia, IT

"Molecular simulations of $CO_2/N_2/H_2O$ gaseous mixture separation in multilayer graphtriyne membranes"

10:05-10:25 **IL7: Karinne Miqueu** – Université de Pau et des Pays de l'Adour, FR

"New reactivities and new bonding situations of gold complexes: The key role of the theory–experiment synergy"

10:25-10:45 **OC6: Luis Cerdán** – Universidat de València, ES

"GMM-NEA: Reconstruction of nuclear ensemble approach absorption spectra using unsupervised machine learning"

10:45-11:05 **OC7: Josep M. Bofill** – Universitat de Barcelona, ES

"Controlling chemical reactivity with optimally oriented electric fields: A generalisation of the Newton trajectory method"

11:05-11:30 Coffee Break

11:30-13:35 Session 5. Chairman: Iñaki Tuñón (Universitat de València)

11:30-12:15 **PL5: Fernando P. Cossío** – Euskal Herriko Unibertsitatea, ES

"Bicolor fluorescent sensors for barium tagging in neutrinoless double beta decay nuclear reactions: A fruitful interplay between theory and experiment"

Sponsored by the Chemistry & Computation division of the RSEQ

12:15-12:35 **IL8: Emilio Martínez-Núñez** – Universidade de Santiago de Compostela, ES

"AutoMeKin: An open-source program for automated reaction discovery"

Sponsored by the Chemistry & Computation division of the RSEQ

12:35-12:55 **IL9: Inés Corral** – Universidad Autónoma de Madrid, ES

"Structure-photophysics relationships in genetic building blocks: The keys to the current composition of nucleic acids"

12:55-13:15 **OC8: María Fumanal** – École Polytechnique Fédérale de Lausanne, CH

"Optimizing the thermodynamics and kinetics of the triplet-pair dissociation in donor-acceptor copolymers for intramolecular singlet fission"

13:15-13:35 **OC9: Jon Uranga** – Georg-August-Universität Göttingen, DE

"A lysine-cysteine redox switch: The NOS bridge"

13:35-15:30 Lunch

15:30-21:00 Trip to Illas Cíes

15:30 h Departure from Vigo at Estación Marítima

16:30 h Arrival on Illas Cíes

16:30-20:30 Guided visit to Illas Cíes

20:30 h Boat ride on the estuary with appetiser

June 23 – Thursday

9:00-11:05 Session 6. Chairman: Antonio Largo (Universidad de Valladolid)

9:00-9:25 **IL10: Manuel Yáñez** – Universidad Autónoma de Madrid, ES

"A fight of Be versus B for tetracoordination: Stability of $(BeX_2)_m$:$(BX_3)_n$ (n=0,1,2; m=0,1,2) clusters"

9:25-9:45 **OC10: Enrique M. Arpa** – Linköping University, SW

"Computational design of more efficient solar energy storage molecules based on the dihydroazulene/vinylheptafulvene photoswitch"

9:45-10:05 **IL11: Barry Carpenter** – Cardiff University, UK

"The influence of conical intersections on ground-state chemical reactions"

10:05-10:25 **IL12: Àngels González-Lafont** – Universitat Autònoma de Barcelona, ES

"Understanding how reticulocyte 15-lipoxygenase-1 catalyzes the production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway"

10:25-10:45 **OC11: Tomás González-Lezana** – CSIC, ES

"Ca^{2+} ions solvated in helium: The observation of the largest shell around an impurity"

10:45-11:05 **OC12: Carles Curutchet** – Universitat de Barcelona, ES

"Determination of the energy ladder in cryptophyte photosynthetic antenna complexes from multiscale simulations"

11:05-11:30 Coffee Break

11:30-13:35 **Session 7**. Chairman: Panaghiotis Karamanis (Université de Pau)

11:30-12:15 **PL6: Peter Gill** – The University of Sydney, AU

"Two approximations for accelerating quantum chemistry calculations"

12:15-12:35 **IL13: Eduard Matito** – DIPC, ES

"Correlation-driven spin-component-scaled second-order Møller-Plesset perturbation theory"

12:35-12:55 **IL14: Ángel Martín-Pendás** – Universidad de Oviedo, ES

"An open quantum subsystems view of atoms (or fragments) in molecules: Application to the local spin problema"

12:55-13:15 **OC13: Pedro Salvador** – Universitat de Girona, ES

"Unified treatment of spin-polarization in wavefunction analysis"

13:15-13:35 **OC14: Coen de Graaf** – Universitat Rovira i Virgili, ES

"GronOR: A massively parallel and GPU-accelerated program for non-orthogonal configuration interaction"

13:35-15:30 **Lunch**

15:30-17:35 **Session 8**. Chairwoman: Aurora Costales (Universidad de Oviedo)

15:30-16:15 **PL7: Julia Contreras-García** – Sorbonne Université, FR

"Insight into superconducting behaviour from topological analysis"

16:15-16:35 **IL15: Chiara Cappelli** – Scuola Normale Superiore, IT

"Computational spectroscopy of complex systems: Breaking the complexity barrier"

16:35-16:55 **IL16: Vicent Moliner** – Universitat Jaume I, ES

"Towards the computation-assisted design of new enzymes"

16:55-17:15 **OC15: José Plata** – Universidad de Sevilla, ES

"Exploring the role of chemical composition in the lattice thermal conductivity of thermoelectric materials assisted by machine learning"

17:15-17:35 **OC16: Samantha C. S. Lemos** – Universitat Jaume I, ES

"In_2O_3 as multifunctional material: Fundamentals and progress of a versatile semiconductor"

17:35-19:00 **Poster Session 2 + Coffee Break**

PO64-PO149

21:00 h **Gala Dinner at Hotel Los Escudos**

June 24 – Friday

9:15-11:05 **Session 9.** Chairwoman: Mª. Teresa Roca Moliner (Universitat Jaume I)

9:15-10:00 **PL8: Núria López** – ICIQ, ES

"Simulations of materials for CO_2 electrochemical reduction"

10:00-10:20 **IL17: Erina Rosta** – University College London, UK

“Reaction mechanism and dynamics of phosphate catalytic enzymes”

10:20-10:40 **OC17: Carmelo Naim** – Université de Bordeaux, FR

“Electric-field induced second harmonic generation responses of push–pull polyenic dyes: theoretical characterizations and comparison with experiments”

10:40-11:00 **OC18: Marco Marazzi** – Universidad de Alcalá, ES

“Solar-Thermal fuels in the spotlight: Novel methods for standard systems and standard methods for novel systems”

11:00-11:30 Coffee Break

11:30-13:15 Session 10. Chairwoman: Olalla Nieto (Universidade de Vigo)

11:30-11:50 **OC19: Fabrizio Silveri** – Gemmate Technologies s.r.l., IT

“From Atom to Anode: the MODALIS2 multiscale approach to modelling Si/C anodes for lithium-ion batteries”

11:50-12:10 **IL18: Manuel Melle-Franco** – Universidade de Aveiro, PO

“Bridging the divide between models and experiments”

12:10-12:30 **IL19: Alessandro Erba** – Università di Torino, IT

“Spin current density functional theory of weyl semimetals: Spin-orbit coupling in TaAs”

12:30-13:15 **PL9: Laura Gagliardi** – The University of Chicago, US

“Multireference methods for quantum materials”

13:15-13:30 Closing Ceremony

PLENARY LECTURES
ESPA2022

New Methods for Quantum Mechanical Photochemistry

D. G. Truhlar[1,*]

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PL1

We have developed new methods for photochemical dynamics, including:

Time-derivative coherent switching with decay of mixing (tCSDM) and curvature-driven coherent switching with decay of mixing (κCSDM) [1–4]. These methods calculate nonadiabatic dynamics without nonadiabatic coupling vectors, and **κCSDM** (aka “NACs for free”) does not require wave function overlaps either. They are based on a mean-field trajectory with decoherence of the density matrix by a semiclassical Liouville-von Neumann equation. Both methods are available in the free, open-source SHARC-MN software.

Compressed-state multi-state pair-density functional theory (CMS-PDFT) [5,6]. This allows accuracy comparable to XMS-CASPT2 at the cost of state-averaged CASSCF. Because it is based on MC-PDFT, which uses an MCSCF reference function, it does not suffer from the spin mixing problem of Kohn–Sham TDDFT for photodissociation problems, and because the final step is a diagonalization in a small model space, it gives the correct topology of interacting surfaces at and near conical intersections. Fast analytic gradients are available in the free, open-source *OpenMolcas* program.

Direct diabatization by neural network (DDNN) [7,8]. Machine intelligence is used to simultaneously find and fit the diabats such that the eigenvalues of the diabatic potential energy matrix agree well with the adiabatic potential energy surfaces. The only required inputs are the adiabatic energy surfaces and specification of weakly coupled geometries where the diabats may be set equal to the adiabats. From the output one gets all the energies, gradients, and couplings needed to run very fast quantal or semiclassical multi-surface dynamics in either the adiabatic or diabatic representation.

References

[1] Y. Shu, L. Zhang, S. Mai, S. Sun, L. González, D. G. Truhlar, *J. Chem. Theory Comput.* 2020, 16, 3464.
[2] L. Zhang, Y. Shu, S .Sun, D. G. Truhlar, *J. Comput. Phys.* 2021, 154, 094310.
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[8] Y. Shu, Z. Varga, S. Kanchanakungwankul, L. Zhang, D. G. Truhlar, *J. Phys. Chem. A* 2022, 126, 992.

This work was supported in part by the U.S. Dept. of Energy, the National Science Foundation, and the Air Force Office of Scientific Research.

PL2

Mechanisms of Enzymatic Reactions

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We know that we can establish catalytic mechanisms of enzymatic reactions and, in doing so, explain the findings of experimentalists, but can we actually predict them accurately? This talk is concerned with the computational needs that we come across to figure out results within computational enzymology. Calculations devised to study protein interactions and circumvent problems in some relevant systems will be reported as well as recent developments in the establishment of some catalytic mechanisms. We have resorted to QM/MM [1,2] as well as other calculations [3,4], in order to analyse the energetics of processes related to the systems under study and evaluate their feasibility according to the available experimental data.

References

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Chirality Tranfer Mediated by Plasmonic Electromagnetic Fields

PL3

A. García-Etxarri[2], J. J. Sáenz[1], V. Mujica[3] and J. M. Ugalde[1,*]

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Chirality imprinting in nanomaterials is a well documented, though poorly understood phenomena. Thus, circular dichroism and optical rotatory signatures have already been observed on substrates with chiral molecules absorbed on-top [1]. Likewise, it has also been reported that handedness can be imparted on excited states upon excitation with circularly polarized light. When the chemistry of those excited states takes place in a time scale shorter than the de-excitation time scale, that chemistry is imprinted by the handedness of the exciting light [2].

A newer phenomena concerns with the transfer, over large distances compared to atomic scale lengths, of chirality in hybrid nanoparticle systems. Recent experiments [3] have reported on chirality information transfer mediated by plasmonic metallic nanoparticles, from a chiral tag-molecule to an achiral probe-molecule located at more than 20 nm away, a distance long enough as to render chirality transfer mediated by local bond formation and/or breaking, impossible. The chirality transfer was detected by the Raman activity of the achiral probe-molecule.

In this talk we will present the fundamentals of a theory along with its computational support [4,5] for the mechanism of this kind of chirality transfer, as mediated by the electromagnetic field arising from photon absorption and re-emission by the plasmonic nanoparticle, surface-decorated with a chiral molecule. Using a semi-classical model, we will show that the re-emitted plasmonic electromagnetic field carries chirality coherently over long distances, which is ultimately reflected as a chiral-dependent distinct electric-field intensity at the achiral probe-molecule. This model provides a simple and surprisingly robust description of this type of re-emitted plasmonic electromagnetic-field mediated chirality-transfer, which can unambiguously be detected by Raman spectroscopy on distant achiral probe-molecules.

References

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[4] A. García-Etxarri, J. M. Ugalde, J. J. Sáenz, V. Mujica, *J. Phys. Chem. C* 2020, 124, 1560.
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Beyond Chemical Accuracy at DFT Cost: Models Combining Connectivity-based Fragmentation and Graph-based Machine Learning

PL4

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The failure of available density functional (DFT) methods to compute accurate electronic structures and energies for complex systems is well documented. While newly developed dispersion corrected and long-range corrected density functionals offer improved results, the errors in thermochemical properties computed with DFT are often greater than 5 kcal/mol for many chemical processes. In this talk, we discuss a new fragmentation-based molecular representation framework “FragGraph” for QM/ML methods involving embedding fragment-wise fingerprints onto molecular graphs. Our model is specifically designed for delta machine learning (Δ-ML) with the central goal of correcting the deficiencies of approximate methods such as DFT to achieve high accuracy.

Our framework is based on a judicious combination of ideas from fragmentation, error cancellation, and a state-of-the-art deep learning architecture. Broadly, we develop a general graph-network framework for molecular machine learning by incorporating the inherent advantages prebuilt into error cancellation methods such as the generalized Connectivity-Based Hierarchy. More specifically, we develop a QM/ML representation through a fragmentation-based attributed graph representation encoded with fragment-wise molecular fingerprints. For the thermochemistry of the 130k molecules in the GDB9 dataset, our method predicts an out-of-sample mean absolute error significantly lower than 1 kJ/mol compared to target G4(MP2) calculated energies, rivaling many deep learning methods with reduced computational scaling. Our QM/ML framework and its performance for theoretical thermochemistry are analyzed and assessed in this talk.

Bicolour fluorescent sensors for barium tagging in neutrinoless double beta decay nuclear reactions: a fruitful interplay between theory and experiment

PL5

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Neutrinoless double beta decay (*ββ0ν*) processes constitute a very promising method (perhaps the only practical way) to demonstrate that neutrinos are they own antiparticles. Demonstrating this hypothesis would constitute a major discovery in physical sciences and cosmology. One useful *ββ0ν* nuclear reaction is shown in Figure 1A. This process involves the Xe-136 isotope and leads to the emission of two electrons, whose drift and energy can be monitored [1] in an ETD (Energy-Tracking Detector), together with a barium cation. Therefore, the second essential component of the TPC (Time Projection Chamber) to monitor this reaction is the BTD (Barium Tagging Detector, Figure 1A).

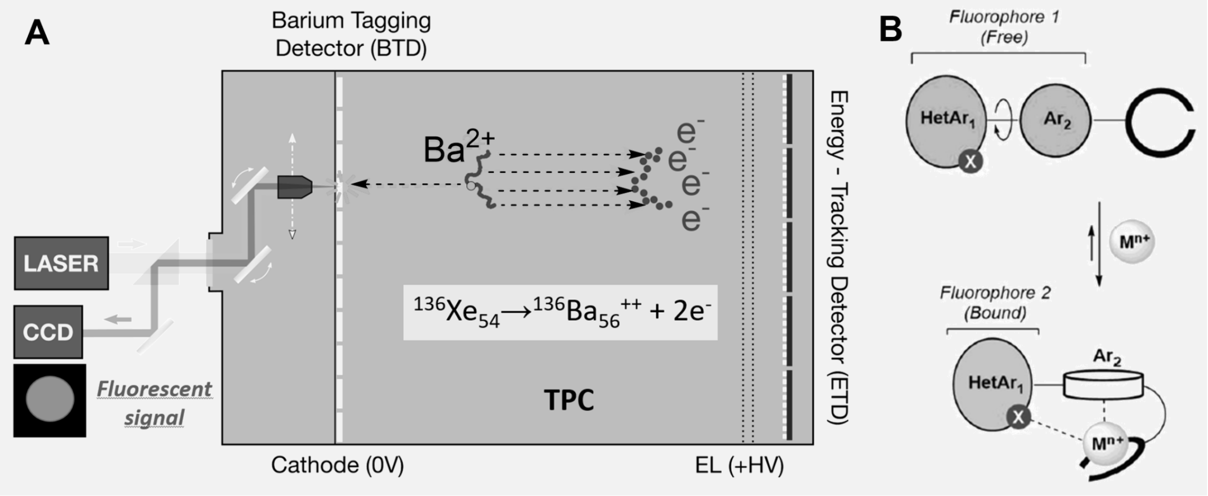

Figure 1. Basic components of a bicolor fluorescent indicator for Ba($^{2+}$) tagging in *ββ0ν* experiments.

The BTD must incorporate a fluorescent sensor [2] whose photophysical properties are adequate to distinguish the free and Ba^{2+}-bound states (Figure 1B), thus giving rise to a bicolour fluorescent indicator (FBI) potentially useful for barium tagging [3] in NEXT-BOLD experiments. The different emission spectra for the free and coordinated states stem from the decoupling between the aromatic components of the fluorophore upon barium coordination (Figure 1B). In this lecture, details about the design and chemical synthesis of FBIs, their photophysical properties and structure-activity relationships will be presented, with special emphasis on DFT and TD-DFT calculations that provide a rationale for the observed behaviour.

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Accelerating Quantum Chemistry Calculations via Highly Localized MOs

PL6

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In most quantum chemical calculations, all of the molecular orbitals (MOs) are expanded in a large set of basis functions, typically contracted gaussians that are centred on the nuclei [1]. However, we contend that this is computationally inefficient and conceptually unhelpful, and we argue that it is preferable to expand each MO in a small set of relevant functions [2]. In order to accomplish this in the context of Hartree-Fock theory [3], one needs to abandon the traditional Roothaan-Hall energy formula [4] and avoid diagonalization in the self-consistent field procedure [5]. A disadvantage of this approach is that it usually gives a higher energy than that obtained from the full basis set. The twin advantages are: (1) the HF calculations are much faster (2) they yield localized MOs [6,7] with clear chemical interpretations.

A selection of results for various molecules and basis sets will be presented.

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PL7

From quantum topology to properties. A focus on superconductivity

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A room temperature superconductor is probably the most desired system in solid state physics. So far, the greatest advances, cuprates, pnictides and number of others were obtained in a serendipitous way. As there is no clear theory for these superconductors, it is difficult to predict where progress will be made. In contrast the Bardeen-Cooper-Schrieffer (BCS) theory gives a clear guide for achieving high Tc, and hydrogen seems to be a main clue. Within this approach, the recently reported superconductivity at 190 K in compressed H2S [1] has been arguably the biggest discovery in the field since the superconducting cuprates nearly 30 years ago.

However, a microscopic understanding of why this particular material features such a strong coupling is still missing. We have recently shown that the underlying chemical structure and bonding need to be characterized for a good comprehension of the chemical composition-superconductivity relation.

We have constructed simple metal and BCS models showing that the Electron Localization Function [2] can be used to define a quantity called the networking value, which should provide insight into the superconducting activity.

By analyzing through DFT calculations the structural and electronic properties of nearly 200 compounds predicted to be superconductors in the literature, we have shown that the networking value correlates well with the predicted critical temperature, much better than any other descriptor analyzed thus far. And this, for all bonding types [3].

The discovery of the positive correlation between superconductivity and the bonding network offers the possibility of screening easily hydrogen-based compounds and, at the same time, sets clear paths for chemically engineering better superconductors.

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Atomistic modeling in Electrochemical Systems

PL8

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Electrochemical conversion of CO_2 by renewable energies holds the key to close the C-cycle. And yet, so far only Cu has been reported as being able to generate C-C bonds that would allow the formation of long chain hydrocarbons. Still, Cu only generates ethanol and ethylene with small amounts of C3 fractions not containing alkenes. In my presentation I will present the challenges in the modelling of such complex interfaces paying attention to (i) the surface restructuring of the materials under potential, (ii) the complex reaction networks and (iii) the role of cations in the reactivity observed. I will show which are the main challenges in the field and how Machine Learning techniques can help at developing better atomistic models for very complex systems.

Multireference Methods for Quantum Materials

PL9

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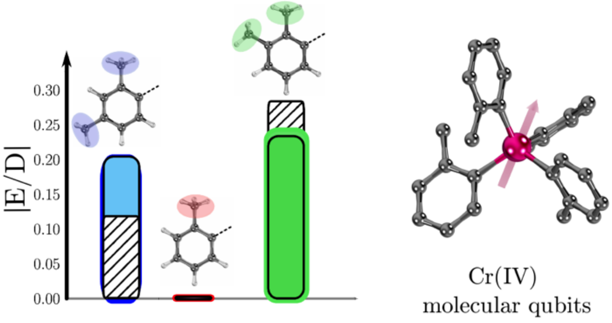
Quantum chemistry calculations of large, strongly correlated systems based on multireference wave functions are typically limited by the computation cost that scales exponentially with the size of the active space used to describe the phenomena of interest. One way to reduce the cost is to use fragmentation methods. The localized active-space self-consistent field (LASSCF) method [1] is an example of such a strategy. LASSCF is designed for applications in which electrons are strongly correlated in different weakly interacting physical regions of a molecule. I will describe our recent advances in localized active space methods, and their combination with pair-density functional theory to compute the total electronic energy. Applications to potential quantum materials [2], including molecular qubits [3] will be discussed.



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INVITED LECTURES
ESPA2022

IL1

Modelling Membrane Transport and Protein Binding

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The simulation of lipid membrane and protein processes is a complex task which requires the combination of different quantum and classical mechanical techniques. Moreover, these hybrid calculations are often performed within a dynamic framework to account for vibrational and conformational sampling. In the case where the process under investigation takes place on a long-time scale, the application of enhanced sampling approaches, such as umbrella sampling and accelerated molecular dynamics, may also be needed. In this contribution, the application of many of these approaches will be illustrated by discussing the mechanisms of some biological events recently investigated by our research group, including the permeation of the antitumoral drug cisplatin though a lipid bilayer [1,2], the binding of different inhibitors to the RNA-dependent RNA polymerase protein of SARS-CoV-2 [3], and the binding of photoswitches to a voltage-gated ion channel [4].

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New computational tools for chemical kinetics: The cathedral package

IL2

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The improvement of hardware capabilities has allowed including simultaneously most of the elementary reactions involved in complex mechanisms and predicting the corresponding rate constants, which has given rise to a new era of *ab initio* kinetics. Unfortunately, although it is possible to deal with a significantly high number of reactions, the accurate determination of their rate constants remains a key challenge even for gas-phase processes. The reasons are not just the approximations involved in their calculation, but also the steps required to achieve these rate constants. In general, manual actions and deep knowledge of chemical dynamics are required for such tasks, restricting them to *advanced users*. This situation creates a demand for **automated codes** and **user-friendly** interfaces.

We have been working on integrated computational codes able to bring theoretical studies of chemical kinetics closer to *non-expert users*. Specifically, we have developed ***The Cathedral package***, available at *Github* [1], consisting on the following programs:

- **Pilgrim** [2], employs direct-dynamics to calculate thermal rate constants of chemical reactions and to simulate chemical kinetics mechanisms;
- **Torsiflex** [3,4], searches for and locates all the conformational isomers of flexible acyclic molecules;
- **Q2DTor** [5], treats torsional anharmonicity in flexible molecules with two coupled torsions by means of the *extended two-dimensional torsional* (E2DT) method [6].

These codes can be applied to different fields, as organometallic catalysis, gas-phase mass spectrometry, the simulation of microwave spectra, the calculation of thermodynamic properties, and to the study of many chemical reactions occurring in the gas phase. At the moment, we are concentrating our efforts in applying the methods to combustion chemistry and to processes taking place at ultra-low temperatures.

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Determining the mechanism of the catalytic reduction of CO_2 by Zn molecular complexes. Difficulties and options

IL3

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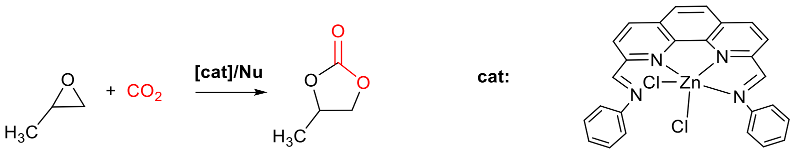
To stop the global warming, a complementary alternative to the decrease of CO_2 production is the reduction of its amount in the atmosphere by capture and transformation into consumer products. But given that CO_2 is a very stable molecule, its transformation into other products needs the use of catalysts and/or other highly reactive substances. The catalysed cycloaddition of carbon dioxide to epoxides is the greenest, cheapest and most atom-economy efficient way of synthesising carbonates [1], compounds of high industrial interest due to their applications as polar aprotic solvents, electrolytes in lithium-ion batteries, industrial lubricants, monomers for polymer synthesis or as useful intermediates for the preparation of a wide variety of organic chemical products [2-4].

It is well known that computational chemistry is a powerful tool that can contribute in the design of new and more efficient catalysts. To help in this endeavour, structural and mechanistic studies must be developed. But the complexity of the experimental systems and of the mechanisms of these reactions lead to the need of using models and approximations [5].

With the background of an experimental catalytic study developed in our department, we will use a specific case as an example to analyse the effects on the reaction profile of some of the factors that determine the computational model used on the calculations.

We present in this contribution the study of the mechanism of the cycloaddition of CO_2 to epoxides to form cyclic carbonates catalysed by a Zinc(II) complex with a tetra-aza donor ligand bearing a phenanthroline bis(aniline) skeleton (Figure 1).



Nu: tetrabutylammonium bromide (TBAB)

Figure 1. Reaction studied.

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ATP synthase: A moonlighting enzyme with unique functions

IL4

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This talk underscores the biological role of the electric potentials of enzymes beyond their roles as catalysts. Recent structures of ATP synthase from 5 species are used to compare their electrostatic potentials (ESP) and fields. Striking patterns emerge including a role of ATP synthase beyond its known catalytic function in mitochondrial energy transduction. ATP synthase's intrinsic ESP is of the order of magnitude of the chemiosmotic ESP and, hence, it is suggested to add a term to the traditional ΔG expression of chemiosmotic theory (Fig. 1):

$$\Delta G = \Delta G_{\text{chem.}} + \Delta G_{\text{elec.}} + \Delta G_{\text{ATPase}} = 2.3\,nRT\Delta\text{pH} + n\mathscr{F}Z\Delta\psi + \boxed{\underbrace{n\mathscr{F}Z\Delta\psi_{\text{ATPase}}}_{\text{NEW TERM}}}$$

Thus, we can assign three complementary roles to ATP synthase:

(1) Its putative role, and that is catalysing the phosphorylation of ADP into ATP.
(2) A novel role, which is, altering the ΔG of the reaction of translocation of protons from the inter-membrane gap to the mitochondrial matrix.
(3) Another novel role, and that it to create a potential barrier regulating the rate of proton translocation itself.

Thus, ATP synthase functions over and above its role as an enzyme as a biological catalyst.

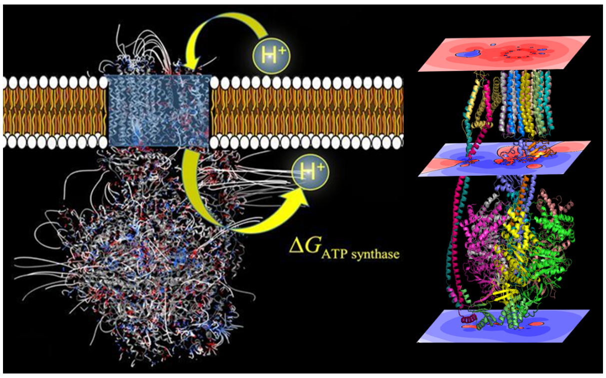

Figure 1. (Left) ATP synthase with representative electric field lines in relation to the inner mitochondrial bilayer membrane. (Right) A representation of the corresponding electrostatic potential (red/blue indicates positive/negative potential values in the displayed planes, respectively). The entering proton "sees" a positive potential (red) and a negative one (blue) on exit of the membrane-bound F_0 unit of ATP synthase

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Fine-Tuning Deep Eutectic Solvents for CO_2 Capture Using Machine Learning Tools

IL5

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Deep eutectic solvents (DES) are found as promising green solvents for CO_2 capture, especially in large scale industrial applications [1]. Indeed, compared to conventional ionic liquids (IL), DES exhibit similar favourable solvent properties but they are much cheaper, easy to prepare, and more environmentally friendly than IL. Yet, the major drawback is related to their high viscosity which difficult their management not fulfilling industrial demands. Further efforts are thus required to develop new DES solvents that hold together high capacity for CO_2 uptake and low viscosity. In this communication, we move a step forward and present results of a practical machine learning approach to simultaneously cope with these two properties. Such approach relies on the application of a multi-objective optimisation (MOOP) technique based on Derringer's desirability function [2]. We began by setting up quantitative structure-property relationship (QSPR) models targeting the two properties for a dataset of known binary DES. Both models were shown to have a high overall accuracy and predictivity, as well as to provide key information responsible for the DES' viscosity and CO_2 capture ability. Then, desirability functions derived from the individual QSPR models were found and combined to virtual screen (VS) and rank two libraries, one comprising experimentally reported DES and another one with newly designed DES. The latter enabled us to propose novel efficient DES for CO_2 uptake, *i.e.*, with the most suitable trade-offs between CO_2 absorption capacity and viscosity. Finally, and most importantly, this work demonstrates the usefulness of the MOOP-based approach for the rational discovery of deep eutectic solvents or other materials to suit particular sustainable applications.

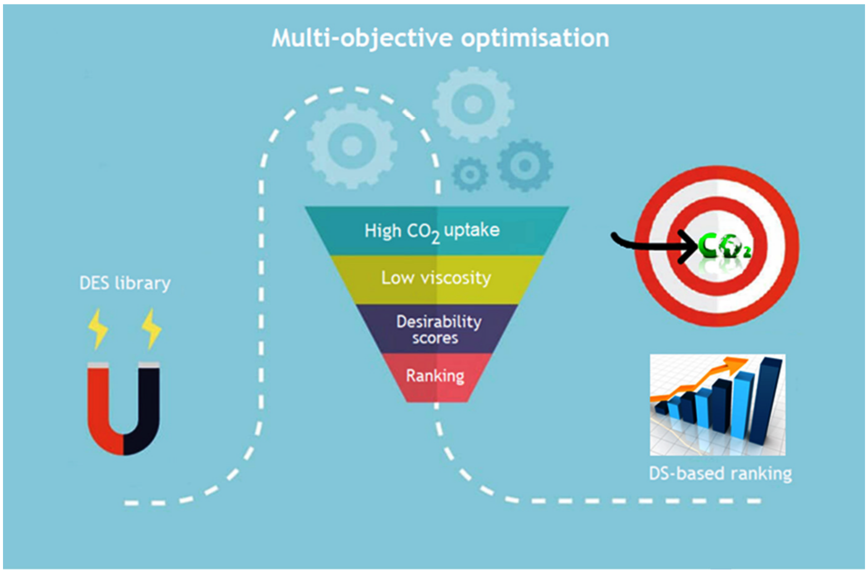

Figure 1. Flowchart showing the desirability MOOP-based approach and VS ranking

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Molecular simulations of $CO_2/N_2/H_2O$ gaseous mixture separation in multilayer graphtriyne membranes

IL6

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Graphynes are porous derivatives of graphene that can be considered as ideal 2D nanofilters. Here, we investigate by theoretical methods graphtriyne single/double and three layer, proposing them as membranes featuring pores of subnanometer size suitable for CO2/N2/H2O separation and CO2 uptake. The potential energy surfaces, representing the intermolecular interactions within the CO2//N2/H2O gaseous mixtures and between the graphtriyne layers and the molecules, have been formulated in an internally consistent way, by adopting potential models far more accurate than the traditional Lennard-Jones functions, routinely used to predict static and dynamical properties of matter. In this work, we have exploited the Improved-Lennard Jone formulation[1].

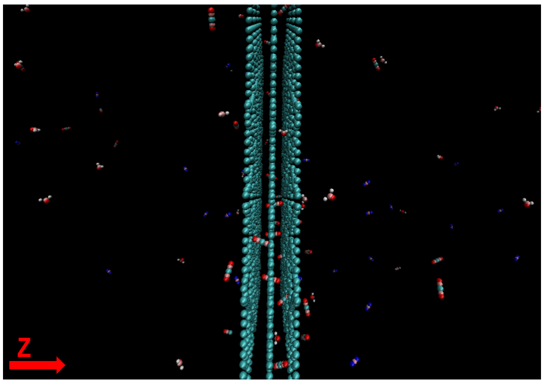

Figure 1. Snapshot of configurations for the trilayer system at 4.62 atm and 353 K

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New chemical reactivities and new bonding situations of gold complexes : the key role of the theory-experiment synergy.

IL7

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Transition metal catalysis has spectacularly progressed over the past century and nowadays occupies a forefront position in organic synthesis. For a long time, gold was considered to be too chemically inert to be used in catalysis. Hopefully, the situation has changed dramatically since 2000 and homogeneous gold catalysis has become a very active field [1].

In collaboration with Didier Bourissou's team, and through a synergetic experiment-theory approach, we initiated in 2014 a research program aiming at opening new facets in Au(I) and Au(III) chemistry through the design of new P-chelated ligands [(P,C), (P,P), (P,N)]. In this context, we have described in detail unknown reactivities (oxidative addition, migratory insertion, β-H elimination…)[2] and new intermediates with unusual bonding situations (agostic interaction [3], hydrogen bonding[3], π-alkene and π-allyl complexes …).

This presentation will be focused on the description of the electronic structure and bonding situation of Au(III) π-allyl complexes with (P,C) ligand and the study of their reactivity towards β-diketo-enolates, by DFT [4]. Impact of the ligand [(P,N)] will be discussed.[4] The hemilable (P,N) ligand also enabled access to a wide range of stable Au(I) π-complexes with unbiased alkenes, electron-rich and for the first time electron-poor ones. The direct and linear response of the (P,N) ligand to the Au/alkene coordination has been evidenced and will be discussed thanks to structural, electronic and spectroscopic data [5].

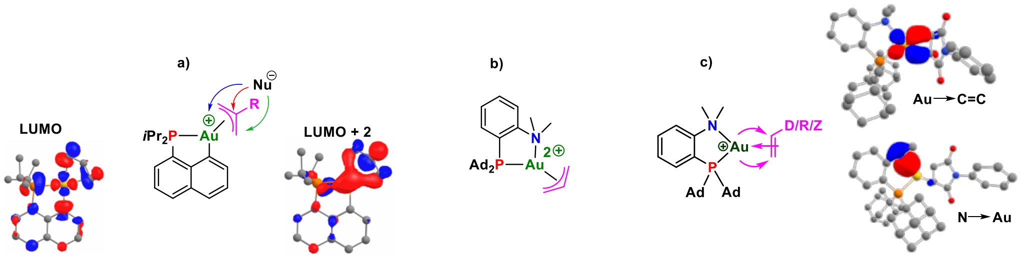

Figure 1. Au(III) π-allyl complexes with (P,C) ligand (a) or (P,N) ligand (b). (P,N)Au(I) π-complexes (c).

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AutoMeKin: An open-source program for automated reaction discovery

IL8

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A computational protocol is proposed in this talk for use in discovering reaction mechanisms. The method does not rely on either chemical intuition or assumed a priori mechanisms, working in a fully automated fashion.

The pipeline consists of three steps:
- i) Exploration of reaction mechanisms through MD simulations or chemical knowledge-based algorithms.
- ii) Use of Graph Theory to build the reaction network.
- iii) Kinetics simulations.

The method has been successfully employed to study combustion chemistry, cycloaddition reactions, photodissociations, organometallic catalysis, radiation damage of biological systems, simulation of mass spectrometry experiments, and astrochemistry, and a few examples will be given in this talk.

This methodology has been implemented in the open-source program AutoMeKin [1,2].

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Structure-photophysics relationships in genetic building blocks: The keys to the current composition of nucleic acids

IL9

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The current genetic alphabet is a reflect of the endurance of DNA and RNA monomers against multiple environmental pressures striking early Earth, among which UV light exposure played a prominent role[1]. Despite being strong UV absorbers, native nucleobases are highly photostable systems that have developed extremely efficient mechanisms to dissipate the absorbed energy, preventing this way nucleic acids' damage[2].

The scrutiny of the photophysical and photochemical properties of non-canonical purine- and pyrimidine-derivatives can help establishing the origin of the photostability of life building blocks, and at the same time identifying potential prebiotic genetic ancestors that might have participated in the primordial soup.

In this communication, we will discuss the impact of the nature, position and number of substituents in the relaxation mechanisms of nucleobases, through the inspection of the topography of the ground and excited potential energy landscapes and deactivation dynamics of a selected group of purine and pyrimidine nucleobase derivatives[3, 4, 5, 6].

These results can help establishing functionalization-photophysics relationships in purines and pyrimidines, which are key to determine the electronic and structural factors that established the superiority of the five contemporary DNA and RNA nucleobases against other organic chromophores.

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IL10

A fight of Be versus B for tetracoordination: Stability of $(BeX_2)_m$:$(BX_3)_n$ (n=0,1,2; m=0,1,2) clusters.

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Beryllium and boron are highly electron-deficient elements with distinctive peculiarities, that are clearly seen when analyzing the structures, bonding and stability of $(BeX_2)_m$:$(BX_3)_n$ (n = 0,1,2; m = 0,1,2; X = F, Cl, CN, NC, CCH) clusters. CCSD(T)/ aug-cc-pVTZ calculations show that these peculiarities are already manifested when looking at the possible dimers since, whereas $(BeX_2)_2$ homodimers are very stable, BeX_2:BX_3 heterodimers are systematically less stable than Be-homodimers, and $(BX_3)_2$ homodimers are in almost all cases not prone to form. These dissimilarities are a reflection of the strongly electropositive nature of Be compared to B. For larger clusters the differences between Be and B are also evident. Whereas no stable $BeX_2(BX_3)_2$ trimers can be found with two BX_3 monomers being neighbors, all $(BeX_2)_2(BX_3)$ trimers present, as a global minimum, a structure in which the $(BeX_2)_2$ moiety is bonded to the BX_3 monomer, and for the $(BeX_2)_2(BX_3)_2$ tetramers the $(BeX_2)_2$ subunit is at the center of the cluster (See Figure 1).

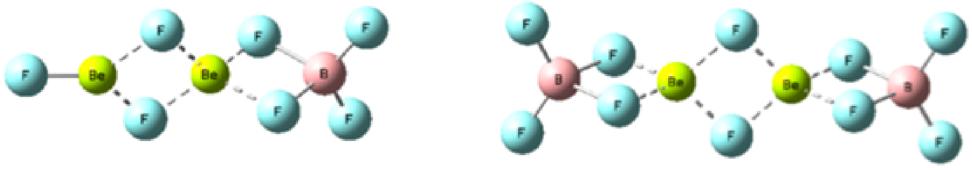

Figure 1. Optimized structures of the $(BeF_2)_2(BF_3)$ trimer and $(BeF_2)_2(BF_3)_2$ tetramer showing the preference for formation of $(BeF_2)_2$ subunits that interact with either one or two BF_3 molecules.

The relevance of this binding pattern in the global stability is supported by an excellent correlation between the stabilization energies and the number of Be-Be and Be-B interactions the clusters present, with a clear preference for maximizing facing Be subunits. One obvious consequence is that the stability of the complexes increases dramatically with their size in a fashion that can be easily predicted.

The Influence of Conical Intersections on Ground-State Chemical Reactions

IL11

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We are used to the idea that complex, multi-step reactions might have more than one mechanism. However, it is less well known that seemingly elementary steps, such as an internal rotation or a single bond homolysis can also have more than one transition state on the ground state potential energy surface. Two examples will be discussed: internal rotation in allene (Fig. 1) and homolysis of the C_1–C_5 bond in bicyclo[3.1.0]hexa-1,3-diene (Fig. 2).

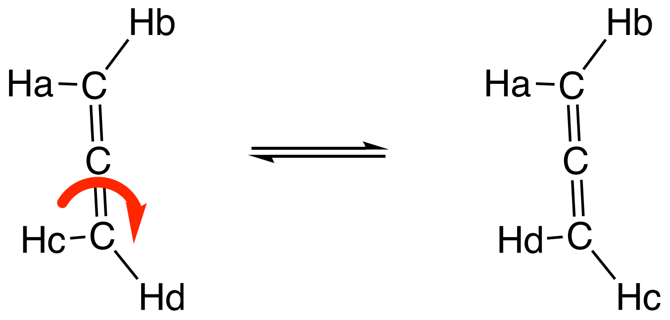

Figure 1. One of the reactions for which there are two transition states.

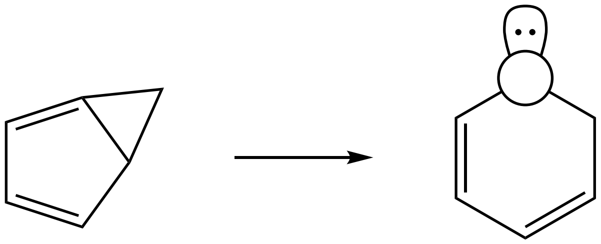

Figure 2. A second reaction for which there are two transition states.

In each of these cases, there are two different transition states which correspond to the two possible paths around the lower cone of a conical intersection [1]. In the case of the allene internal rotation, one of these paths was previously known. The new one has a higher barrier and so does not significantly alter the expected kinetics of the reaction. However, it does serve to show how allene rotation is mechanistically linked to two other reactions: ring opening of cyclopropanylidene and hydrogen migration in propenylidene.

In the case of the bicyclo[3.1.0]hexa-1,3-diene ring opening, the newly discovered path has a transition state that is 10 kcal/mol lower than the previously known one. Consequently, the new discovery does have significant impact on the calculated reaction kinetics. This is important, because the reaction in question plays a significant role in soot formation during hydrocarbon combustion.

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Understanding how reticulocyte 15-lipoxygenase-1 catalyzes the production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway

IL12

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Local acute inflammation in living organisms is a mechanism of defense in response to a tissue lesion or against an invasion of microbial pathogens. If it gets out of control, it evolves into chronic and may lead to a wide range of diseases that can be attributed to a failure of resolution. So, inflammatory processes are a first-order health problem.

The specialized pro-resolving lipid mediators (SPMs), which are cell signaling molecules formed in cells by the metabolism of polyunsaturated fatty acids, are crucial for causing the resolution of inflammation, so alleviating chronic inflammatory diseases. 5S,6R,15S-Trihydroxy-7E,9E,11Z,13E-eicosatetraenoic acid and 5S,14R,15S-trihydroxy-6E,8Z,10E,12E-eicosatetraenoic acid were the first SPMs discovered. These products are now termed lipoxinA_4 (LXA_4) and lipoxinB_4 (LXB_4), respectively, and derive from arachidonic acid. The biosynthesis of these lipoxins (lipoxygenase interaction products) requires catalysis by lipoxygenases (LOXs).

In this study, we intend to progress in understanding the lipoxin formation mechanism by means of the 5(S),15(S)-diHpETE biosynthetic pathway at a molecular level. To this aim, we have combined molecular dynamics (MD) simulations and quantum mechanics/molecular mechanics (QM/MM) calculations to explore the different reactions that reticulocyte 15-LOX- 1 can catalyze when either 5(S),15(S)-diHpETE or 5(S),15(S)-diHETE acts as a substrate.

Our results do not predict the formation of lipoxins by means of the dehydration mechanism. This result is compatible with the fact that no epoxide has been directly detected as an intermediate in the catalytic formation of lipoxins from 5(S),15(S)-diHpETE. The formation of lipoxins takes place by the oxygen molecule's addition to the π nonatetraenyl radicals derived from 5(S),15(S)-diHpETE by the C_{10} hydrogen abstraction. The antarafacial oxygen addition to C_{14} is very easy, leading later to the formation of LXB_4. However, the oxygen molecule's addition to C_6 is blocked by C_4 of 5(S),15(S)-diHpETE and the side chains of Leu408 and Leu597. There is also an important reorganization of C_6 and C_7 to adjust to the entry of oxygen at C_6. That is the reason why LXA_4 cannot be formed from 5(S),15(S)-diHpETE by 15-LOX-1

For comparison, we have also studied the behavior of 5(S),15(S)-diHETE as a substrate. In this case, the oxygen addition to C_{14} is not feasible and no oxygen access channel leading to C_6 exists. Consequently, 15-LOX-1 cannot convert 5(S),15(S)-diHETE into a lipoxin, which is in good agreement with the experimental results.

Correlation-Driven Second-Order Møller-Plesset Perturbation Theory

IL13

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The second-order Møller-Plesset perturbation theory (MP2) is one of the most widely employed computational methods, offering a convenient accuracy/cost ratio to introduce electron correlation starting from a Hartree-Fock wavefunction (HF) [1]. Although the HF wavefunction incorporates Pauli's exclusion principle, it treats electron pairs of the opposite spin as independent particles. Hence, same-spin and opposite-spin electron pairs are not treated at the HF level on equal grounds. Grimme and co-workers developed the spin-component scaled MP2 (SCS-MP2) to compensate for this fact [2]. SCS-MP2 includes two parameters that control the fixed amounts of the second-order correlation energy depending on the spin case. Typically, the same-spin and opposite-spin MP2 correlation energies are scaled by 0.33 and 1.2 [2], respectively. Other authors have suggested alternative parameterizations but also kept the values fixed [3-5]. This work suggests a system-dependent scaling factor determined by the amount of dynamic and nondynamic correlation as determined by the correlation indices recently developed in our group [6-7]. The resulting method is a correlation-driven SCS-MP2 (CD-SCS-MP2) that only requires two parameters and the natural orbital occupancies obtained at the MP2 level. As a calibration set to optimize the two parameters, we have employed the diet-GMTKN55 set [8]. Our results on the GMTKN55 [9] show a significant improvement compared to either MP2 or SCS-MP2.

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Questioning the orbital picture of magnetic spin coupling: a real space alternative

IL14

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The prevailing magnetic spin coupling paradigm is based on a one-electron picture, thus being orbital dependent and unsatisfactory from a physical point of view. We examine it under a truly invariant real space perspective, focusing on the role of electron delocalization. We show that this view overcomes its limitations, and that it is electron delocalization that drives any singlet-triplet gap. Delocalization and ionic mixing are two sides of the same reality. In the case of superexchange-mediated coupling through atomic bridges, the non-essential role of the bridge's electrons in setting up singlet-triplet preferences is highlighted. We show that the use of real space thinking allows for tuning singlet-triplet gaps using knobs that are not easily grasped from the orbital point of view [1].

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IL15

Computational Spectroscopy of Complex Systems: Breaking the Complexity Barrier

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The spectral response of molecular probes strongly depends on the surrounding environment. A successful approach to computational spectroscopy of systems in the condensed phase consists of resorting to focused models, where the focus is on a specific portion of the system, which is described at the Quantum Mechanical (QM) level, whereas the remaining portion is treated classically, through ad-hoc Molecular Mechanics (MM) force-fields [1]. Polarizable QM/MM approaches, where the mutual polarization between QM and MM layers is considered [2, 3], are particularly successful in modelling spectral properties of molecular systems embedded in complex external environments [2, 3].

I will discuss the most recent developments of the fully polarizable QM/FQ(Fμ) approach to computational spectroscopy [2-4], by resorting to pilot applications [5-10], which highlight the method's potentialities.

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IL16

Towards the Computation-Assisted Design of New Enzymes.

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Over the past decades, the interest in designing new enzymes to solve practical challenges in all branches of science and technology has increased notably, most importantly due to large strides made in directed evolution approaches in contrast to more traditional rational design approaches. We will present in this communication a new computational strategy to design novel biocatalysts based on the sum of the best electrostatic properties of different enzymes that show certain catalytic activity on a common reaction [1-5]. The computational protocol has been applied on the re-design of the protein scaffolds from existing promiscuous enzymes. The free energy landscape obtained with QM/MM multiscale methods for proposed new variants predicts measured increased catalytic activity over the original wild-type enzyme. Our computational predictions have been experimentally confirmed by comparing the kinetic data measured with the wild-type and the mutated enzymes. Regardless of the intrinsic limitations, the simplicity of the presented approach offers a new route based on computational technique to (re)design new enzymes.

Recent results obtained in our laboratory oriented towards the design of new enzymes, in collaboration with experimentalists, will be summarized in this communication.

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IL17

Reaction mechanism and dynamics of phosphate catalytic enzymes

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The formation and cleavage of phosphate bonds are essential in most biological processes including nucleic acid processing. Many enzymes that catalyze phosphate hydrolysis require bound divalent metal ions. Most commonly, Mg^{2+} ions are required for catalysis, while similar Ca^{2+} ion abolishes the catalytic activity. To elucidate the often controversial mechanism of these ubiquitous metal ion catalyzed reactions, we carry out hybrid quantum-classical QM/MM free energy simulations. In our calculations, we focus on specific prototype systems, including Ribonuclease H (RNase H) [1] and Ras [2].

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Bridging the Divide between Models and Experiments.

IL18

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Atomistic computer modelling has emerged as a key feature at the forefront of molecular sciences due to its ability to rationalize and predict the properties of new materials and molecules. Yet, despite the considerable and continuous advances in the field and the pervasive presence of high-performance computing, a large paradoxical divide between experimental science and computer modelling remains.

We will discuss how different factors, like an open mentality, scientific curiosity, common sense and a holistic view of science together with a well-grounded knowledge of the experiments and their limitations are powerful ingredients to bridge this divide. This will be illustrated with examples of our recent work in porous covalent organic frameworks [1-2] and inorganic nanomaterials [3].

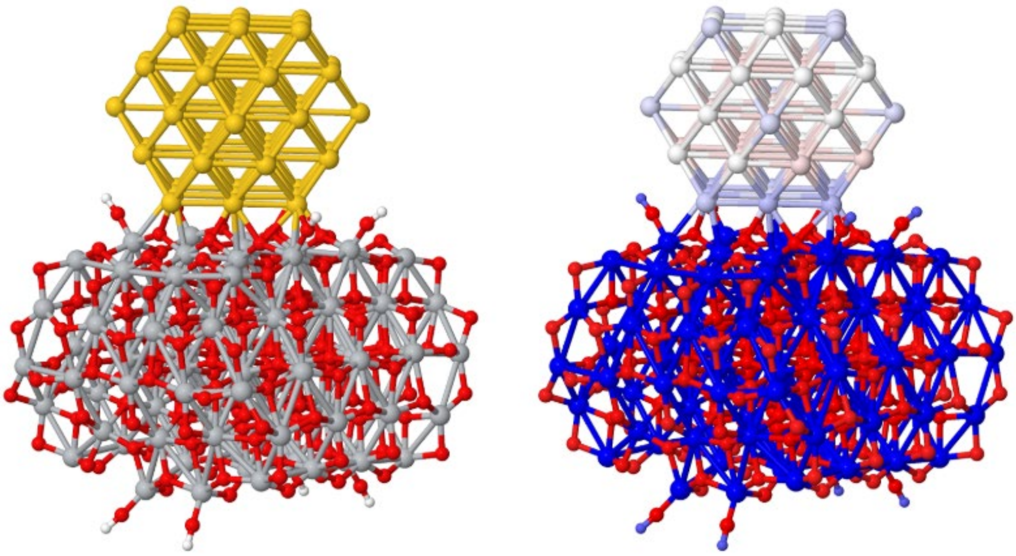

Figure 1. Tight binding model (left) of a gold nanoparticle adsorbed on a titania nanoparticle and color-coded charge transfer (right) in water [3].

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Spin Current Density Functional Theory of Weyl Semimetals: Spin-Orbit Coupling in TaAs

IL19

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The self-consistent treatment of spin-orbit coupling (SOC) in solids, within a two-component (*2c*) spinor approach, is presented, as recently implemented in the CRYSTAL program [1]. The fundamental role of non-local exact Fock exchange is highlighted in the framework of the spin current density functional theory (SCDFT) [2-3].

Weyl fermions are massless solutions of the Dirac equation described by *2c* complex spinors. Such elusive objects emerge as quasi-particles in so-called Weyl semi-metals (WSM) [4-5].

We formulate a practical version of the SCDFT that can be used to characterize WSMs. We show how a 3D doubly-degenerate bulk Dirac node is present in the TaAs WSM in the absence of SOC, lying on the $k_x = 0$ mirror plane, which is split into two singly-degenerate Weyl nodes off the mirror plane by the SOC. This breaking of the degeneracy and the corresponding splitting of the two Weyl nodes with opposite chirality offers a measurable way to assess different theories. We show how an SCDFT formulation is essential to a correct quantitative description of the electronic features of WSMs [6].

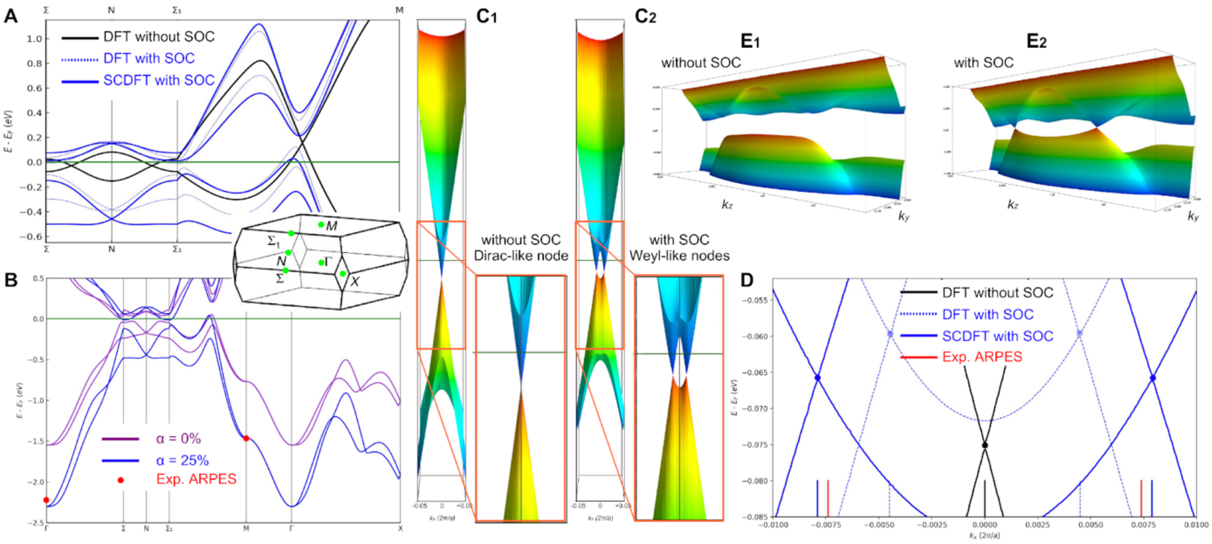

Figure 1. Electronic structure of the TaAs WSM upon treatment of SOC within the SCDFT versus standard DFT.

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ORAL COMMUNICATIONS

ESPA2022

Ru(II)- and Os(II)-polipyridil photosensitizers with highly photocytotoxic ^{3}ILCT states in both normoxia and hypoxia: theoretical insights

OC1

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Photodynamic Therapy (PDT) is an emerging treatment whose light-triggered anticancer activity relies on the massive generation of reactive oxygen species (ROS). Its minimal invasiveness, simplicity, selective destruction of neoplastic tissue through direct cellular damage and immune response, have contributed to boost a worldwide interest on this topic. The efficacy of conventional PDT is, however, strictly dependent on the availability of sufficient tissue oxygen, therefore the acute hypoxia conditions characterizing some of the most aggressive and drug-resistant tumours hamper the treatment outcome. To face this issue, the design and development of light-responsive compounds that can directly work at very low oxygen tension is of paramount importance.

The unprecedented hypoxia activity displayed by new Os(II)- and Ru(II)-compounds bearing quaterthiophene chains proposed and characterized in joint experimental and theoretical studies [1-3] are herein presented. DFT results reveal the pivotal role of the switch in the nature of lowest-lying triplet excited state from a metal-to-ligand charge transfer (^{3}MLCT) to intraligand charge transfer one (^{3}ILCT) at n=3, with a lower energy and longer lifetime for n=4, for both Os(II) and Ru(II) families. Moreover, they provide fundamental insights into their dual normoxia/hypoxia activity, demonstrating as it does not rely on a photoinduced ligand loss mechanism as the better-known photoactivated cancer therapy (PACT or PCT).
Results show that the excited-state dynamics of the most active compounds (n=4) are governed in large part by the ^{3}IL/^{3}ILCT state hence questioning the generally accepted correlation between the hypoxia phototoxicity and the population of ^{3}MC dissociative states.

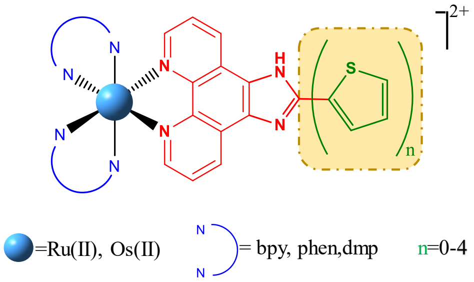

Figure 1. Schematic representative of the Ru(II)- and Os(II)-based complexes proposed as Hypoxia-Active PS[1-3]

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OC2

Navigating the Conformational Landscape of Interacting Biomolecules: Millisecond Time Scale Activation of Allosterically Regulated Enzymes

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(Bio)molecular recognition is a key concept in chemistry and biology. Life processes such as enzyme catalysis and allosteric regulation are critically dependent on the association of (bio)molecules. Binding finely tunes the biomolecule dynamic conformational ensemble by reshaping the relative populations of the conformational states and/or the timescales of conformational transitions. Understanding the mechanisms through which (bio)molecules interplay to attain stable (and often transient) bound states involve deciphering the interplay between fast and slow dynamics and rearrangements of networks of inter- and intramolecular interactions that control biomolecular function. The transient nature and usually slow millisecond timescale interconversion between functional states hamper their detailed experimental and computational characterization. Experimental methods give information on stable structures or binding affinities but cannot offer a complete description of biomolecular recognition at the required atomic detail. Molecular dynamics (MD) simulations can provide an atomistic dynamic view of such processes. However, a tremendous amount of conformational sampling is required to reconstruct the conformational landscape of interacting biomolecules.

Here, we design a computational strategy (Figure 1) that combines enhanced sampling techniques and dynamical networks to describe the millisecond allosteric activation of imidazole glycerol phosphate synthase (IGPS) from substrate binding to the formation of the enzyme active complex[1]. IGPS is a heterodimeric enzyme complex whose HisH subunit is responsible for hydrolysing glutamine and delivering ammonia for the cyclase activity in HisF. Essential molecular details of the long-range millisecond allosteric activation of IGPS remain hidden. Without using *a priori* information of the active state, our simulations uncover how IGPS, with the allosteric effector bound, spontaneously captures glutamine in a catalytically inactive HisH conformation, subsequently attains a closed HisF:HisH interface, and finally forms the oxyanion hole in HisH for efficient glutamine hydrolysis. We show that the combined effector and substrate binding dramatically decreases the conformational barrier associated with the oxyanion hole formation, in line with experimentally observed 4500-fold activity increase in glutamine hydrolysis. This computational strategy tailored to describe millisecond timescale events can be generalized to study other allosterically regulated enzymes.

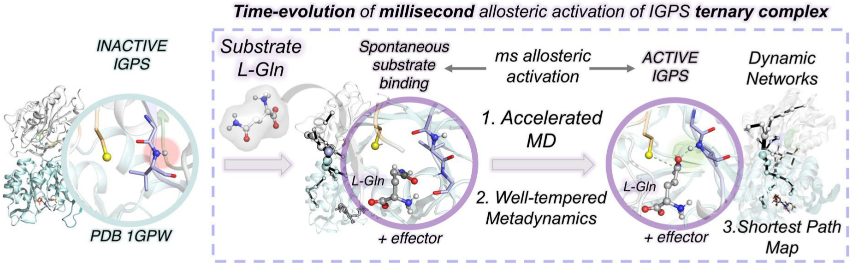

Figure 1. Computational simulations unravel the millisecond allosteric activation of IGPS

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Mapping Guanine Oxidation in Nucleosomal DNA using Multiscale Simulations

OC3

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Light, oxidative stress or exogenous molecules can modify the well-designed structure of DNA by inducing nucleobases lesions. The accumulation of these damages can hinder the DNA transcription or replication and lead to mutations, cell apoptosis or cancers. As a consequence, numerous studies focus on the elucidation of the mechanisms of damages formations or their repair by dedicated proteins. Because of the complexity of the DNA molecule in its biological context, the problem becomes rapidly combinatorial, involving sequence, structural and dynamical effects. Indeed, beyond the double strand structure, the DNA polymer is wrapped around a core of eight proteins call histones to form nucleosomes[1]. This specific and dynamical environment mechanically constrains the DNA conformation and creates an heterogeneous electrostatic field. Then, the physicochemical properties of the nucleobases and their reactivity can become strongly dependent on their position around the histone core (see for example [2]), especially the redox properties of the nucleobases.

The recent efforts to increase computational power of simulations have permitted the first all-atom classical simulations of a nucleosome at a microsecond timescale[3], and our group also perform long timescale classical simulations of damaged DNA [4-6]. We present here our guanine oxidation map obtained using efficient FO-DFTB/MM approach [7] over 20 µs all-atom simulations. We focus on the importance of different parameters such as sequence, nucleobase position and tail proximity on the guanine redox properties. All our data will be used to feed machine learning algorithm to provide a better understanding of the environmental factors which can play a role on these properties and facilitate the analysis of our complex simulations.

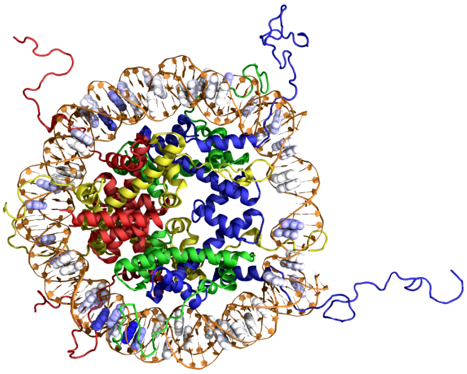

Figure 1. Nucleosome particle with guanine colored depending on their ionization potential from white (low ionization potential) to blue (high ionization potential)

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Identifying electromagnetic and chemical contributions to SERS

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OC4

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Surface Enhanced Raman Spectroscopy (SERS) is a molecular spectroscopic technique based on the enhancement of the Raman scattering of a molecule located near a metallic particle[1]. This enhancement is the result of two different mechanisms: the chemical (CHEM) mechanism due to the chemical interaction between the metallic surface and the molecule, and the electromagnetic (EM) mechanism due to the extremely localised electromagnetic fields induced near the metallic particle by collective oscillations of the electron density (plasmon resonances). Frequently-used approaches to calculate the CHEM contribution to the total SERS enhancement are based on Density Functional Theory (DFT) calculations and ignore the role of the EM mechanism, although the latter can also influence the obtained results [2].

In this work, we present an approach to identify the role of the CHEM and EM mechanisms in the total SERS enhancement obtained within DFT calculations. We apply this approach (which uses Time-Dependent Density Functional Theory (TDDFT) calculations of the optical response of metallic clusters [3]) to study the changes in the Raman spectrum of the molecule biphenyl-4,4'-dithiol (BPDT) (Fig. 1a) sandwiched between two gold clusters (Fig. 1b). We show that for small cluster sizes the total SERS enhancement is mainly driven by the CHEM mechanism (Fig. 1c), but the EM contribution grows with cluster size. Thus, being able to separate between EM and CHEM contributions becomes increasingly important for DFT simulations involving larger metallic clusters.

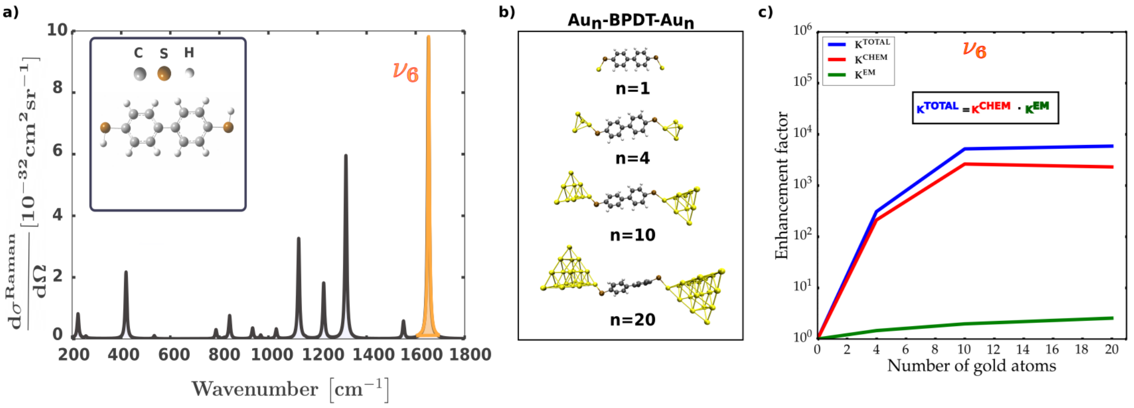

Figure 1. SERS enhancement factors of biphenyl-4,4'-dithiol (BPDT) sandwiched between two gold clusters. Panel a: Raman spectrum of BPDT between 200 cm^{-1} and 1800 cm^{-1}. In the inset, a molecular model of the minimum energy structure of BPDT, where grey, white and brown spheres represent carbon, hydrogen and sulfur atoms, respectively. The most intense Raman line within the selected spectral range (ν_6) is highlighted (orange area). Panel b. Molecular models of the minimum energy structures of BPDT sandwiched between two gold clusters of different size Au_n-BPDT-Au_n, n=1, 4, 10 and 20, where yellow spheres represent gold atoms. Panel c. Evolution of the total SERS enhancement factor (solid blue line, K^{TOTAL}), the chemical enhancement factor (solid red line, K^{CHEM}) and the electromagnetic enhancement factor (solid green line, K^{EM}) with the number of gold atoms per cluster for the vibrational mode ν_6.

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Computational study on the affinity of potential drugs to SARS-CoV-2 main protease

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Herein, we report a computational investigation of the binding affinity of dexamethasone, betamethasone [1,2], chloroquine, and hydroxychloroquine [3,4] to SARS-CoV-2 main protease using Molecular and Quantum Mechanics as well as Molecular Docking methodologies. We chose dexamethasone as reference drug that have shown promising results in the treatment of COVID-19, while we selected chloroquine and hydroxychloroquine as reference drugs where no benefit was observed in patients with mild COVID-19.

We aim to provide information on the anti-COVID-19 mechanism of the abovementioned potential drugs against SARS-CoV-2 coronavirus. Hence, the 6w63 structure of the SARS-CoV-2 main protease was selected as potential target site for the Docking analysis. The study includes an initial conformational analysis of dexamethasone, betamethasone, chloroquine and hydroxychloroquine. For the most stable conformers, a spectroscopic analysis has been carried out. In addition, global and local reactivity indexes have been calculated to predict the chemical reactivity of these molecules.

The Molecular Docking results indicate that dexamethasone and betamethasone have a higher affinity than chloroquine and hydroxychloroquine for their theoretical 6w63 target. Additionally, dexamethasone and betamethasone show a hydrogen bond with the His41 residue of the 6w63 protein, while the interaction between chloroquine and hydroxychloroquine with this amino acid is weak. Thus, we confirm the importance of His41 amino acid as a target to inhibit the SARS-CoV-2 Mpro activity. We hope that the present study sheds light on the understanding of the interactions that take place between potential drugs and the main SARS-CoV-2 protease, facilitates the design of inhibitors of the activity of this enzyme and, ultimately, it contributes to the advance towards a possible treatment of the disease caused by SARS-CoV-2.

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GMM-NEA: Reconstruction of Nuclear Ensemble Approach Absorption Spectra using Unsupervised Machine Learning

OC6

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The theoretical prediction of molecular electronic spectra by means of quantum mechanical (QM) computations is fundamental to gain a deep insight into many photophysical and photochemical processes. A computational strategy that is attracting significant attention is the so-called Nuclear Ensemble Approach (NEA), that relies on generating a representative ensemble of nuclear geometries around the equilibrium structure and computing the vertical excitation energies (ΔE) and oscillator strengths (f), and phenomenologically broadening each transition with a line-shape with empirical full-width δ [1]. Frequently, the choice of δ is carried out by visually finding the trade-off between artificial vibronic features (small δ) and over-smoothing of electronic signatures (large δ). Nevertheless, this approach is not satisfactory, as it relies on a subjective perception and may lead to spectral inaccuracies, overall when the number of sampled configurations is limited due to an excessive computational burden (high-level QM methods, complex systems, solvent effects, …). We have recently developed a new approach to reconstruct NEA spectra, dubbed GMM-NEA, based on the use of Gaussian Mixture Models (GMMs), a probabilistic Machine Learning algorithm, that circumvents the phenomenological broadening assumption and, in turn, the use of δ altogether [2]. In this communication I will revisit the fundaments and philosophy behind NEA and our new methodology, I will highlight some relevant peculiarities, aspects and results of GMM-NEA, and will show how it outperforms other approaches such as KDE [3] or the KREG model [4], especially for small datasets (Figure 1).

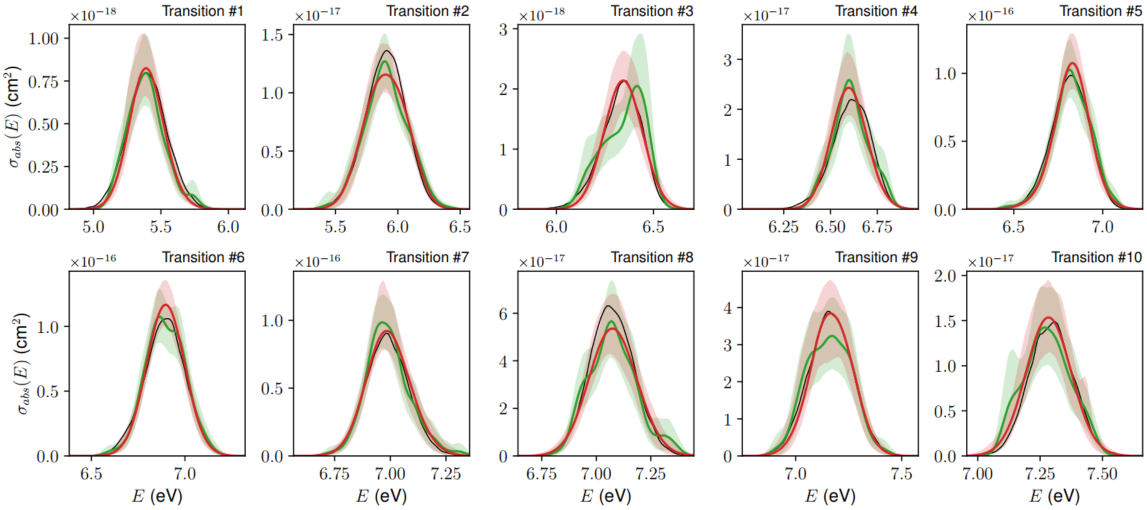

Figure 1. TD-DFT absorption cross section spectrum for each of the transitions in benzene reconstructed from 250 geometries using GMM-NEA (red lines) and KDE (green lines). The shaded areas represent the reconstruction 95% confidence intervals. The target spectrum (black lines) is included for comparison purposes.

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Controlling Chemical Reactivity with Optimally Oriented Electric Fields: A Generalisation of the Newton Trajectory Method

OC7

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The application of oriented external electric fields (OEEF) to accelerate chemical reactions is of interest to understand enzymatic processes and catalysis in which an activated process becomes essentially barrierless. Recently, a recent landmark single–molecule experiment by Aragonès et al.[1] has shown that OEEFs created by a bias voltage between an electrode and an scanning tunnelling microscopy tip can catalyze a Diels–Alder reaction. Inspired by this work, we have developed a new model to calculate the optimal OEEF of the least intensity to induce a barrierless chemical reaction path [2]. In this model, which is an example of optimal control of a chemical process, a suitable ansatz is provided by defining an effective potential energy surface (PES) that considers the unperturbed or original PES of the molecular reactive system and the action of a constant OEEF on the overall dipole moment of system. Based on a generalization of the Newton Trajectories (NT) method previously developed by some of us [3], we show that the optimal OEEF can be determined upon locating a special point of the potential energy surface (PES), the so–called optimal bond–breaking–point (optimal BBP) [2]. Two different algorithms are proposed and applied to a 2–dimensional model (Fig. 2), to an SN_2 reaction and the 1,3–dipolar retrocycloaddition of isoxazole to fulminic acid plus acetylene reaction (Huysgen mechanism). It is concluded that the knowledge of the orientation of optimal OEEF provides a practical way to reduce the effective barrier of a given chemical process. Finally, in contrast to previous models that focus on the TS of the reaction [4], the oBBP structure represents the essential point in the PES to understand the effect of the OEEF applied to the molecular system. This model has potential utility to understand the basic mechanisms of enzymatic catalysis.

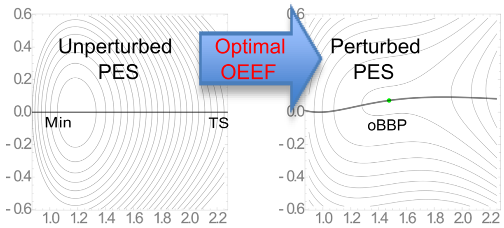

Figure 1. An activated 2D process becomes barrierless by an optimally oriented external electric field (OEEF)

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Optimizing the thermodynamics and kinetics of the triplet-pair dissociation in donor-acceptor copolymers for intramolecular singlet fission

OC8

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Singlet fission (SF) is a two-step process in which a singlet (S_1) splits into two triplets ($2T_1$) throughout the so-called correlated triplet-pair (^{1}TT) state (see **Figure 1**). Intramolecular SF (iSF) materials, such as oligomers and donor-acceptor (D-A) copolymers in particular[1-2], have attracted growing interest as they can be implemented in single junction solar cells and boost their power conversion efficiency beyond the Shockly–Queisser 33% limit up to 45%. In this context, previous work has been devoted to establishing molecular design rules[3-5] and determining the mechanism that optimizes the S_1-to-^{1}TT splitting process in these systems[6-7]. These consist in appropriate *energetics*, $E(S_1) > E(2T_1)$, and D-A *coupling*, which can be achieved with well-balanced charge-transfer (CT) and local contributions[3-7]. Still, their practical implementation in photovoltaic applications directly depends on their ability to go beyond the ^{1}TT intermediate and generate free triplets ($2T_1$), which mechanism remains poorly understood. Traditionally, the ^{1}TT binding energy is considered the minimal energy required for the separation of the triplet-pair state and is usually evaluated as the ^{5}TT-^{1}TT vertical energy difference. In this work[8], we show that considering the ^{1}TT binding energy is not enough to anticipate favourable intramolecular triplet-triplet dissociation rates in D-A copolymers. First, we show that both *thermodynamics* and *kinetics* play a crucial role in the intramolecular triplet-pair separation process. Second, we discuss whether it is possible and how to optimize both features simultaneously, and finally, we propose a simple model based on sequential T_1 potentials to rationalize and predict their behaviour. Overall, these results provide a better understanding of the intramolecular ^{1}TT dissociation process in D-A copolymers and establish a new paradigm for the development of novel iSF active materials.

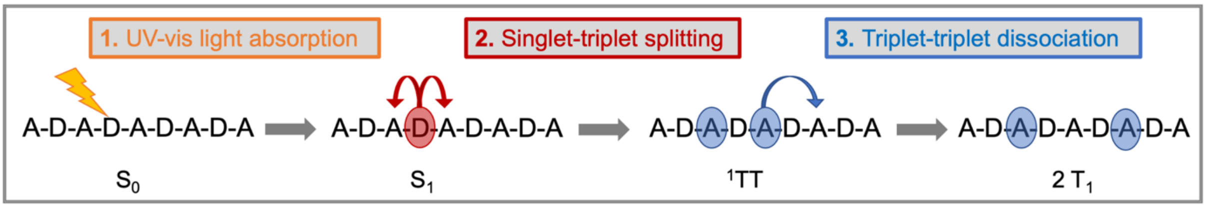

Figure 1. Schematic representation of the intramolecular singlet fission (iSF) steps in donor-acceptor (D-A) copolymers. First, UV-vis light absorption promotes S_0 to S_1, characterized by strong D-to-A charge-transfer (CT) sideways. Second, S_1 decays via a spin-allowed process towards the triplet-pair state ^{1}TT, localized in adjacent A. Third, the ^{1}TT state spatially dissociates and become two independent T_1 triplets.

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A Lysine-Cysteine Redox Switch: The NOS Bridge

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OC9

Recently, a new naturally occurring covalent linkage in peptides was characterised, involving a cysteine and a lysine bridged through a single oxygen atom. The latter was coined as *NOS bond*, reflecting the individual atoms directly involved in this rather uncommon bond which finds little parallel in lab chemistry [1]. It is found to form under oxidising conditions and reversible upon addition of reducing agents. Further studies have shown that this bond is found over a large variety of systems and organisms, potentially playing an important role in regulation, cellular defense and replication [2]. Herein, QM based key structural data for the identification of the NOS is shown, which allows to differentiate it from the reduced Cys and Lys residues. Moreover, double NOS bonds have recently been identified as a regulatory unit in the main protease of SARS-COV-2 (Mpro)[3], playing an important role in the catalytic activity of the enzyme and its oligomerization. Finally, with the aim of characterizing the reaction mechanism that leads to the formation of the *NOS bond*, we present a reaction network with more than 30 intermediates which provides one of the most encompassing pictures for cysteine oxidation pathways to date.

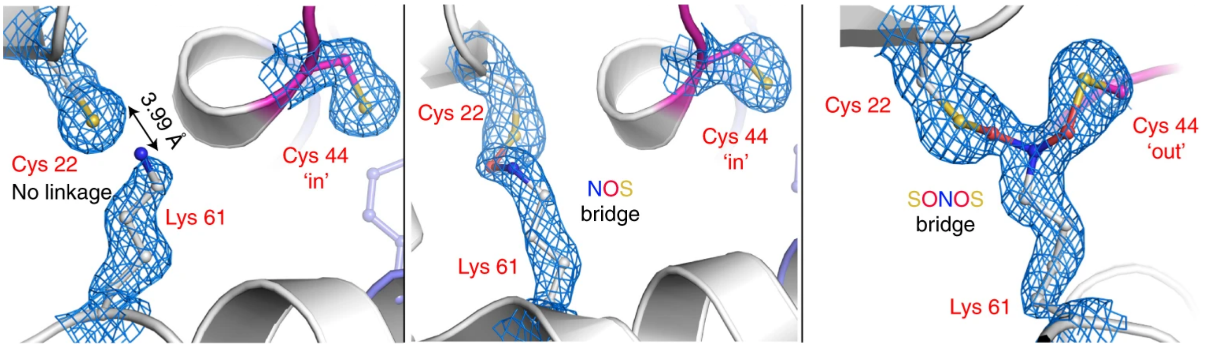

Figure 1. NOS and SONOS bridges in Mpro from SARS-CoV-2. The corresponding 2mFo–DFc electron density maps are shown in blue at a contour level of 1σ. Left: structure of Mpro in the reduced state (PDB: 7JR3) showing the redox switch at the protein surface formed by residues Cys 22, Cys 44 and Lys 61 (highlighted in red). Center: Structure of Mpro in a mono-oxidized state with an NOS bridge formed between Cys 22 and Lys 61 (PDB: 6XMK). Right: Structure of Mpro in a dioxidized state with a SONOS bridge formed between Cys 22, Lys 61 and Cys 44 (PDB: 7JR4).

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Computational design of more efficient solar energy storage molecules based on the dihydroazulene / vinylheptafulvene photoswitch

OC10

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Solar energy has been the main fuel for life forms on Earth since the rise of chlorophylls. The 20th century brought us the first solar cells, an attempt to replicate plants' ability to turn sunlight into profitable energy. While the scope of different kinds of solar cells has markedly broadened in the last decades, most of them are suited to create an immediate electric current. Thus, unless this current is used to charge a battery, there is no intermediate energy storage. In contrast, molecular photoswitches offer a way to pile up solar energy as chemical energy [1]. Light-driven photoisomerization enables the formation of a metastable isomer, and (part of) the solar energy is stored as the energy difference between the two isomers. Thermal or catalyzed back-reaction enables delayed energy release. These photoswitches are often referred as MOlecular Solar Thermal energy (MOST) systems.

One of these MOST systems is based on the dihydroazulene / vinylheptafulvene (DHA/VHF, Figure 1) couple [2]. UV-A irradiation of DHA triggers electrocyclic ring opening via C_1-C_{8a} bond breaking, leading to the more energetic VHF isomer, which can revert to DHA in a thermal fashion. The main limitation of this photoswitch is its low energy storage density (the energy difference between both isomers), meaning that a very large portion of the absorbed solar energy is lost. Attempts to increase this energy storage density by increasing the energy of the VHF isomer usually end up in too fast VHF → DHA back-reactions [3], as the activation energy of this process is simultaneously decreased.

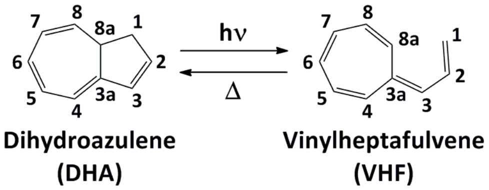

Figure 1. Structure of the dihydroazulene / vinylheptafulvene photoswitch.

In this work, using DFT and TD-DFT approaches, we conducted a systematic search for a substitution pattern in the DHA/VHF couple able to provide acceptable energy storage densities and thermal back-reaction activation energies. Moreover, we introduced a new MOST descriptor, the spectral overlap integral, to quantify the differences in the absorption spectra of both isomers. For the most promising candidates we found, we investigated the photochemical/thermal reaction pathways for the DHA → VHF → DHA operation cycle. We also proposed a possible retrosynthetic analysis for the preparation of these molecules, including ways for their derivatization to gain additional properties such as water solubility.

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Ca^{2+} ions solvated in helium: The observation of the largest shell around an impurity

OC11

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A combined experimental and theoretical investigation on the He_NCa^{2+} clusters has detected the formation of stable closed structures of the helium atoms at specific values of N : Icosahedrons for N = 12 and 44, a dodecahedron for N = 32 and an icosidodecahedron for N = 74. The existence of up to fourth solvation shells around the Ca^{2+} impurity ion yield obtained by means of mass spectrometry of multiply-charged helium nanodroplets [1, 2] is confirmed by calculations performed by classical optimization algorithms and Monte Carlo techniques [3]. Up to our knowledge this work constitutes the first detection of such large structures [4].

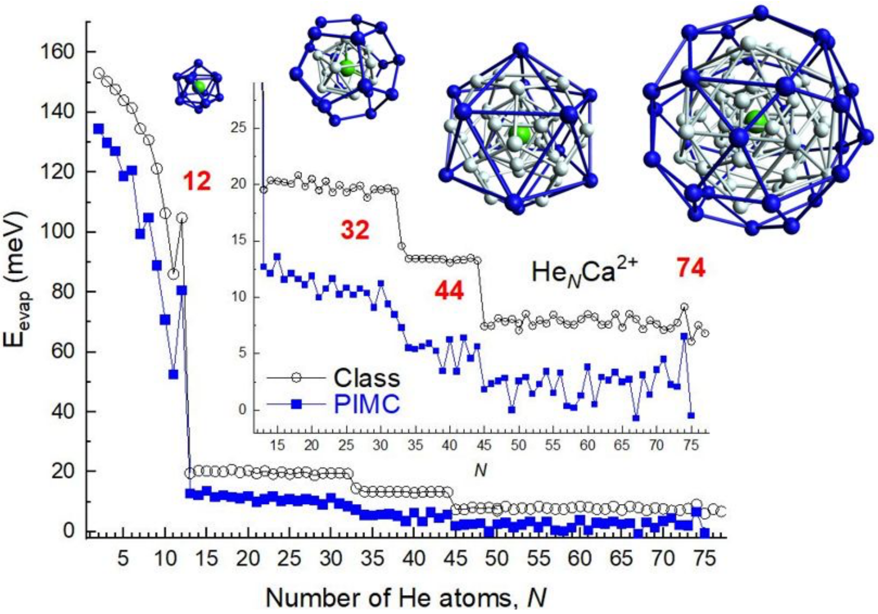

Figure 1. Evaporation Energies as a function of the number of Helium atoms

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Determination of the energy ladder in cryptophyte photosynthetic antenna complexes from multiscale simulations

OC12

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Quantitative models of light harvesting in photosynthetic antennae depend critically on the excitonic Hamiltonian adopted to describe the exciton states in the system. Beyond excitonic couplings, pigment site energies are key to understand energy migration pathways and characterize excitons in terms of pigments contributions. The determination of site energies from structure-based simulations is however considerably challenging, as the protein scaffold can tune them by direct pigment-protein interactions or indirectly by constraining the conformation of the pigments, effects in turn coupled to the multiple time scales characterizing protein motions.

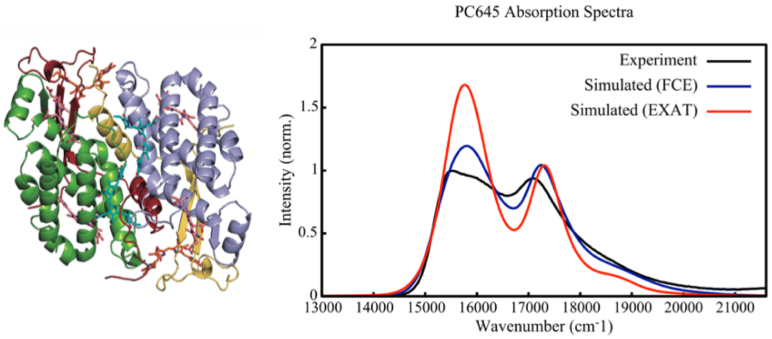

Figure 1. Absorption spectra simulated for the PC645 antenna complex.

In this contribution, we overview efforts performed to characterize the light harvesting properties of the PC577, PC612, PC630 and PC645 phycobiliproteins from cryptophyte algae, notably characterized by either an "open" or "closed" quaternary structure that drastically changes the excitonic interaction in the central bilin pair of these complexes [1,2]. Different simulation strategies based on polarizable quantum/molecular mechanics (QM/MMPol) excited state calculations are discussed, emphasizing the importance of how input geometries are obtained, either from QM/MM optimizations of the pigments in the protein crystal structure or from classical and Born-Oppenheimer molecular dynamics (MD) simulations.

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Unified treatment of spin-polarization in wavefunction analysis

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Current wavefunction analysis techniques treat the alpha and beta electrons separately, in particular those designed to extract oxidation states from first principles [1,2]. With this common approach the classical electron pair picture is often blurred by spin contamination or spin polarization.

Unrestricted Kohn-Sham DFT methods can readily capture spin-polarization in singlet states by recurring to the so-called broken symmetry approach (BS). BS-DFT calculations are routinely used when studying magnetic interactions in e.g. dinuclear TM compounds, and can also describe diradicals, an extreme case of spin polarization. All these cases result in a non-zero spin density. On the contrary, the latter vanishes when turning to a proper description of these singlet states, namely a multireference wavefunction. In this case, the spin polarization is introduced by populating the antibonding orbitals, while keeping the restricted framework. Consequently, the alpha and beta parts of the density are exactly equivalent (as it should be for a singlet state), so the fate of the alpha electrons resulting from any analysis is the same for the beta ones.

We propose a change of paradigm by replacing the alpha and beta densities by some paired and unpaired densities in wavefunction analysis techniques. This alternative strategy permits treating on equal footing broken-symmetry and truly correlated wavefunctions, providing rationale for the formal homolitic split of the electron pair in spin polarized/diradicaloid systems. An improved algorithm based on our effective oxidation states analysis scheme (uEOS) is introduced [3]. Several numerical examples involving transition metal (TM) and main group element complexes will be discussed.

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GronOR: A massively parallel and GPU-accelerated program for non-orthogonal configuration interaction

OC14

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After the initial explorations in the 1980s, non-orthogonal configuration interaction (NOCI) was recognized as an interesting approach for treating electronic structure problems where orbital relaxation plays a fundamental role, e.g., core-hole excitations, metal-to-metal charge transfer excitations. However, the method was never applied extensively because of the huge computational cost of releasing the restrictions on the orthogonality of the molecular orbitals. However, recently NOCI is going through a revival, witnessed by the large number of studies that has been published over the last decade. This renewed interest is in part due to the increased computer power, but also to the development of new algorithms and new (faster) variants of NOCI.

Our implementation of NOCI in GronOR [1,2] is based on the use of multi-electron basis functions built in terms of anti-symmetrized spin-adapted products of multi-configurational fragment wave functions. So far, it has been applied to electron and energy transfers in ensembles of molecules to describe singlet fission, magnetic exchange coupling, charge transfer processes [3], but the method is not restricted to these applications.

GronOR has been specifically designed for execution on distributed memory massively parallel and GPU-accelerated computer architectures, using an MPI+OpenACC/OpenMP programming approach. The task-based execution model used in the implementation allows for linear scaling with the number of nodes on the largest pre-exascale architectures available, provides hardware fault resiliency, and enables effective execution on systems with distinct CPU-only and GPU-accelerated partitions. The code interfaces with OpenMolcas to provide optimized molecular fragment orbitals, configuration interaction coefficients and the required integrals. The current version of the code can handle systems with more than 100 atoms and perform a full NOCI is less than 30 minutes on supercomputers available through PRACE.

After a short introduction to the calculation of non-orthogonal matrix elements and the most important characteristics of the implementation in GronOR, we will present some NOCI applications to illustrate the possibilities of the method and the advantages it has when it comes to the interpretation of the results in comparison to other multiconfigurational methods based on orthogonal orbitals.

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Exploring the role of chemical composition in the lattice thermal conductivity of thermoelectric materials assisted by machine learning

OC15

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Chalcogenides and oxychalcogenides represent a large chemical space with potential application as thermoelectric materials due to their low thermal conductivity and low-cost. However, the nature of this behaviour is still under debate. Understanding the origin of the anharmonicity of these materials is key to developing new materials improving their thermoelectric efficiency. In this work [1,2], we combine machine learning with first principles calculations to explore chalcogenides and oxychalcogenides materials. To afford accurate predictions across this large family of compounds, we solve the Boltzmann transport equation with force constants derived from density functional theory calculations and machine learning-based regression algorithms, reducing by between 1 and 2 orders of magnitude the computational cost with respect to conventional approaches of the same accuracy. Machine learning not only accelerates the prediction of the lattice thermal conductivity for large chemical spaces with high accuracy, but also catalyzes the development of design principles to discover new thermoelectric materials. Using this approach, lattice thermal conductivity has been directly connected to the effect of each species in the material, using atomic projections of the scattering rates

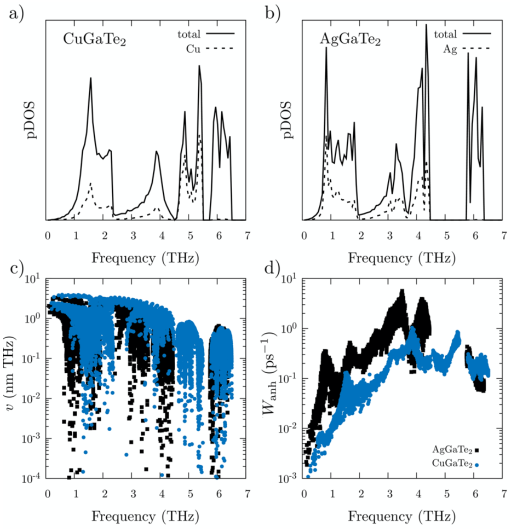

Figure 1. Phonon density of states for (a) CuGaTe$_2$ and (b) AgGaTe$_2$, showing the projections on the Cu/Ag metal atoms. (c) Group velocities vs mode frequency. (d) Scattering rates vs mode frequency for the same two compounds.

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In_2O_3 as multifunctional material: Fundamentals and progress of a versatile semiconductor

OC16

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Indium oxide (In_2O_3) based materials have attracted a remarkable interest for their unique features and multifunctional properties, which can be finely tuned by controlling the interplay between their structure, morphology and composition. To enable their widespread practical usage, significant efforts have been devoted to finding relationships among the nature of chemical bonds, geometrical arrangements and their unique properties.

A detailed insight into chemical/physical properties by using advanced experimental techniques and first principle calculations provide significant advantages from both a fundamental and an applicative point of view [1,2].

The modulation of morphology, surface modification, doping process, formation of solid solutions, constructions of heterojunctions have been discussed in detail. They were employed to promote the optical properties, gas sensor capacity and to enhance the (electro-, photo-, and catalytic-) activity [3,4].

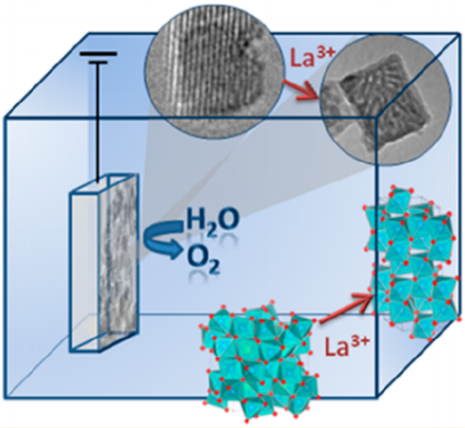

Figure 1. A schematic representation of the structure and morphology changes along the doping process of La^{3+} in In_2O_3 to enhance the oxygen evoluction reaction (OER).

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Electric-field induced second harmonic generation responses of push–pull polyenic dyes: theoretical characterizations and comparison with experiments

OC17

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The second-order nonlinear optical properties of four series of amphiphilic cationic dye involving different push–pull extremities and increasingly large polyenic bridges have been investigated experimentally by electric-field induced second harmonic generation (EFISHG) and theoretically by using a computational approach combining classical molecular dynamics (MD) and quantum chemical calculations based on time-dependent density functional theory (TD-DFT). These systems have an enhanced second-harmonic response and therefore they are prone to be used as probes in biological systems such as lipid membranes[1]. Experimental measures are made possible for these cationic chromophores by using a solvent with a low relative permittivity (chloroform), which induces the formation of neutral ion pairs including the positively-charged dye and its iodine counterion[2].

The computational approach is based on a methodology developed in previous works[3]: MD simulations are carried out on a reference iodine complex which brings key information on the average relative position of two ions, as well as on the effect of dynamical structural fluctuations on the NLO properties. Then, systematic TD-DFT calculations performed on the whole set of systems provide a rationale to experimental data and allow to establish precise relationships between the structure of the dye and the magnitude of the second- and third-order contributions to the EFISHG intensity. The good agreement between experimental and theoretical results shows that this computational scheme might prove highly useful for a rational design of amphiphilic systems for SHG imaging.

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Solar-Thermal Fuels in the Spotlight: Novel Methods for Standard Systems and Standard Methods for Novel Systems

OC18

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Molecular solar-thermal systems (MOST) are becoming increasingly noticeable for the development of renewable energy technologies. The most relevant property of MOST is the direct conversion of solar energy into chemical stored energy within a single process, thus offering a potential solution to the main drawback of solar cells: energy storage, usually relying on expensive lithium-ion batteries [1].

The MOST mechanism is based on the conversion of a low-energy isomer, by light irradiation, into a high-energy isomer. Afterward, by heating or catalytic conversion, the system comes back to his low-energy form and the energy is released (see Figure 1). Although highly attractive for its environmental sustainability (*i.e.*, their cyclic use is in principle illimited), multiple properties need to be fulfilled to propose an efficient MOST: *i*) light-absorption of the low-energy isomer within the solar spectrum range, *ii*) thermal and photochemical stability of the high-energy isomer to enable long-time energy storage, *iii*) cyclability should be ensured by avoiding by-products, *iv*) a high density storage can be achieved only if low molecular weight can be attained.

Hence, due to their desirable limited molecular weight and the tuneable optimization of their physicochemical properties, MOST molecular design is highly attractive for both main interests in theoretical chemistry: on one side, the development of novel theoretical tools to improve the properties of existing MOST and, on the other side, the application of *ab initio* multiconfigurational methods to test the proposal of new MOST.

Here, we show the latest results concerning the application of our developed mechanochemical predictive tools to propose substitution patterns and environment media to improve the MOST properties of an archetypal photoswitch (azobenzene [2]) and of the so far best known MOST (norbornadiene-quadricyclane [3]). Also, we propose the design of new MOST based on ring straining isomerization, as an attempt of paradigm shift in this research field.

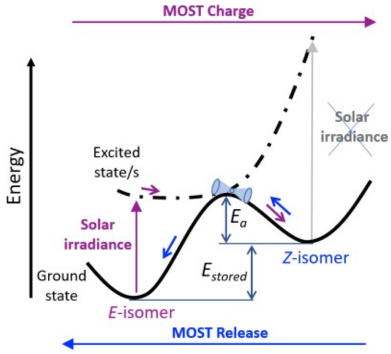

Figure 1. Mechanistic principles of a MOST device.

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From Atom to Anode: the MODALIS^2 multiscale approach to modelling Si/C anodes for lithium-ion batteries

OC19

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MODALIS^2 is a Horizon 2020 research and innovation program spanning 4 countries and 10 institutions across Europe for the development, validation, and implementation of a multi-physics, multi-scale toolchain for the modelling of lithium-ion batteries. The project aims to fast-track the implementation of new materials into next-generation lithium-ion batteries by building bridges between various modelling levels, from atomic detail to battery pack integration in electric vehicles. Within this project, Gemmate Technologies is tasked with the Density Functional Theory (DFT) modelling of the electronic structure and mechanical properties of the composite anode constituents, as well as with the Finite-Elements Method (FEM) multi-physics modelling of the ionic diffusion of lithium within the Si/C anodic material.

Building on the information gathered by the experimental characterization of the Si/C composite anode, atomic models of each material were created in the Quantum Espresso plane-wave DFT code. While atomic models could easily be obtained for the identified crystalline phases, ab-initio molecular dynamics (AIMD) simulations were needed to reflect the amorphous nature of the silicon-based phases. An analysis of the unit cell structures resulting from the AIMD simulations, combined with the calculation of elastic tensors for all lithiated and delithiated phases, laid the basis for the overall multi-scale approach to battery modelling at the atomic level: the DFT investigation could provide mechanical parameters for the evolution of each individual phase within the electrode as the anode is charged and discharged, through the determination of elastic properties and volumetric expansion as a function of lithium content.

The DFT-based mechanical parameters were successfully implemented into FEM multi-physics models of a single Si/C particle created in the COMSOL™ software. These models were built on the experimental characterization of the anodic materials, replicating the characteristic core-shell structure of the specific materials used in the MODALIS^2 project. Through the implementation of bespoke diffusion equations, FEM simulations could model the penetration of lithium ions through the three phases of the Si/C particle, and investigate the response of the particle to battery cycling in terms of mechanical stress and geometric changes. Parametrization of these results as a function of lithium content allows for the modelling of larger portions of the anode material, further strengthening the link between different modelling scales in the MODALIS^2 project.

In this talk we present the results of the modelling work performed at Gemmate Technologies for the MODALIS^2 project, their integration into the broader toolchain, and how the multi-scale approach shaped the investigation at all levels, so as to tailor the modelling to the specific battery components used in the project. In the future, the MODALIS^2 project will move to the next generation of battery components, and its toolchain of carefully chosen models, parameter integration and experimental validation will allow faster time-to-market for next-generation battery cells.

POSTERS
ESPA2022

The production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway. A combined Molecular Dynamics and QM/MM study.

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Chronic inflammation is now widely recognized to play important roles in many commonly occurring diseases, including COVID-19. The resolution response to this chronic inflammation is an active process governed by specialized pro-resolving mediators (SPMs) like the lipid mediators known as lipoxins. The biosynthesis of lipoxins is catalyzed by several lipoxygenases (LOXs) from arachidonic acid. However, the molecular details of the mechanisms involved are not well known yet. In this work, we have combined molecular dynamics (MD) simulations and quantum mechanics/molecular mechanics (QM/MM) calculations to analyze how reticulocyte 15-LOX-1 catalyzes the production of lipoxins from 5(S),15(S)-diHpETE. Our results indicate that the dehydration mechanism from 5(S),15(S)-diHpETE, via the formation of an epoxide, presents huge energy barriers even though it was one of the two a priori synthetic proposals. This result is compatible with the fact that no epoxide has been directly detected as an intermediate in the catalytic formation of lipoxins from 5(S),15(S)-diHpETE. Conversely, the oxygenation of 5(S),15(S)-diHpETE at C_{14} is feasible because there is an open channel connecting the protein surface with this carbon atom, and the energy barrier for oxygen addition through this channel is small. The analysis of the following steps of this mechanism, leading to the corresponding hydroperoxide at the 15-LOX-1 active site, indicates that the oxygenation mechanism will lead to the formation of lipoxin B_4 after the final action of a reductase. In contrast, our calculations are in agreement with experiments that lipoxin A_4 cannot derive from 5(S),15(S)-diHpETE by either of the two proposed mechanisms and that 5(S),15(S)-diHETE is not an intermediate of lipoxin biosynthesis catalyzed by 15-LOX-1.[1]

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PO2

Boron vs. Carbon chemistry: A story in 2D

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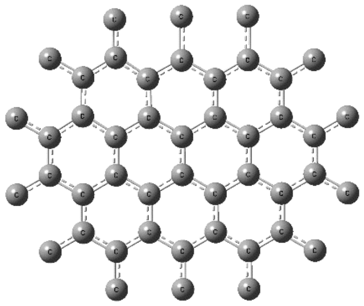
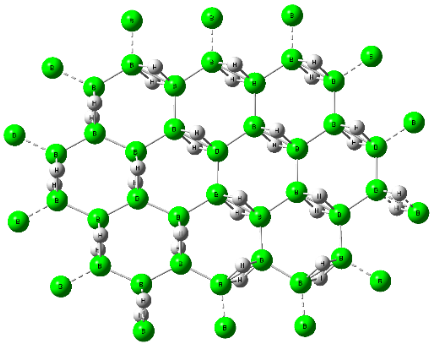
The "classical" organic and inorganic chemistries of carbon and boron, respectively, are well known in university courses and referenced in highly cited university textbooks [1,2]. Thus, thousands of reaction mechanisms are known in the world or organic (carbon) chemistry, but only a few of them are known in the world of boron chemistry. Nowadays, boron chemistry [3] is classified according to (i) organoboron chemistry, and (ii) polyhedral heteroboranes. In (i), a few boron atoms appear in organic molecules and metal complexes, leading to a wide variety of reaction mechanisms and catalysis processes. In (ii), the molecules involved are open and closed polyhedral boranes, with some substitutions of boron atoms by heteroatoms and metals. For the case (ii) the usual known reaction mechanisms of organic chemistry cannot be applied given the complex manyelectron multicenter bonding in the clusterized boranes, since there are no transferability patterns as in organic chemistry. Here we will present some peculiar examples of planarization of boranes, B_xH_y compounds, from the "classical" curved 3D structures, to 2D structures [4,5]. This "planarization" is relevant, because recently a 2D borophane layer $(BH)_1$ – see Figure – has been isolated from superconducting MgB_2 [6]. Borophane is isoelectronic with graphene, and the question then arises naturally: If a quasi-infinite 2D $(BH)_1$ structure can be isolated, can we then isolate finite "planar" molecules derived from borophane? The answer to this question within carbon chemistry is YES! Because benzene, naphthalene, anthracene, etc…exist, and an infinite sequence of fused benzene molecules is simply graphene. However, for boron the answer is by no means straightforward. We will describe, compare and discuss the electronic structure of planar conjugated hydrocarbons vs. planar H-conjugated boranes.



graphene



borophane

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PO3

Electronic structure and magnetic coupling in selenium substituted pyridine-bridged bisdithiazolyl multifunctional molecular materials

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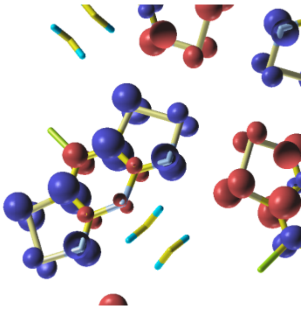
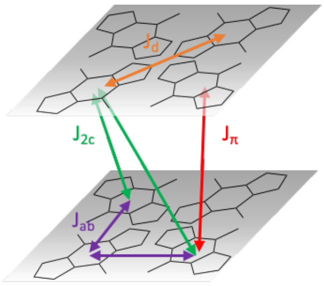
Bisdithiazolyl radicals have furnished in recent years multiple examples of molecular materials with promising conductive and magnetic properties. The electronic band structure and magnetic ordering in four different isostructural pyridine-bridged bisdithiazolyl and Selenium substituted compounds [1,2] have been studied by means of hybrid DFT based methods as implemented in the CRYSTAL code [3]. The full rationalization of the properties of these multifunctional magnetic molecular materials requires a careful description of their complex open-shell electronic structure. The present study [4] is one of the very few attempts dealing with multifunctional magnetic molecular materials whose unpaired electrons that are delocalised over neutral molecular π-systems which are also responsible for the electronic conductivity of the materials. This merges in a single compound two of the most difficult problems faced by current DFT methods: open-shell systems and electron localisation/delocalisation. The results show that the systems are narrow band open-shell semiconductors with a gap of 1.15- 1.40 eV. A low energy closed-shell metallic solution is found at 0.25-0.35 eV above the magnetic solutions thus suggesting a complex mechanism for electric conduction with band and hopping contributions. For all the systems the spin density is well localised on the molecular units and is independent of the magnetic solution. Thus the system can be described as an ensemble of well-defined S=1/2 magnetic centres using a two-body Heisenberg-Dirac-van Vleck spin Hamiltonian. The lowest energy electronic solutions are in line with the observed magnetic behaviour a low temperature. The set of competing magnetic exchange interactions that emerges from using a suitable mapping to consistently describe the low energy magnetic solutions explains the variety of magnetic responses (absence of long-range magnetic order, antiferromagnetism or ferromagnetism) of the four studied compounds at low temperatures.





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Description of conformational ensembles of disordered proteins by residue-local probabilities

PO4

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The study of proteins with intrinsically disordered regions (IDRs) has emerged as an active research field during the last twenty years [1] since they do not obey the well-established paradigm that related the protein function with a well-defined and folded three-dimensional structure of the polypeptide chain encoded in its amino acid sequence. On the contrary IDRs explore dynamically their conformational space but are nevertheless functional and they are prevalent in eukaryotic genomes so that they should be properly considered as a new class of proteins with biological mechanisms different from the traditional structured proteins. Consequently, it has been necessary to adapt or elaborate experimental and theoretical methods able to face the subtleties and challenges introduced by the IDRs.

In particular this work is focused on what we can consider the most fundamental characteristic of any protein, that is, its conformational structure. While ordered proteins show a folding free energy landscape with a deep absolute minimum, the folding funnel picture, IDRs populate many different local minima each of them corresponding to a particular molecular conformation which are separated by free energy barriers that can be overpassed at room temperature. Therefore, IDRs have to be modeled structurally as dynamic conformational ensembles [2]. In practice resolving those conformational ensembles from either experiment or simulations is a difficult task with plenty of uncertainties.

We show through extensive Molecular Dynamics simulations how the molecular conformational ensembles can be properly described through probabilistic expressions by using conformational preferences of each residue depending on the nearest neighbor residues. This modelization allows us to directly detect Molecular Recognition Features (MoRFs) [3] and to follow the time evolution of the thermodynamic magnitudes of the system during its exploration of the conformational space [4].

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QM/MM Study of the Formation of Cyclobutane Pyrimidine Dimers Involving Triplet Thymine

PO5

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Exposure to sunlight radiations induced photodamage to biomolecules and trigger several, well-characterized DNA photolesions in spite of the intrinsic photostability of DNA nucleobases. UV radiation absorption by DNA leads to genetic lesions that impact DNA transcription and replication. But the damage can be repaired by specifically designed proteins (photolyases, BER and NER mechanisms) in living cells [1]. Among all of the DNA damages, the formation of the thymine dimer is one of the predominant and most harmful types of photochemical damage [2]. It corresponds to a [2 + 2] photocycloaddition between two adjacent pyrimidine nucleobases [3].

In this project, we first investigate the stability of triplet thymine along a TTTT track [4] owing to QM/MM-MD simulations, where all the four adjacent thymines are included in the QM subsystem. Thus, we could analyze the energy alignment and the spin localization of the lowest triplet state of thymine embedded in a B-DNA environment successfully [4]. We then investigated the free energy along the reaction coordinate for the formation C6-C6 bond and C5-C5 between two adjacent pyrimidine bases (TT and CT). To do that, we compute the potential of mean force (PMF) by using umbrella sampling. Our simulations account for the embedding of the B-DNA helix, whereas other studies in the literature have usually considered a model system featuring two π-stacked thymines [5].

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Doping Platinum with Germanium: An Effective Way to Mitigate the CO Poisoning

PO6

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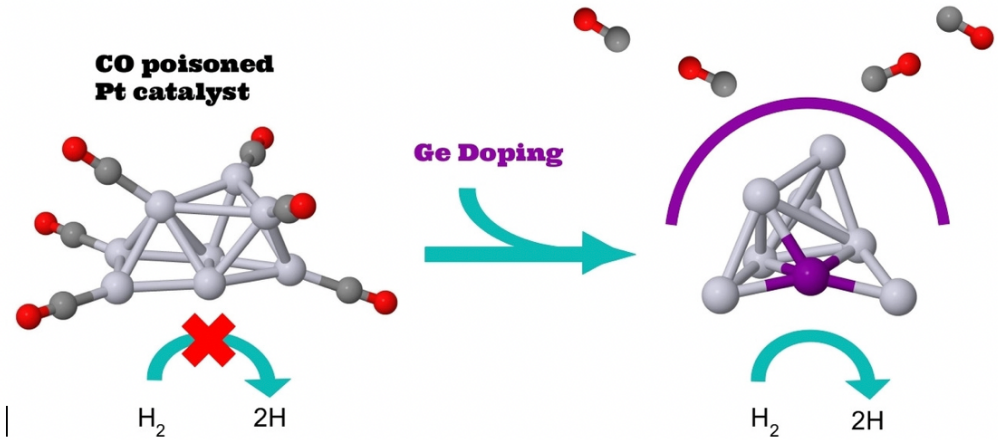
The high catalytic activity of Pt is accompanied by a high affinity for CO, making it extremely susceptible to poisoning. Such CO poisoning, is one of the major obstacles for the commercialization of Fuel Cells. In the first part of this work, using global minima search techniques, exhaustive electronic structure characterization, and mass spectrometric experiments, it is demonstrated that Ge doping mitigates the CO poisoning propensity of Pt nanoclusters, while they remain catalytically active for H_2 dissociation.



In the second part, we show how the dopant concentration is a crucial factor to improve the CO tolerance of Pt catalysts. Analyzing different size and composition PtGe nanoclusters we found that, in clusters with roughly the same amount of Pt and Ge, the binding to CO is weakened significantly. The strong covalency and electrostatic stabilization of equimolar Pt-Ge mixing, make these clusters highly resistant towards CO poisoning. Being these novel catalysts more resistant to deactivation, maintain the catalytic activity towards hydrogen oxidation. Various properties of representative clusters are also analyzed deposited on graphene and the interaction with CO is dramatically weakened for those compounds with 1:1 Pt:Ge ratio. We conclude that Ge can be a promising alloying agent to reduce the deactivation of Pt catalysts.

Theoretical Study of the Sulfonylurea Family of Herbicides

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PO7

This poster presents a study of the structures and chemical properties of sulfonylureas, which are a group of herbicides derived from sulphonamide and ureas with a triazine substituent. They act as inhibitors of acetolactate synthase. Some of the molecules that form this family are amidosulfuron, cinosulfuron, tritosulfuron, prosulfuron, sulfometuron methyl or chlorimuron ethyl [1].

We have determined the most stable tautomers and most stable conformations for each tautomer using the CREST and CENSO programmes [1,2]. The molecules were studied in gas-phase, in octanol and water. Finally, the final properties are obtained at the B3LYP-D3/6-311+G(d,p) level of theory.

As a result, the NH-CO-NH structure is obtained as the most stable tautomer. The use of different properties as gibbs free energies, HOMO/LUMO gap, cavity size, polarizability... to predict properties of environmental interest as the octanol/water partition coefficient for a large family of compounds are also discussed.

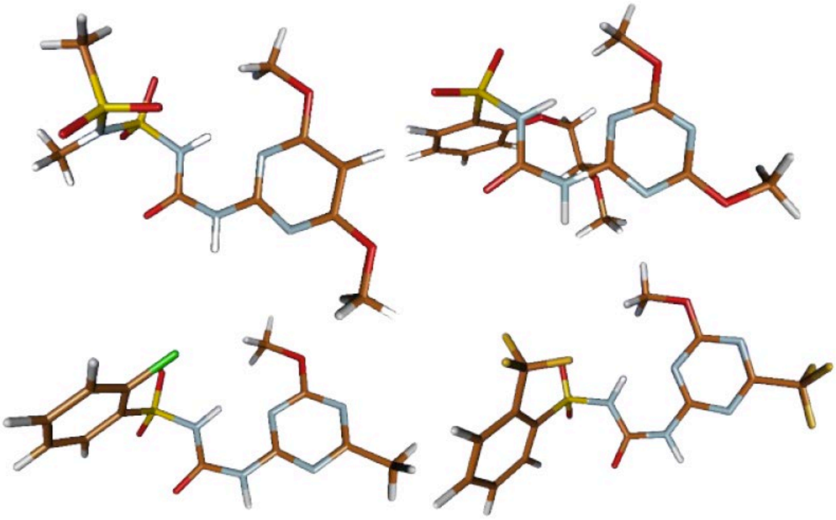

Figure 1. 3D structure of the amidosulfuron, chlorosulfuron, cinosulfuron and tritosulfuron molecules.

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DNA-bases interaction with aminoacids: An exploration of the HB strength.

PO8

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The ability of amino acids to interact with nucleic bases allows proteins to play an important role in processes such as DNA replication, mediated by a set of proteins known as the replisome. This property can also be explored in drugs that target DNA chain. Indeed, exploring the strength of interaction between amino acids with these bases could shed light on their efficacy. Our main aim in the present work is to recover the interaction between some amino acids (glycine, serine, and cysteine) with the four known nucleic bases (adenine, cytosine, guanine and thymine). By means of Density Functional Theory calculations at B3LYP/6-311+G(d,p) level of theory we optimize the structure of the minima that can take place and the most stable ones in each case. We have also calculated the interaction energy between the bases as well as between the base and the chosen amino acids. It has been confirmed that OH as a hydrogen bond donor plays an important role in the stability of the complexes formed. By a thorough Natural Bond Orbital population analysis the origin of these interactions could be detected.

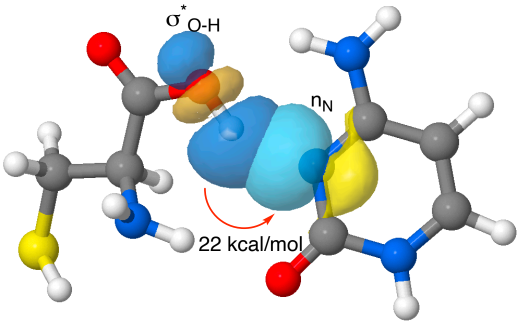

Figure 1. Donation of Nitrogen lone pair of cytosine to the OH antibonding orbital of Cysteine

An Alternative Approach to the g-Matrix: Theory and Applications

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PO9

The g-factor (often called g-value or g-Matrix) is a magnitude that parameterizes the Zeeman effect, involving the interaction of the spin magnetic moment with a magnetic field. One of its most known applications is its use in electron paramagnetic resonance (EPR) spectroscopy [1], in which anisotropic shifts of the g-values relative to the free electron g-value provide significant information about the environment of unpaired electrons.

In the last years, g-factors have been mostly calculated by ab initio methods based on density functional theory (DFT) or wavefunction theory approaches [2]. In this work, Hélène Bolvin's procedure for the calculation of the electronic g-matrix is applied [3]. Herein, molecular wave-functions whose ground state is a non-degenerate spin doublet (and thus can be expressed as Kramer doublets) are determined in a two-step method: firstly the spin-free states are determined and then spin-orbit coupling between these states is introduced. This method allows the analysis of the contributions of each excited state to the anisotropy of the g-matrix.

For the first time, this procedure is applied using restricted active space spin-flip (RAS-SF) method [4]. Different molecules g-values are compared with experimental results and with previous highly correlated results.

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Photophysics and Photoinduced Rotation of a Metallacarborane Cluster. Light-Induced Control of the Surfactant Properties without Covalent Bond Alteration

PO10

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Molecular photo-switches are defined as molecules capable to change their structure upon light irradiation, altering their chemical or photochemical properties. Traditional photo-switches rely on *cis*/*trans* photoisomerisations taking place in organic molecules, such as the famous case of retinal, responsible of animal vision. This phenomenon is however not limited only to organic molecules, and, in the last years, several inorganic systems, including borane[1] and metallacarborane systems[2], have been identified as molecular photo-switches with potential applications in technology and medicine.

The *orto*-cobaltabis(dicarbollide) anion ([*o*-COSAN]⁻, Figure 1) is a well-known metallacarborane that exists in different arrangements, namely the *cisoid*, *gauche*, and *transoid* rotamers, according to the relative positions of the two $[C_2B_9H_{11}]^{2-}$ units that sandwich the Co^{III} atom[3]. In the dark, the most favourable *cisoid* arrangement has amphiphilic properties, allowing the formation of vesicles and micelles. In this talk we will demonstrate that the population of triplet excited states induces a *cisoid* to *transoid* rotation, switching temporarily off the surfactant properties of the molecule[2]. These properties can be recovered *via* the non-radiative repopulation of the ground state.

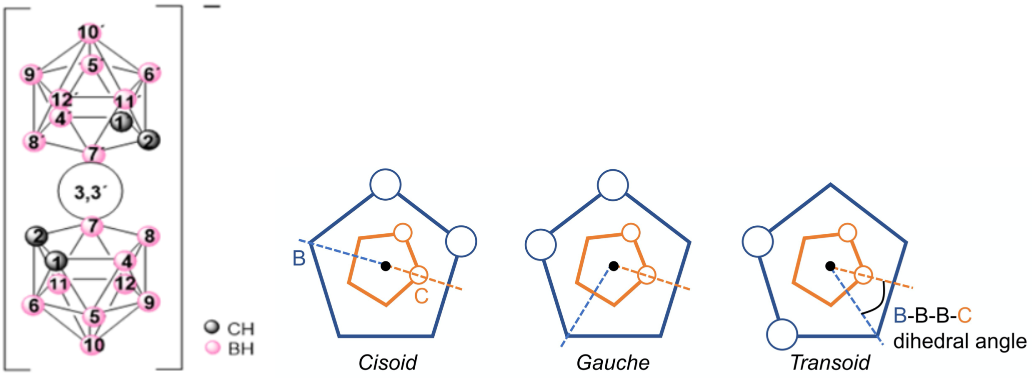

Figure 1. Chemical structure of ([*o*-COSAN]⁻ (left) and disposition of the carbon atoms, shown as circles in blue and orange, for the three rotamers (right).

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Naphthalene-rare gas interaction: intermolecular potential energy surfaces and clusters' structures

PO11

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The noncovalent intermolecular interaction of naphthalene with Helium, Neon and Argon is investigated for selected dimer configurations by means of high level electronic structure calculations and exploiting complete basis set extrapolation techniques. The main features of the intermolecular potential have been identified, with two equivalent global minima (for each side of the naphthalene molecular plane) connected by a low barrier (of the order of 1 meV) which decreases with the size of the involved rare gas (Rg). An analytical formulation of the global potentials, based on simple and efficient atom-atom improved Lennard-Jones expression[1], is also provided by optimizing few and physically meaningful parameters on the calculated interaction energies. The proper representation of the interaction covers the full range of relative configurations of the involved partners and it has been exploited to predict and analyze energies and structures of the low-lying minima in naphthalene-Rg_N (N=1-8) clusters[2] by using Basin-Hopping and Diffusion Monte Carlo approaches.

Preliminary results on clusters involving molecular hydrogen adsorbed on sodium doped naphthalene will be also presented.

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The Role of Sampling in the Computation of Enzymatic Reaction Paths

PO12

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The characterization of reactions is part of the standard repertoire of computational chemists. It enables the verification of proposed reaction mechanisms and, in principle, the calculation of reaction rates and equilibrium constants. Using the Eyring equation, reaction rates can be calculated from the energy difference between the reactant and transition state. However, small errors in this difference lead to large deviations in reaction rates.

We address here two major challenges in the computational characterization of enzymatic reaction paths: (1) the selection of an appropriate starting configuration and (2) the necessity for sampling to accurately describe complex reactions [1,2]. As model reaction, the starting step of the enzymatic desuccinylation catalyzed by Sirtuin 5 was investigated.

For biochemical reactions, an initial frame is usually selected from a molecular dynamics simulation based on chemical intuition, e.g., with the goal of finding a ‘near-attack configuration.’ Screening and testing multiple frames is very tedious and ineffective, mainly because of the highly biased choice of selection criteria. In order to automate and reduce the bias in selecting the starting configuration, which is the basis for all subsequent computations, we present a machine learning based approach, that supports the selection process and also distinguishes relevant structural features.

Starting from the previously chosen frame(s) minimal energy paths are calculated. Because a single path may not be representative, it has been established that exponential averaging is recommended to approximate the true barrier [3,4]. In a second recent study, we computed the free energy barrier using Umbrella Sampling [5] evaluated with the Multistate Bennett's Acceptance Ratio [6] and compared the ‘true’ barrier to the results from 150 minimum energy paths used in our previous work to train the machine learning model and 7501 barriers predicted by this same model. This direct comparison highlights the importance of sufficient sampling. Furthermore, it was shown that the initial step of the desuccinylation reaction proceeds in a S_N2-type mechanism.

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Towards the description of mixed valence in hydrogen-bonded metallocenes

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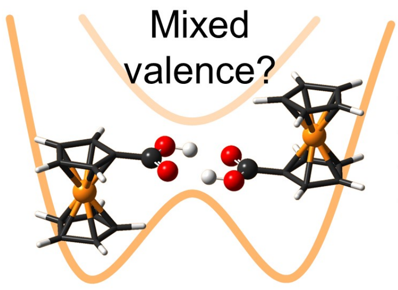
PO13

In the study of mixed-valent (MV) multiferrocenyl systems, much attention has been paid to the impact of covalent bridging units on the observed MV behaviour, particularly focusing on the type of atoms and the nature of the bridge [1-3]. Surprisingly, the effect of non-covalent bridges in MV metal compounds is much less studied, and therefore, less understood [4-6].

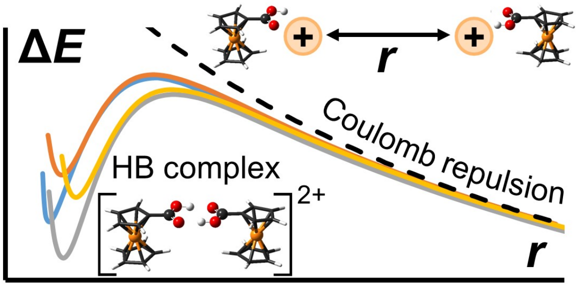
We have started to fill this gap in knowledge by studying several non-covalently bonded metallocene dimers. As a first step, we have focused on ferrocene and other isoelectronic closed-shell species, such as the manganocene anion or the cobaltocenium cation.

The first challenge we address is the choice of method, since those appropriate for the study of non-covalent interactions can many times work poorly when describing transition metal complexes [7]. We have run extensive ab initio calculations in order to choose an appropriate DFT functional for our work.

Remarkably, some of the studied closed-shell dimers can be considered "electrostatics-defying", systems where two anions or two cations can remain bonded through weak non-covalent interactions [8,9]. We have examined how these interactions are influenced by the type of bridge, the metal center and charge of the metallocene, or the substituents on the ring. Once these relationships are well established for the closed-shell cases, we will take a look into the MV behaviour of some of these species.



✓ Metal/Charge
✓ Linking group
✓ Substituents
✓ Method



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Dinitrogen Activation Mediated by the (P_2P^{Ph})Fe Complex: Electronic Structure, Isomerization Mechanism, and Magnetic Coupling

PO14

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We have studied the extent of dinitrogen activation by different charged and structural forms of the (P_2P^{Ph})Fe biomimetic catalysts, which in the presence of light exhibit significant yield in the N_2-to-NH3 conversion[1]. CASSCF calculations have been used to evaluate the electronic structure of the mononuclear complex $(P_2P^{Ph})Fe(N_2)_2$. These calculations revealed the formation of Fe^{2+}-$(N_2)_2{}^{2-}$ species, where the dinitrogen is activated because of the back-bonding from the Fe^0 centre. Using DFT calculations, the mechanism and energy profile of the isomerization between models of the mononuclear $(P_2P^{Ph})Fe(N_2)_2$ adduct and the dinuclear mono-N_2-bridged $[(P_2P^{Ph})Fe]_2(\mu\text{–}N_2)$ one has also been figured out (Figure 1). The isomerization process was found to involve a spontaneous three step mechanism thermodynamically favoured (ΔG_{isomer} = -30.49 kcal·mol^{-1}).

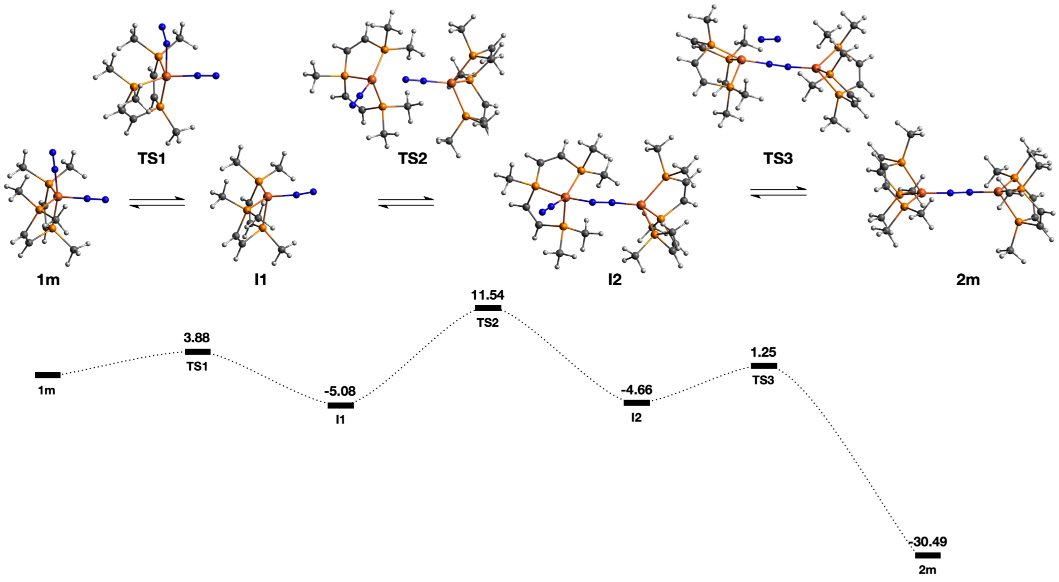

Figure 1. Gibbs free energy profile (kcal·mol^{-1}) for the isomerization mechanism between the mononuclear complex 1m and the dinuclear mono-N2-bridged adduct 2m.

We have also estimated a strong antiferromagnetic coupling in the model diiron $(\mu\text{–}N_2)$ complex (J = -1528 cm^{-1}) by means of NEVPT2 calculations. The electronic structure of this dinuclear system is in line with a dominant Fe^+-$N_2{}^{2-}$-Fe^+ species, i.e., a highly activated dinitrogen, with two electrons on the π* orbitals of N_2 moiety and a low spin d^7 configuration on each Fe atom. These local spins on the irons and dinitrogen account for the antiferromagnetic behaviour[2].

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Extending the MST model to large biomolecular systems: parametrization of the ddCOSMO-MST continuum solvation model

PO15

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Continuum solvation models are popular to describe solvation effects in computational chemistry and are widely applied to study either small molecules and large biomolecular systems. Whereas the study of large systems is usually done adopting the Poisson-Boltzmann or the Generalized Born formulations of continuum models, apparent surface charge (ASC) methods like PCM or COSMO are used in quantum chemical implementations addressed to small molecules, its cost preventing their application to large systems. The novel domain decomposition (ddCOSMO) formulation of COSMO,[1] however, speeds up calculations by several orders of magnitude, thus paving the way for its application to very large systems. Here, we report the parametrization of ddCOSMO to the prediction of hydration free energies based on the MST solvation model developed in Barcelona,[2,3] which has been previously successfully applied to a variety of biological problems,[4,5] e.g. tautomeric equilibria, octanol-water partition coefficients, acidity constants, or the definition of 3D hydrophobic/hydrophilic profiles of biomolecules. Beyond ddCOSMO electrostatics, we introduce several novelties in MST, like a new definition of atom types for non-electrostatic contributions based on hybridisation and an automatic adaptation of the cavity size for charged regions of ions. The training set includes 229 neutral molecules and 122 ions, and the model is parametrized at the DFT B3LYP/6-31+G(d) and semi-empirical PM6 levels of theory. Finally, we test the parametrizations using the sets of hydration free energies proposed in the previous SAMPL2 and SAMPL4 blind challenges, with a total of 91 molecules. Our results provide excellent mean unsigned errors of 1.65 and 1.90 kcal/mol for SAMPL2 and SAMPL4, respectively, using B3LYP/6-31+G(d), and 2.56 and 1.77 for SAMPL2 and SAMPL4, respectively, using PM6.

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Electronic structure of realistic C-doped Anatase TiO_2 Nanoparticles from first principles: Implications for Photocatalysis

PO16

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Semiconducting photocatalysts have generated great expectation during last decades due to their potential applications in different areas, including energy and environment. In particular, titania (TiO_2) is considered one of the workhorses in heterogeneous photocatalysis. However, its limited light absorption in the UV region hinders several commercial applications. Different strategies have been proposed to overcome this drawback, including crystal facet engineering, tailoring size and morphology of photoactive nanostructures and either metal or non-metal doping, just to name a few. The common goal of these approaches is to reduce the energy band gap (E_{gap}) promoting the activation of the nanostructures in the VIS region. Among the different options we focus here on doping with non-metal elements, their incorporation into the photoactive crystal framework reduces E_{gap} by creating intermediate energy levels between valence and conduction bands. In particular, we focus on structural and electronic modifications of TiO_2 triggered by carbon doping (C-doped TiO_2).

Experiments have confirmed that the presence of C atoms in the TiO_2 crystal frame- work promotes photoactivation in the VIS region. This feature has been understood from theoretical analysis of C-doping in anatase and rutile bulk systems and also in anatase extended surfaces [1-3]. However, these solid-state models involve situations that are not sufficiently representative of the experimental photoactive finite nanostructures where several active regions such as corners or edges are missing. The aim of the present study is to investigate the influence of C-doping on TiO_2 by making use of more realistic models. Thus, we investigate C doping on a $(TiO_2)_{84}$ nanoparticle featuring the experimental bipyramidal morphology and a size within the scalable regime [4]. Our results show that the substitution of Ti atoms by carbon (C_{Ti}) is thermodynamically more favorable than the doping in intersticial sites (C_i) and the substitution of O atoms by carbon (C_O), in agreement with previous works. Nevertheless, the reduction of the energy gap is more pronounced for NPs with C_O and C_i sites. Clearly, the atomic environment and structure of titania framework can play an important role in the stability of C-doping as shown by these studies.

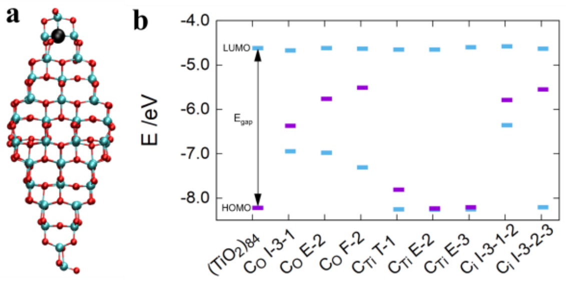

Figure 1. a) Sketch of the optimized C-doping $(TiO_2)_{84}$ NPs. Blue, red, and black spheres denote titanium, oxy- gen, and carbon, respectively..b) Kohn-Sham orbital energy level diagram of $C@(TiO_2)_{84}$ NP as predicted by hybrid density functional.

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PyQchem: a python interface for Q-Chem

PO17

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Q-Chem[1] is a popular general-purpose quantum chemistry software written in FORTRAN, C and C++. As in many other scientific codes, it relies on a simple input/output text user interface. This interface is sufficient for simple human usage, but it has several inherent limitations when automation is desired. In the last decade, Python has experienced a wide adoption within the scientific community due to its flexible and simple syntax. The increasing number of libraries being written in this language makes it a more suitable language for scientific applications. Well-known codes such as LAMMPS[2], Psi4[3], GROMACS[4], among others have native Python interfaces, however Q-Chem still do not have a well-stablished one.

In this poster I present PyQchem, a Python library that allows to interact with Q-Chem using Python scripting. This includes generating inputs, running calculations and parsing the outputs. The aim of PyQchem is to offer a simple and flexible interface for Q-Chem to easily write scripts to automate quantum chemistry workflows linking outputs and inputs of different calculations. This library can also be used to combine data from different software or to create post-analysis scrips taking advantage of the wide variety of available Python tools.

PyQchem is designed to work out-of-the-box by reading the Q-Chem environment without requiring any additional configuration. This makes it easy to install in cluster computers with a pre-existent installation of Q-Chem.

GitHub repository: http://github/abelcarreras/PyQchem
Online Manual: https://pyqchem.readthedocs.io/

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Characterization of halogen bonding between fluorescent pyridine-functionalized fluoroborate dyes and perfluorohalobenzenes

PO18

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In the last two decades halogen bonding has gained importance in the scientific community due to its role in material science, organic synthesis, organocatalysis and medicinal chemistry [1], to name a few areas. Theoretical methods can be invaluable in understanding of various aspects of interactions and bonding, thus contributing to the design of new structures with tailored properties. In the present work we study a set of complexes composed of fluorescent dyes presenting BF_2 group (halogen bond acceptors) and halogenated fluorobenzenes (halogen bond donors). This set of dyes has been studied recently on experimental basis. The experimental results demonstrated a link between formation of halogen bond and Stokes shifts thus making a stimulus for development of theoretical model.

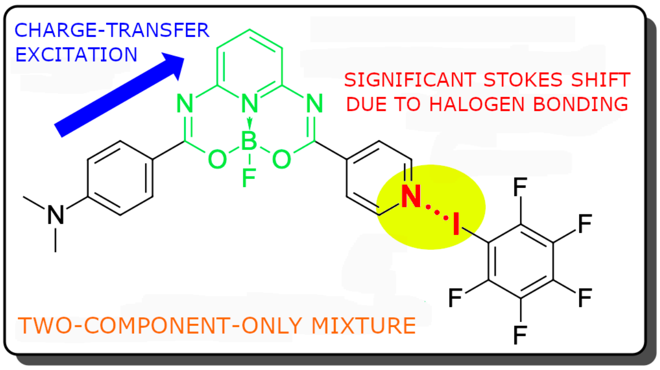

Figure 1. Structure of the system and its properties

In order to understand this interesting phenomenon, we applied quantum chemistry methods to study intermolecular interactions for these complexes and their photophysical properties. In order to gain insight into the nature of intermolecular interactions several schemes have been developed, where the interaction energy is partitioned into different physical terms. One of the most commonly used approaches is the Symmetry Adapted Perturbation Theory (SAPT) [2]. We used a SAPT-based Variational-Perturbational Energy Decomposition Scheme (VP-EDS) which allows to decompose MP2 interaction energy into terms of clear physical interpretation. The Time-Dependent Density Functional Theory was used to study photophysical properties. The results of computations rationalize the origin of experimental significant band shift in the emission spectra on passing from one complex to another and we demonstrate a link with strength on halogen bond.

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Structure and Spectroscopic Properties of Hydrometal Isocyanide Isomers: Plausible Astronomical Ca- and Al-bearing Molecules

PO19

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Metal cyanides and isocyanides play a relevant role in the metal chemistry of the carbon-rich circumstellar envelope IRC+10216. Recently, the first Ca-bearing molecule discovered in space, calcium isocyanide, CaNC, has been detected in the IRC+10216 circumstellar envelope. It is thought that hydrometal cyanides/isocyanides could also be present in these environments; in fact, HMgNC has been detected in the same source that MgCN, MgNC, and AlNC. The aim of this work is to provide information about hydrocalcium and hydroaaluminum cyanide/isocyanide isomers. For this goal, a comprehensive analysis of the energy surfaces of the [Ca, C, H, N] and [Al, C, H, N] systems has been carried out using quantum theoretical methodologies. For the most stable isomers, the stability against dissociation and their interconversion processes have been analyzed. For the [Al, C, H, N] system, our results [1] predict two low-lying isomers, namely, c-HCa–NC ($^1A'$) and hydrocalcium cyanide, HCaCN ($^1\Sigma$), as possible candidates for experimental or radioastronomical detection. In the case of aluminum-bearing molecules, our results [2] show that the most relevant isomers from an experimental point of view are HAlCN ($^2A'$) and HAlNC ($^2A'$). For the most stable isomers, we provide predictions for their vibrational and a complete set of relevant spectroscopic parameters for rotational spectroscopy mandatory to guide an eventual laboratory or interstellar detection. The predicted dipole moment of HCaCN (3.42 D) is very similar to that for the detected HMgNC (3.49 D), whereas the c-HCa–NC isomer has a lower dipole moment, and its identification could be difficult in space. Both HAlCN and HAlNC isomers present sizable μ_a dipole moment components (3.7 and 3.3 D, respectively), which are large enough to enable a characterization by means of rotational spectroscopy, further increasing their interest as interstellar candidates. Despite the technical difficulties of detecting these new species with currently available telescopes, they are potentially interesting molecules to search for, so we expect their spectroscopic information is very valuable.

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Synthesis of Protonated Glycine Isomers in the Interstellar Medium

PO20

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The question whether amino acids are present or not in space is one of the most pursued targets for astrochemists. Despite several radioastronomical searches, so far, the smallest amino-acid, glycine, has not been conclusively identified in the interstellar medium (ISM). Nevertheless, there is observational evidence of amino acids in extraterrestrial objects, such as meteorites or comets. Furthermore, different experiments have shown the formation of amino acids after UV irradiation of interstellar ice analogues. Therefore, even though no conclusive detection of an amino acid in the interstellar medium has been reported, it is conceivable that they could be present in space. The observation of amino acids in the ISM and in solar system bodies should be of crucial importance for revealing the chemistry that may have led to life's origin. There is a question as to whether glycine will ever be detectable even if present, given the difficulties for its possible detection in space. One of these difficulties arises from its rotational spectrum features with relatively weak lines due to its large molecular partition function. Thus, search of the target transitions could be hindered by the emission of other molecules. Second, amino acids are highly susceptible to UV photodestruction and they will likely be destroyed during the lifetime of a typical interstellar cloud and they only survive in shielded environments. Finally, it might happen that efficient synthetic routes to produce amino acids under interstellar conditions do not exist. In this regard, exothermic ion−molecule reactions between positive ions and neutral molecules play a crucial role in the synthesis of organic interstellar molecules in the gas phase since these processes tend to have no activation energy barrier. Herein, we report a computational study [1] of the products obtained from reaction between protonated hydroxylamine and acetic acid. These products are structural isomers of protonated glycine. We have carried out a comprehensive structural and spectroscopic description for all the isomers of protonated and neutral glycine with the aim to aid their laboratory or astronomical detection by radioastronomy or infrared spectroscopy. Our study predicts neutral N-hydroxyacetamide as a candidate molecule to be searched for in the interstellar medium.

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PO21

Computational design of conjugated molecules with lower (or isoenergetic) S_1 than T_1 excited-state energies

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Thermally Activated Delayed Fluorescence (**TADF**) process has been recently identified as one of the most promising strategies to achieve 100% internal quantum efficiency in Organic Light-Emitting Diodes (**OLEDs**)[1, 2]. The TADF process enhances the upconversion of triplet-excited states to singlet emitting states via a Reverse Inter-System Crossing (**RISC**) mechanism[2]. As molecular template, we selected the (open-shell) Clar's Goblet **(CG)** nanographene, to tune the molecular properties upon substitution; which is been exceedingly used in organic electronics and spinelectronics[3]. In this contribution, we will mainly discuss the influence of both the type and site of heteroatoms substitution on CG molecules in order to decrease the energy difference between the first singlet excited state **S1** and the first triplet excited state **T1** (**ΔE^{ST}**) and allow RISC mechanism to occur, by using various quantum chemical methods such as **TD-DFT (e.g. PBE0, M06-2X or double- hybrid functionals)**, **CIS(D)** and **SCS-CC2**. Overall, the topology of substitutions is found to be the key to alter the excited-state energies, while concomitantly disclosing the accuracy of the various methods assessed as well as the importance of double excitations[4].

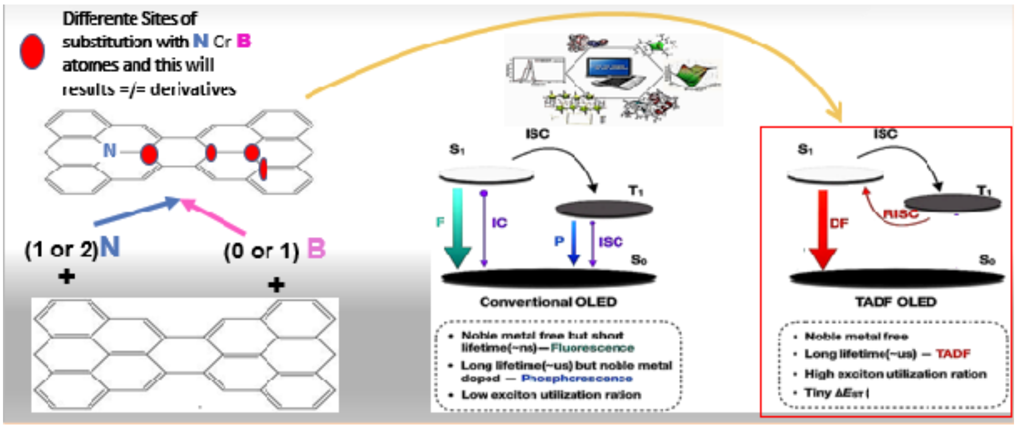

Figure 1. Schematic illustration of the study

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Enthalpy-Entropy compensation in metal-bound neurofilament peptides

PO22

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In the last decades aggregation of Intrinsically Disordered Proteins has been found to be close-related with some neurodegenerative disease such as Alzheimer's and Parkinson's[1]. However, despite of the considerable amount of work that has been done, aggregation mechanisms remain yet unknown. Here, we have utilized a multi-scale approach (QM + MD) to unravel the possible implications of the $Al^{(3+)}$ cation in the conformational changes of a neuropeptide involved in the Alzheimer's disease, following the metal-ion hypothesis. Results show that binding type leads to different spatial arrangements which entails variable aggregation probabilitiy[2]. Furthermore, these spatial arrangements modify inevitably the accesible conformational space[3]. Thus, we aim to quantify the contributions of both enthalpy and entropy magnitudes and characterize the balanced interplay that determine the population of the most favorable species.

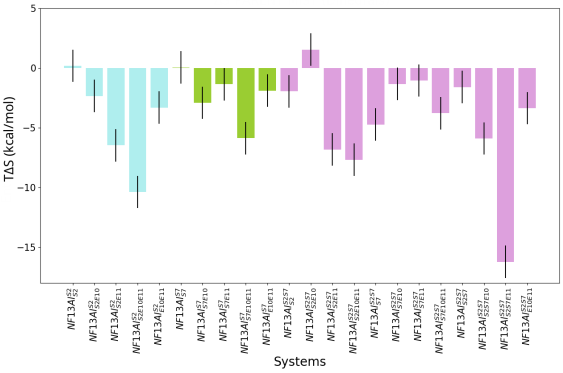

Figure 1. TΔS values for the studied systems. Larger negative bars correspond to entropically unfavored systems. Color code correspond to phosphorylation type: single phosphorylation at serine 2 (blue), single phosphorylation at serine 7 (green), double phosphorylation in both serine 2 and serine 7 (pink.)

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Benzene, an unexpected binding unit in anion–π recognition: The critical role of CH/π interactions

PO23

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Anion–π interactions are a prominent type of attractive non-covalent force that were put in the spotlight of the scientific community from the pioneering computational studies that appear back in 2002[1-3]. Anion–π interactions are also very frequent in biological systems, with more than half of the biomolecular complexes of the protein data bank containing at least one anion–π contact, i.e., one anion–π interaction for every 50 anionic residues in the PDB[4]. The CH/π interaction is a type of force which is shown to be crucial as the driving force in crystal packing, host-guest chemistry, conformation, and reaction selectivity of organic compounds. Moreover, due to the omnipresence of both alkyl and phenyl groups in biomolecules, many evidences for the CH/π interaction in biological systems have been reported [5].

Here, we report a theoretical study using high-level ab initio calculations in which we address cooperativity effects between anion–π and CH/π interactions and analyze their importance in biological systems due to the ubiquity of CH bonds (as in methyl groups), phenyl rings (as in the side chains in Phe and Tyr) and anions (as in Asp and Glu). We selected the benzene molecule as a model of phenyl moieties, methane molecule as a model of an alkyl chain and formate and nitrate anions as models for carboxylate anions. Moreover, the SAPT partition scheme was used to analyze the different energy contributions to the binding energies and to investigate the physical nature of the interplay between both interactions. Finally, the AIM theory and the NCI approach were used to further analyze the two interactions.

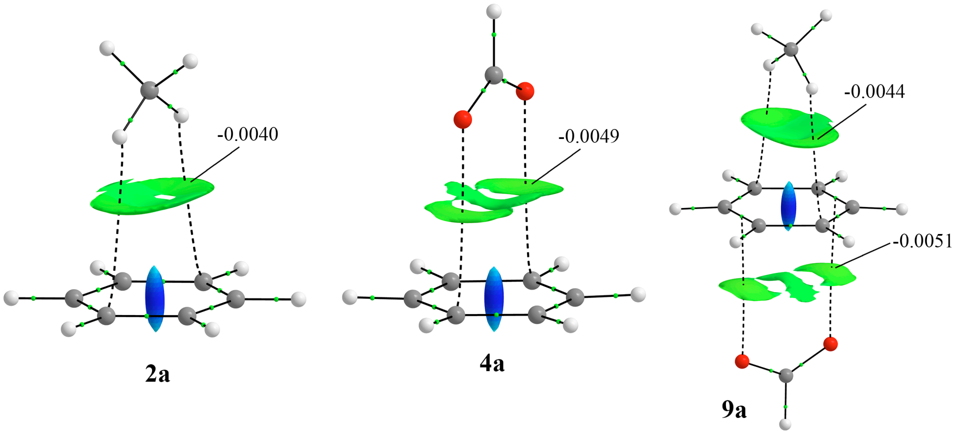

Figure 1. NCIPLOT gradient isosurfaces (isovalue = 0.5 au). Green and blue indicate weak and strongly repulsive interactions, respectively. Values of sign(λ_2)ρ indicated are in au.

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Competing photolytic degradation and photostability, the case of the C4-oxo substituted pyrimidine.

PO24

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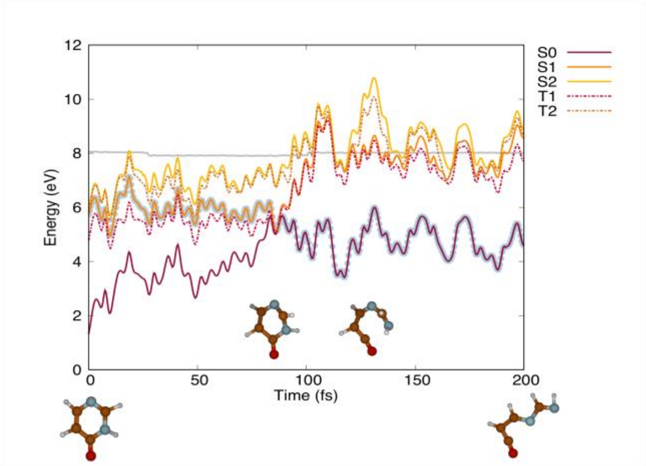
Natural DNA nucleobases are characterized by its intrinsic photostability upon the continued UV irradiation. The efficient internal conversion process through those biomolecules dissipate the absorbed energy, highly prevents hazard secondary photoreactions which can give place to genetic mutations[1]. Stablishing the electronic and structural keys which control the interesting photophysics and photochemistry of these systems has constituted an important researching line for years. In this way, the study of the deactivation mechanism in modified nucleobases has allowed to reveal the role that different chemical groups play in the exceed energy dissipation[1]. Among the ensemble of non-natural nucleobases, 4-pyrimidinone and its equivalent purine, hypoxanthine, have been proposed as nucleobases' ancestors[2]. Those systems classified as photostable system present short excited state lifetimes, comparable to the fastest DNA bases[3,4].

In this communication, we investigate the photophysics of the modified nucleobase, 4-pyrimidinone, by means of multidisciplinary study which combines static and dynamics simulations at one of the most sophisticated multiconfigurational method, XMS-CASPT2[5], with femtosecond transient absorption spectroscopy. Experimental observations and our non-adiabatic molecular dynamics results provide strong evidences for the photodegradation of this system[6]. These unexpected results shedding light on the effect of functionalization of pyrimidine core and establish one of the first examples of photolabile nucleobase derivate.



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Ultrafast electron dynamics in molecules adsorbed on metal surfaces: a Wave Packet Propagation Approach

PO25

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Quantum chemical calculations are typically carried out in the framework of the Born-Oppenheimer approximation, where the electron density adapts instantaneously to the coordinates of the nuclei. Thus, electron dynamics are not considered in standard calculations. However, for some chemical processes they can play an important role and more sophisticated methods must be used.

Here, we present a methodology based in Wave Packet Propagation (WPP) to study electron dynamics with the possibility of an explicit consideration of the atomic structure of the system [1]. Some examples of possible applications of WPP are also presented. Specifically, we show the importance of the electron dynamics in the lifetime of excited states of molecules adsorbed on surfaces, a reason behind the quenching of the signal in the STM-induced fluorescence [2]. Thanks to WPP calculations, it has been possible to provide a detailed explanation of these experimental observations [3], as well as to understand the role of the electronic structure of the surface on the electronic decay [4].

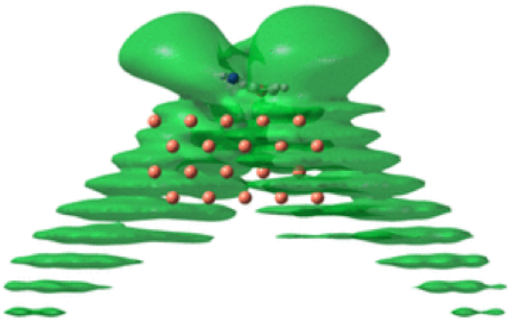

Figure 1. Decay path of an excited electron in a molecule adsorbed on a metal surface.

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Frustrated Lewis Pairs: An efficient and controllable carbon dioxide capture and activation

PO26

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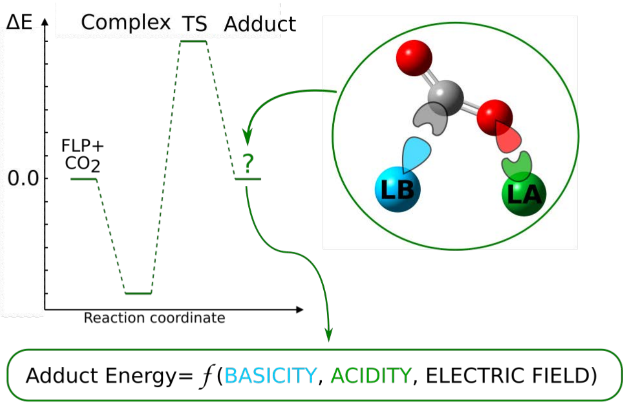

Since their discovery in 2006 by Stefan *et al.* [1], Frustrated Lewis Pairs (FLP) gained a lot of interest in the scientific community due to their large range of applications: capture and sequestration of several small molecules [2], reversible capture and rupture of H_2 [3] and ability to work as a catalyst to hydrogenate non-saturated bonds [4]. The main property that gives a bright future to those systems is their metal-free character that integrates them in the "green chemistry" tendency. Due to the constant growing of CO_2 concentration in the atmosphere and the several problems induced by this increase [5], one possible application of the FLP is the capture and activation of CO_2 molecules. The main techniques to capture CO_2 nowadays are the use of nitrogen-based compound, ammonium carbamate salts, carbamic acid, and amine [6]. Nitrogen being a Lewis base, due to its lone pair, one can expect that a FLP based on nitrogen can be also a candidate to capture CO_2. For that reason, FLP can be used as a possible storage supply, as well as a catalyst that enables to capture CO_2 and to activate it, making its transformation easier [7]. In the literature, there is a plethora of FLP. From the original $P(^tBu)_3/B(C_6F_5)_3$ [1], to the 5,10-Disubstituted dibenzophosphaborines [8], passing by the $R_3P\text{-}CH_2CH_2\text{-}BR_2$ linked FLP [9] and more exotic FLP couples like N/Si and N/Ge [10], the importance and the versatility of FLP is a certainty in the chemistry world. During the study of several FLP reacting with CO_2 [9-10], it was shown that the capture of carbon dioxide molecules by FLP can be controlled by playing with the acidity and basicity of the Lewis acid and base or by imposing an internal or external electric field. One can pass from a non-favorable, to a thermodynamically favorable reaction, and the concept of reversibility capture can be accessed.

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Statistically Optimal Analysis of the Extended-system Adaptive Biasing Force (eABF) Method

PO27

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The extended-system Adaptive Biasing Force (eABF) method [2] and its newer variants [3,4] offer rapid exploration of the configuration space of chemical systems. Instead of directly biasing the dynamics of collective variables (CVs), they are harmonically coupled to fictitious particles which are biased vicariously.

In this contribution [1] we show how to recover the full statistical information from extended-system simulations using the Multistate Bennett's Acceptance Ratio (MBAR) [5], putting their post-processing on one level with other frequently used sampling methods. Thus, we extend the application of this class of sampling algorithms from the calculation of potentials of mean force (PMFs) to ensemble averages in general.

We apply this formalism to the prediction of nuclear magnetic resonance (NMR) shieldings, which are sensitive to molecular geometries and often require extensive sampling [6]. Additionally, we show how PMFs can be reweighed to other collective variables of interest, which yields mechanistic insight into complex chemical processes. The results show that the combination of enhanced sampling by means of extended-system dynamics with the MBAR estimator is a highly versatile tool for the calculation of ensemble properties [1].

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Computational Methodologies for Describing Supramolecular Host-Guest Encapsulation Processes

PO28

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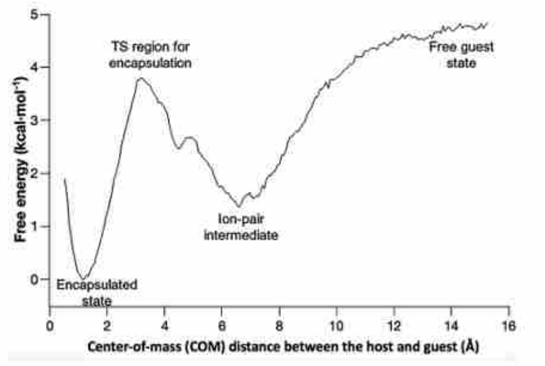
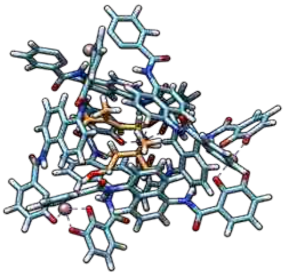
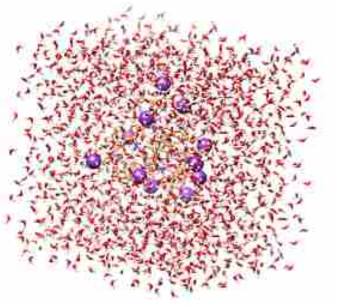
In recent years, studies on synthetic host mediated catalysis have driven into a better understanding of supramolecular catalysis and the effect of chemical microenvironments[1]. However, the initial step must be the guest-encapsulation (reactants-encapsulation). This process undergoes a major challenge in supramolecular systems, requiring a combination of methodologies to accurately overcome host microenvironment conditions and guest diffusion low barriers[2].

The proposed workflow includes the use of all-atom molecular dynamic simulation techniques such as attach-pull-release (APR)[2,3] and the refinement of well-tempered metadynamic methodologies. Both allow us the obtention of accurate binding Gibbs energies in a computationally affordable way. The encapsulation of several guests (charged and neutral) into a set of metallocages have been computed and compared between them and to experimental data. The purpose is testing the viability of these enhanced sampling techniques[2,3]. The results obtained indicate that these methods are properly suited for modelling these processes.







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Theoretical investigation of the electronic and structural factors that govern the photostability of nucleobases

PO29

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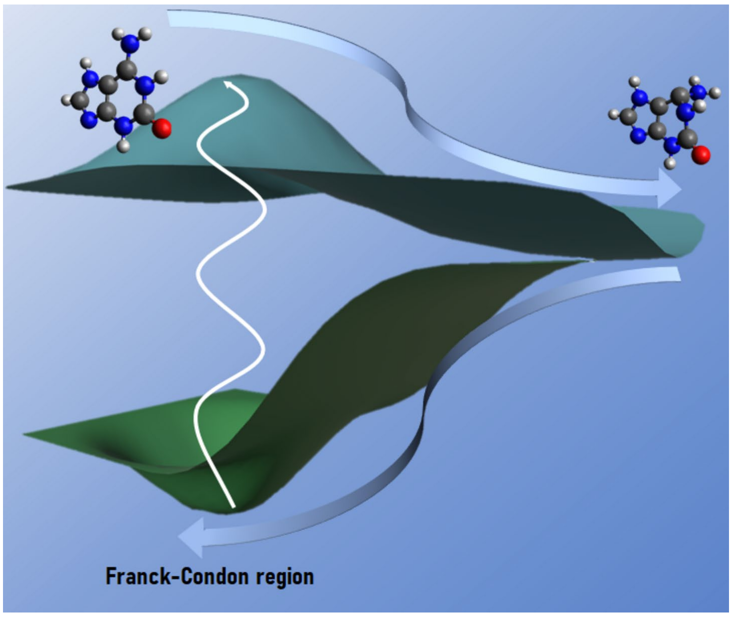
Only five different monomers integrate the canonical nucleic acids' alphabet. This is believed to be, at least in part, due to their notable photostability, which allows the efficient and ultrafast return of the electronically excited population to the ground state, minimizing the photoreaction yields. Efficient ultrafast ground state recovery occurs via internal conversion funnels that need to be accessible along the relaxation of the system from the Franck Condon region[1].

Recent investigations have revealed that the topography of the ground and excited state potential energy surface is related to the substitution pattern of the purine or pyrimidine cores which can strongly modify the photophysics of the formers[2,3]. Studying the effect of the nature and position of the substituents in the shape of the potential energy surfaces can help understanding the mechanisms that govern photostability in nucleobases.

In this communication, we will analyze the potential energy surface landscape of several purines, isoguanine, guanine and xanthine, using state of the art quantum mechanical methods. We will also examine which is the impact of the structural modification of the heterocyclic core in the photophysics of these systems by scrutinizing the potential energy surfaces of 7-deazaguanosine and 5-aza-7-deazaguanine[4].



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Inhibition of the Parkinson's Disease-related alpha-synuclein aggregation by phtalocyanine tetrasulfonate. New Insights from Molecular Dynamics Simulations.

PO30

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Alpha-synuclein (aS) is an intrinsically disordered protein whose aggregation directly related to Parkinson's disease (PD) development[1,2]. One type of neuroprotective therapies under investigation against PD is based on small molecule aggregation inhibitors, which interact with aS and hinder the conformations prone to nucleation.

NMR experiments revealed phthalocyanine tetrasulfonate (PcTS) as a lead candidate against aggregation of aS and several of its mutants[3]. We provide a fully atomistic molecular basis of the aS-PcTS interaction through molecular dynamics and umbrella sampling simulations.

Consistent with the reported NMR experiments, our results reveal new modes of interaction between aS and PcTS. The most stable complex is formed by the simultaneous interaction of two protein regions acting in a tweezers-fashion with PcTS. Additional simulations with aS mutants show that the interaction with PcTS can be interpreted as dynamic equilibria between different aS-PcTS complexes. These findings could be used for the development of aggregation inhibitor-based therapies against PD.

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Conceptual Density Functional Theory under Pressure: XP-PCM method applied to atoms

PO31

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Since its conception, the field of Conceptual Density Functional theory has succeeded in giving rigid definitions to previously vaguely defined chemical concepts such as the electronegativity and the chemical hardness[1]. Within this field, the energy is expanded as a functional of the number of electrons and the external potential and its resulting descriptors have proven their usefulness in retrieving chemical properties and scrutinizing chemical reactivity[2]. In recent years, extensions to this framework are at stake by including external perturbations such as electric fields, magnetic fields, temperature and mechanical forces[3]. By using the XP-PCM (eXtreme Pressure Polarizable Continuum Model) method, developed by Cammi et al. to simulate extreme pressures on the single molecular level, now pressure is introduced into this new set of perturbations and its influence on reactivity descriptors in the conceptual DFT framework can be evaluated[4]. This with the aim of describing and better understanding electronic structure and molecular reactivity in the GPa pressure range.

By applying XP-PCM and conceptual DFT to atoms of the main group elements elements hydrogen to krypton, the first order response function with respect to the pressure, $\left(\frac{\partial E}{\partial p}\right)_{N,v}$, is identified as the electronic volume. The derived electronic radii correlate well with known sets of atomic radii, indicating it as a valid measure of the system extension. This interpretation allows to explain the trends observed for the ionization potentials, electron affinities and electronegativity, all decreasing under pressure. Additionally, the atom-based model used here, succeeds in retrieving some striking findings in high pressure chemistry. The chemical hardness on the other hand was found to increase with pressure and its inverse cube (i.e. the softness) correlates well with the isotropic polarizability for different elements under pressure.

Finally, as a local descriptor, the electron density is analysed under pressure, finding a clear translocation of electron density from the peripheral to the internal regions of atoms. Three different analysis methods, including two rooted in information theory, all find unbiased periodic behavior in the density of elements under pressure with elements early on in a period displaying a more sensitive response to external pressure than their later counterparts.

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Inhibition mechanisms of EGFR Lys745 by sulfonyl fluoride derivative inhibitors: A computational study.

PO32

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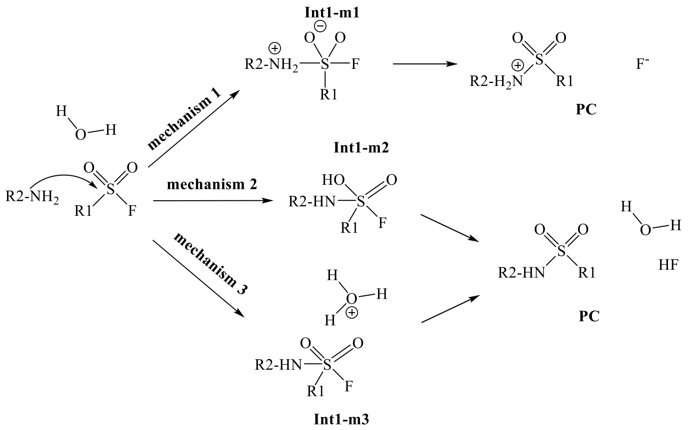
The epidermal growth factor receptor (EGFR) is a tyrosine kinase receptor that transduces proliferation signals [1]. Activating mutations in the EGFR gene concur to the insurgence of non-small cell lung cancer (NSCLC). The emergence of the C797S mutation in EGFR is a frequent mechanism of resistance during the treatment of NSCLC[2]. There is an urgent need to develop an effective treatment for this disease. Thus, the catalytic Lys745 of EGFR has become a promising target for covalent drug design. Efforts in this direction have led to XO44, a sulfonyl fluoride derivative able to covalently modify EGFR$^{L858R/T790M/V948R}$ but with a low selectivity against kinases[3]. In this sense, the sulfonylating agent UPR1444 has emerged as a promising compound, able to irreversibly inhibit EGFR$^{L858R/T790M/C797S}$ by covalent modification of the catalytic Lys745.[4]

We present a computational study of the possible inhibition mechanisms of EGFR Lys745 by the sulfonyl fluoride derivative inhibitors XO44 and UPR1444 (see Scheme 1). The inhibition mechanisms have been studied using a multiscale approach based on molecular dynamics (MD) and quantum mechanical/molecular mechanics (QM/MM) simulations to obtain a complete picture of the free energy profile in terms of a potential of mean force (PMF). The proposed inhibition mechanism, with their corresponding free energy barriers and interactions between the inhibitors and the enzyme has been the subject of a deep analysis in order to improve the design of EGFR Lys745 inhibitors.



Scheme 1. Possible inhibition mechanisms of EGFR Lys745 by sulfonyl fluoride derivative inhibitors.

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Atomic shell structure from Born probabilities: comparison to other shell descriptors and persistence in molecules.

PO33

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Although orbital paradigms lie behind the development of modern quantum chemistry [1], methods that provide orbital invariant pictures provide and independent, likely preferable, image of chemical phenomena [2, 3]. Most of them have been developed in real space, thus providing a suitable playground to interpret the chemical bond. In this work, the atomic shell structure is examined after obtaining the 3N-dimensional maxima of the square of the wave function (or Born probability) in atoms. This has been done by applying the Variational Quantum Monte Carlo method for atoms H to Kr. The shell structure obtained through this procedure has been compared to other shell structure descriptors, like the Laplacian of the electron density, the electron localization function (ELF) and the Localized Orbital Locator (LOL) [1].

The maxima of the Born probability density show that the electrons form very clear quasi-spherical shells for a given principal quantum number *n* (see Fig 1). Same-spin electron blocks in each shell minimize their Fermi repulsion as much as possible separately, and these quasi-rigid opposite spin blocks organize themselves to minimize their smaller Coulomb repulsion. Shell distances are close to the nuclei than in the case of the minima of the Laplacian of the density, being substantially smaller than those found with the ELF or LOL.

Fig 1. Pictorial representation of the position of electrons (spins labeled by color) at the Born maximum for the ground states of Be, Ne, Ar, and Kr as obtained from VQMC HF+J/cc-pVDZ calculations. The two K electrons at the nucleus are not shown. Subfigures are not drawn on the same scale.

Regarding the behaviour observed in the molecules, as they are formed, the atomic valence shells distort considerably. Pauli-based descriptors typically reveal non-bonded concentrations, such as lone pairs, effortlessly, while tending to fuse the shell maxima of the two atoms involved in a bonded concentration. This tendency to fusion is much smaller in the Laplacian, which usually distinguishes the two valence shells of the two bonded atoms. It is fully avoided by the use of Born maxima.

The study of Born probabilities for atoms provides an alternative shell structure descriptor which we think displays many advantages over other available indices. It considers, in principle, the full *N* electron correlations, and this has been seen to lead to sizable effects. Atomic shells are rather impressively preserved in molecules.

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On the decomposition mechanism by photo-oxidation and photoreduction of azetidine derivatives as models of (6-4) photoproduct DNA lesions

PO34

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DNA in living beings is constantly damaged by both exogenous and endogenous agents, such as UV radiation. The photoinduced DNA lesions can be initiated by Paternò–Büchi, or aza-Paternò-Büchi, photocycloaddition between two adjacent pyrimidine bases, forming an oxetane or an azetidine ring, respectively.

Then, the repair mechanism of these lesions can be represented with the inversion of the Paternò-Büchi reaction. Some lesions can be repaired by photolyases also in presence of light and a photosensitizer via a photoprocess whose molecular mechanism is not completely understood yet. In this contribution, we have focused on the aza-version of the Paternò-Büchi reaction. Then, two azabipyrimidinic azetidines have been studied as model compounds of the elusive azetidine intermediates present during the (6-4) photoproducts repair. The first one is obtained by photocycloaddition between 6-azauracil and thymine (AZT-Thy), and the second one arises from the photocycloaddition between 6-azauracil and cyclohexene (AZT-CH). DFT calculations have allowed to interpret the experimental observations. In addition, they also help us to elucidate the ring-opening mechanisms during photoreduction and photo-oxidation processes. On the one hand, regarding the AZT-Thy model, energy barriers lower than 13 kcal mol^{-1} are obtained for both the photoreduction and photo-oxidation processes[1]. On the other hand, regarding the AZT-CH system, energy barriers lower than 14 and 9 kcal mol^{-1} for the *cis*- and *trans*- isomers are obtained for photoreduction, while values of about 36 kcal mol^{-1} are obtained for both isomers in the photo-oxidation process[2].

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Automatic procedure to obtain tight-binding parameters for second-principles simulations. The case of $SrTiO_3$

PO35

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First-principles calculations allow to compute the energy and properties of a compound from essential information about its structure and composition. In principle, even the finite temperature behavior of materials is accessible from first-principles simulations since the early stage of density functional theory (DFT). Nowadays, however, such simulations remain practically limited by computational resources to very small length scales (a few hundreds of atoms per cell) and timescales (a few picoseconds). Nevertheless, many important fundamental and applied problems require to explore these large time and length scales at operating conditions (finite temperature, electric fields, etc). A practical way to overcome these limitations is to work with effective atomistic models, integrating out the electronic degrees of freedom and providing a simple parametric description of the Born–Oppenheimer energy surface in terms of structural degrees of freedom. This might be a constriction in some cases, specially, in those problems where the relevant physics is dominated by the electronic degrees of freedom. Recently, a method has also been proposed to reintroduce explicitly the treatment of the meaningful electronic degrees of freedom in the form of a tight-binding model, while avoiding double-counting with the effective atomic potentials [1].

This tight binding approach is based on the Taylor expansion of the DFT energy around a reference electronic density. The deformation density with respect this reference, as well as the hamiltonian matrix elements, is expressed in a basis of Wannier functions which are obtained from the band manifolds of interest in the problem. Only the relevant electrons to the problem can be retained in the description, reducing by orders of magnitude the computational cost. This gain in efficiency would come at the cost of finding the right parameters in the tight binding hamiltonian matrix elements, that would reproduce as close as possible the first-principle hamiltonian matrix elements.

Here we propose a method implemented in python, the MODELMAKER code, for the automatic parametrization of such tight binding hamiltonian. The starting point is made of first-principles calculations (from the SIESTA code [2]) in training sets with a small number of atoms in the unit cell. Since there is not input coming from the experiment, our method retains full predictive power, and that is why it is coined as second-principles simulations. Both electron-lattice coupling, studied by calculations characterized by geometry distortions, and electron-electron interactions, caught by simulations exploring electronic states beyond the Born-Oppenheimer surface, are included in the parametrization of the electronic model. The obtained parameters are validated comparing the band structures computed from first and second-principles in configurations that are not included in the training set. This methodology has been applied to a paradigmatic functional oxide such as $SrTiO_3$.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” by the European Union.

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Spin-crossover complexes in nanoscale devices: main ingredients of the molecule–substrate interactions

PO36

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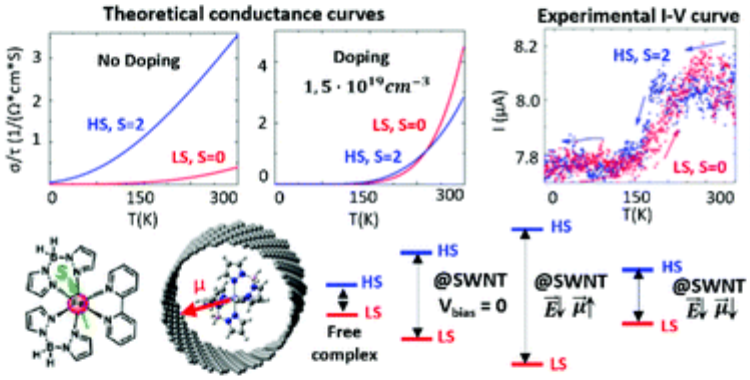
Spin-crossover complexes embedded in nanodevices experience effects that are absent in the bulk that can modulate, quench and even suppress the spin-transition. In this work we explore, by means of state-of-the-art quantum chemistry calculations, different aspects of the integration of SCO molecules on active nanodevices, such as the geometry and energetics of the interaction with the substrate, extension of the charge transfer between the substrate and SCO molecule, impact of the applied external electric field on the spin-transition, and sensitivity of the transport properties on the local conditions of the substrate. We focus on the recently reported encapsulation of Fe(II) spin-crossover complexes in single-walled carbon nanotubes [1], with new measurements that support the theoretical findings. Even so our results could be useful to many other systems where SCO phenomena take place at the nanoscale, the spin-state switching is probed by an external electric field or current, or the substrate is responsible for the quenching of the SCO mechanism.



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PO37

Computational Study of inhibitors targeting PD-L1 and VEGFR-2 proteins

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Immunotherapy and anti-angiogenic agents are two promising therapeutic strategies to treat cancer. Immunotherapy involves the use of immune checkpoint inhibitors (ICIs) to attack the immune system to restore its anticarcinogenic effect and attack the cancer cells to destroy them. One of the immune checkpoints proposed is the programmed cell death-ligand 1 (PD-L1) protein (Figure 1a). Anti-angiogenesis is designed to disrupt the growth of new blood vessels from pre-existing vasculature and starve tumor of nutrients and oxygen. This effect is achieved by blocking the vascular endothelial growth factor receptor 2 (VEGFR-2) protein (Figure 1b). The combination of these therapies, namely addition of anti-angiogenic agents to immune checkpoint inhibitors, improve anticancer efficacy [1].

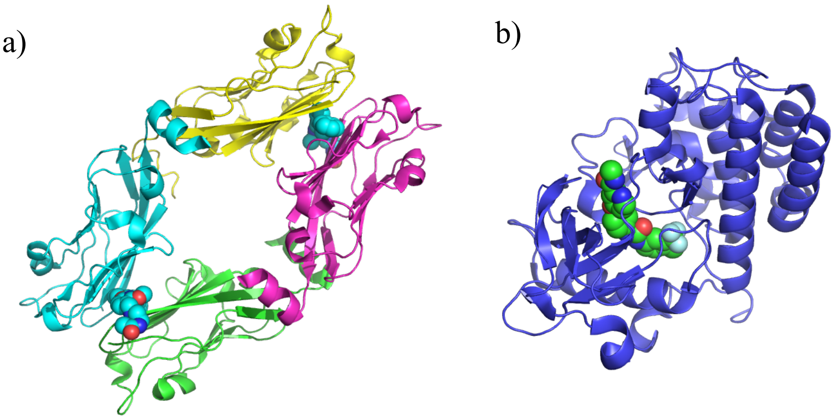

Figure 1. Structures of a) PD-L1 and b) VEGFR-2 proteins with inhibitors.

In this work we present the computational study of possible inhibitors that can be used in both PD-L1 and VEGFR-2 systems. Starting from the structure proposed in Figure 2 with different substituents we have studied the interaction energies using molecular dynamics and hybrid quantum mechanics and molecular mechanics (QM/MM) methodologies. Based on the results obtained, new effective inhibitors will be predicted and designed to treat cancer [2].

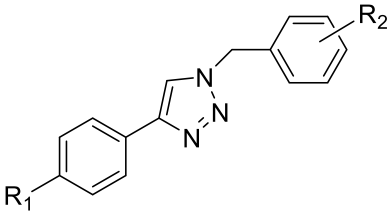

Figure 2. Structure of possible inhibitor of PD-L1 and VEGFR-2 proteins.

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Exploration of Novel Candidates for Photocontrolled Treatment based on Curcumin and Cyclocurcumins

PO38

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Cyclocurcumin is a natural compound extracted from turmeric and presenting an interesting solvent-dependent photoswitching ability. The solvent-dependent photochemistry of cyclocurcumin has been rationalized on the basis of a competition between π-π* and n-π* states[1]. Furthermore, we have reported the synthesis of a biomimetic analogue showing enhanced photochemical properties and in particular presenting photoswitching capacity in various media[2]. In addition, molecular modeling and simulation, including density functional and wavefunction based methods were used to explore the excited states potential energy surface landscape. We realize that with cyclocurcumin, the addition of a carbon-carbon double bond to the core of the natural compound favors the population of the π-π* state, whatever the choice of the solvent, and hence leads to photoisomerization, with fluorescence reduced to only a minor channel comparing with natural derivative[3].

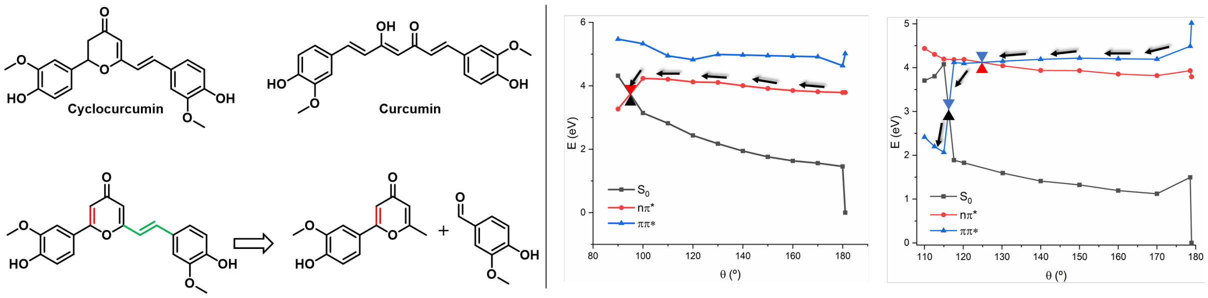

Figure 1. Molecular formula and retrosynthetic design of cyclocurcumin derivatives (left). PES of the rotation scan following n-π* and π-π* states, respectively (right).

In addition, the two-photon absorption (TPA) cross section is also strongly increased compared to the parent compound, paving the way to the use in biologically oriented applications. Apart of that, we are also interested in the interaction between these systems and lipidic membranes as a potential photocontrolled way to destabilize it, which can yield in cellular apoptosis or vesicle drug delivery. Likewise, natural curcumin was studied as a potential photodynamic therapy candidate taking advantage of it larger TPA comparing with other used drugs.

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PO39

Molecular dynamics studies of protein folding under non-enzymatic glycation and oxidative stress conditions.

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Sustained high concentration of free sugars in the organism favors uncontrolled glycation of proteins. The subsequent degradation of the glycation products generates irreversibly modified proteins. Another consequence of high concentration of free sugars is high levels of oxidative stress, which promote protein degradation. From either pathway, chemically modified proteins typically show altered structure, folding equilibria, dynamics and function [1,2].

Molecular dynamics simulations and Markov state models were employed to evaluate how different glycation and degradation products modify the structure, dynamics and folding equilibrium of the Trp-Cage mini protein.

Glycation of Arg16 to carboxymethyl arginine allows native folding structure and core hydrophobic contacts. However, the unfolding kinetics is reduced and the folding kinetics is increased, leading to an over stabilization of the folded state. On the other hand, degradation of Trp6 to N-formylkynurenine dramatically affects the folding thermodynamics and kinetics. The native folded structure is completely lost and the free energy difference between the misfolded and the unfolded states virtually disappears as it becomes similar to the thermal energy.

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DFT Studies on the Metal Ligand Cooperative Effects of Rhodium-NHC-Catalyzed Hydropyridonation of Terminal Alkynes

PO40

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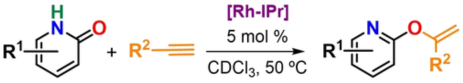
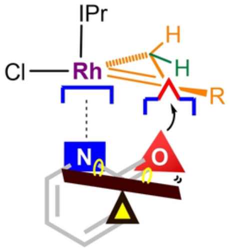
In this work, a detailed theoretical study on the gem-Specific O-Selective hydropyridonation of terminal alkynes catalyzed by Rh N-heterocyclic carbene (NHC) catalyst is presented. In previous works, the Rh(NHC) catalyst was employed for selective alkyne dimerization following C-H oxidative addition, alkyne insertion and reductive elimination steps [1]. More recently, the efficiency of the catalyst was greatly improved by replacement of pyridine by hydroxipyridine, allowing a metal-ligand cooperative mechanism where proton transfer from the alkyne to the base was the rate-limiting step [2]. Surprisingly, the combination of hydroxipyridine and chloride ligands on the Rh(NHC) catalyst does not yield alkyne dimerization but addition of 2-pyridones to the alkyne [3]. Hence, the new catalyst can be used for the development of the synthetic routes to form selectively C-N bonds using the 2-pyridone scaffold.

In this work, a detailed study at the DFT level will be performed to explain the experimental observations. Hence, the presence of hydroxipyridine and chloride ligands favours a proton transfer mechanism to the alkyne and the formation of a metallacyclopropene instead of hydride intermediate. Chemoselectivity control towards the less thermodynamicallyfavoured O-alkenylated products arises from the preferred N- vs. O-coordination of the k1 pyridonato ligand in Rh-IPr systems. Electronic and steric effects of the Rh-NHC catalyst provides an explanation of the preferred reaction mechanism towards gem-Specific O-Selective hydropyridonation of terminal alkynes.





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Automating the decomposition reactions of biofuels: the case of the 2-butanol radical

PO41

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Butanol is an alcohol with similar characteristics to fossil fuels but is less pollutant. It reduces the emission of greenhouse gases and decreases the production of smog when compared to gasoline. It is a bioalcohol that can be obtained from biomass by the acetone-butanol-ethanol (ABE) fermentation process or via a biotechnological route using microorganisms. In particular, 2-butanol is compatible with the current engines and can be obtained from renewable sources.

The decomposition reactions of the 2-butanol radical are key in the study of the combustion process. This radical mainly originates from hydrogen atom abstraction reaction by small radicals (usually H or OH) to the root species.

Starting from the different radical isomers of 2-butanol, we have located several reaction channels for its decomposition. The transition state structures were obtained by AutoMeKin[1]. Specifically, we have found more than 60 channels together with several conformational structures for each of the stationary points.

To compute the rate constants for each of the elementary processes, we have applied the multi-structural canonical variational transition state theory with small-curvature tunneling corrections, as implemented in Pilgrim[2]. In addition, multi-structural torsional anharmonic corrections were evaluated with MsTor[3]. All electronic structure geometry optimizations were performed at the DFT level and corrected by CCSD(T)-F12 single-point calculations.

Finally, branching ratios were estimated employing a kinetic Monte Carlo simulation, a method also implemented in Pilgrim. Our calculations show that the automated search of transition states led to channels not previously described in the literature. The calculated thermal rate constants reflect the importance of incorporating anharmonicity and multiple structures to each of the reaction channels. This study illustrates that the combination of the AutoMeKin + MsTor + Pilgrim codes is a promising tool for studying complex reaction mechanisms.

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Cage-size Effects on the Encapsulation of P_2 by Fullerenes

PO42

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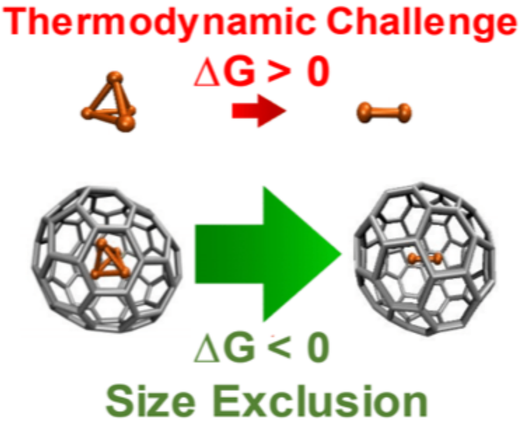
The classic pnictogen dichotomy stands for the great contrast between triply bonding very stable N_2 molecules and its heavier congeners, which appear as dimers or oligomers [1]. A banner example involves phosphorus as it occurs in nature as P_4 [2] instead of P_2 [3]. The synthetic value of the P_2 moiety has brought a number of Lewis base and metal coordination stabilization strategies [4].

Herein, we discuss the unrealized encapsulation alternative using the well-known fullerenes' capability to form endohedral and stabilize otherwise unstable molecules [5]. We chose the most stable fullerene structures from C_n (n = 50, 60, 70, 80, 90, and 100) to computationally study the thermodynamics and the geometrical consequences of encapsulating P_2 inside the fullerene cages. Given the size differences between P_2 and P_4, we show that the fullerenes C_{70} to C_{100} are suitable cages to side exclude P_4 and host only one molecule of P_2 with an intact triple bond. The thermodynamic analysis indicates that the process is favourable, overcoming the dimerization energy. Additionally, we have evaluated the host-guest interaction to explain the origins of their stability using Energy Decomposition Analysis [6].



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Alterations caused by micro-hydration in the electronic structure of 2-aminopurine control its fluorescence

PO43

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2-Aminopurine (2AP) is an isomer of adenine (6AP), which has fluorescent properties in contrast to the latter[1]. Ultrafast electronic excited state deactivation in 6AP make this nucleobase photostable and reduces its fluorescence quantum yield, while 2AP photophysics are markedly different[2]. 2AP fluorescence is pronounced and arises from the hampering of the main deactivation routes compared to adenine, leading to much longer decay times[1]. Thus, interest in 2AP hinges upon its use as a fluorescent probe in DNA by replacement of 6AP sites in the double helix. This replacement has allowed and significantly contributed to achieve time-resolved optical imaging of our genetical material[5,6]. Moreover, 2AP excited state lifetimes show an extraordinary increase[7] moving from the time-resolved ps signals recorded in vacuo to ns or µs timescales in water[1,6,8].

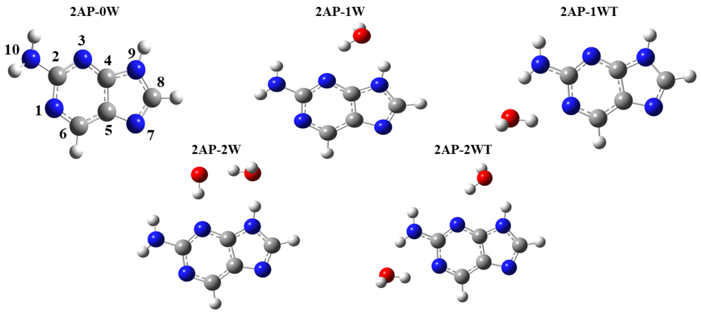

Figure 1. Micro-hydrated 2AP systems studied.

We use extended multistate complete active space second-order perturbation theory (XMS-CASPT2) calculations to include the effects of static and dynamic electron correlation, for each one of the main micro-hydration arrangements available to 2AP (Figure 1). We consider all states regardless of character ($^1n_N\pi^*$ vs $^1\pi\pi^*$) or multiplicity (singlet vs triplet) on an even footing. Our results show 2AP micro-hydration hampers internal conversion by raising the potential energy barrier required to reach the $(^1\pi\pi^*/GS)_{CI}$ conical intersection mediating decay to the ground state, and therefore being responsible for the high fluorescence quantum yield of 2AP in water. Moreover, in those cases where water is near to N_1 and N_{10} in a trans amino position, we observe a significant $^1n_N\pi^*/^1\pi\pi^*$ mixing in the $^1\pi\pi^*$ excited state minimum leading to lower associated oscillator strengths, which result in longer fluorescence lifetimes in agreement with experiment. By comparing with the 6AP isomer in analogous micro-hydration conditions, we observe very similar nuclear distortions which suggest the longer lifetimes in 2AP arise mostly due to electronic effects.

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Fully DFT large-scale pursue of organic cathode materials

PO44

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During the last years a very intense research have been carried out in order to get a new generation of energy storage materials. This would allow the replacement of the traditional batteries, which are based in expensive, rare and polluting inorganic materials. Organic batteries have emerged as a promising alternative due to their unique properties, high energy density (product of the capacity and the working potential), flexibility, processability, sustainability and structural diversity[1]. In this manner, conjugated carbonyl compounds are encouraging candidates for energy storage materials. The highest average potential that can be obtained using carbonyl-based cathode is around 2.8 V(vs. Li+/Li electrode)[2], still far from common inorganic cathode materials (3.5–4 V). In the pursuit of higher energy density, organic materials with high reduction potentials should be still proposed.

Under those circumstances, the contribution of quantum theory and computational science might be crucial to develop organic cathode materials able to improve the ratio cost/efficiency of the current energy storage devices. More specifically, many examples of large-scale computational screenings of databases can be found in the literature. Although it was already successful in other areas[3], this strategy remains as a partially unexplored pathway to follow.

Here we report a fully DFT screening to select all possible cathode materials among the nearly 100 million species available in the PUBCHEM database[4]. As a first step, low time-consuming LDA/STO-3G calculations were carried out to obtain the energy of the LUMO, which is known to correlate well with the first reduction potential[5]. The best performing molecules were chemically classified, allowing the reduction of the final set of successful candidates by removing closely related materials. Practical considerations, such as stability or availability will be also considered in the discussion in order to safe computational efforts. Finally, up to the fourth reduction potential of each of the selected materials was calculated at a B3PW91/aug-cc-pVTZ level of theory over B3PW91/6-31+G(d) optimized structures.

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic through the e-INFRA CZ (ID:90140).

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PO45

Assignment of Oxidation States from Optimally Fragment-Localized Orbitals.

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Oxidation states represent the ionic distribution of charge in a molecule and are significant in tracking redox reactions and understanding chemical bonding. While effective algorithms already exist based on formal Lewis structures, such as the IUPAC's ionic approximation [1-2], as well as using localized orbitals, e.g. Localized Orbitals Bonding Analysis [3], they exhibit differences in challenging cases where effects such as redox non-innocence are at play [4].

In this work we focus on developing a new approach to obtain fragment-localized orbitals, namely oxidation state localized orbitals (OSLO), together with an algorithm for assigning the oxidation state using the OSLOs and an associated fragment orbital localization index (FOLI) [5]. The FOLI evaluation requires fragment populations, and for this purpose we do not only made use of a robust real-space atomic definition, in particular the Topological Fuzzy Voronoi Cells (TFVC) [6], but also introduced a new version of the intrinsic atomic orbital (IAO) scheme in which the IAOs are evaluated using a reference minimal basis formed from on-the-fly superposition of atomic densities (IAO-AutoSAD) in the target basis set and level of theory [5].

The implementation of the OSLO algorithm has been performed in both the Q-Chem and APOST-3D packages and we applied it to a range of challenging cases including high valent metal oxide complexes, redox non-innocent nitrosyl and dithiolate transition metal (TM) systems, a variety of carbene-containing TMs and other examples including the potentially inverted ligand field in $[Cu(CF_3)_4]^-$. The results obtained are generally satisfactory and, in borderline cases, the OSLOs and associated FOLI values provide direct evidence of the emergence of covalent interactions between fragments that nicely complements existing approaches.

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Unraveling the conversion mechanism of LTA$_4$ to LTB$_4$ driven by LTA$_4$H

PO46

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LTA$_4$H is a bifunctional zinc metalloenzyme that converts leukotriene A$_4$ (LTA$_4$) into leukotriene B$_4$ (LTB$_4$), one of the most potent chemotactic agents involved in acute and chronic inflammatory diseases. Through a unique and fascinating mechanism, LTA$_4$H acts as an epoxide hydrolase adding a water molecule to LTA$_4$ in a position several methylene units away from the epoxide moiety in a very stereospecific way.

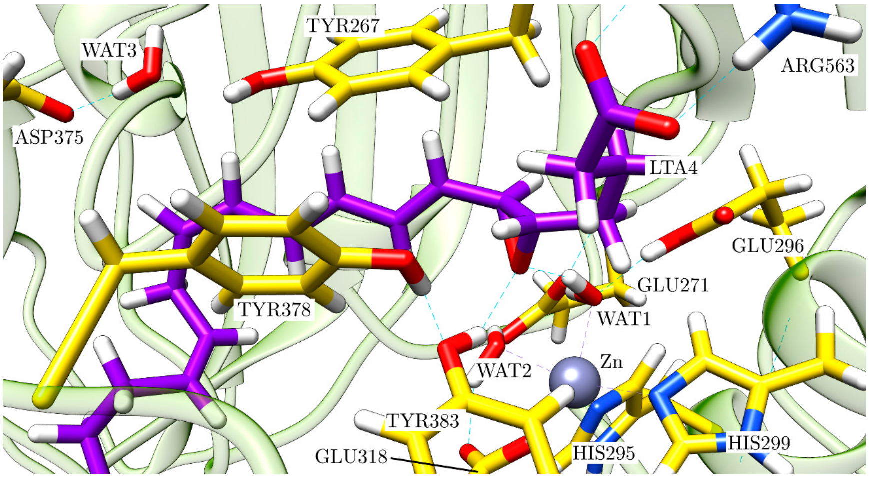

Figure 1. Structure of the reactant of the LTA4:LTA4H system with the most relevant residues labelled

Molecular Dynamics simulations and Quantum Mechanics/Molecular Mechanics calculations have been used to obtain a very detailed molecular picture of the consecutive steps of the conversion. The mechanism takes place in a rather unusual 1,7-nucleophilic substitution following a S$_N$1 mechanism: first the epoxide is opened in such a way that the C$_6$-C$_7$ bond adopts a *cis* (*Z*) conformation and generates a carbocation delocalised over the triene moiety. This generated *cis* conformation exposes the *R* face of C$_{12}$, the extreme methylene unit of the triene to a water molecule, which is activated by a hydrogen bond with ASP375. Then it added as an OH group to the substrate with an *R* configuration [1]. Thus, the *R* stereochemistry of the alcohol group on the C$_{12}$ is determined by the conformation of a bond 5 methylene units away, so both stereochemical features, which are key for the bioactivity of LTB$_4$, appear to be closely related. This unusual relation takes place thanks to non-covalent π-π stacking interactions that occur between the triene and TYR267 and, specially, TYR378. Those TYRs are able to regulate and fix the relative position of the triene. Once again, non-covalent interactions take a fundamental role in the selectivity and reactivity of the enzyme.

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PO47

Multidentate halogen-bond based catalysis: A computational study

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In the field of organocatalysis a green alternative to the typical metal centred catalysis, non-covalent molecular interactions based on halogen bonds (XB) represent a powerful and promising catalytic activation mode. Inspired by the nature of the customary hydrogen bonding, halogen bonding is suggested to be a worthy alternative due to novel features such as directionality[1]. The polarizability of the sigma hole of the XB-donor atom and the electronic effect of the attached organic framework has been explored computationally. The halogen atom (I, Br or Cl) in a symmetrical bidentate organocatalyst was varied and the mechanistic insights as well as the different NCI established upon complexation have been investigated by means of DFT on the Michael addition reaction.

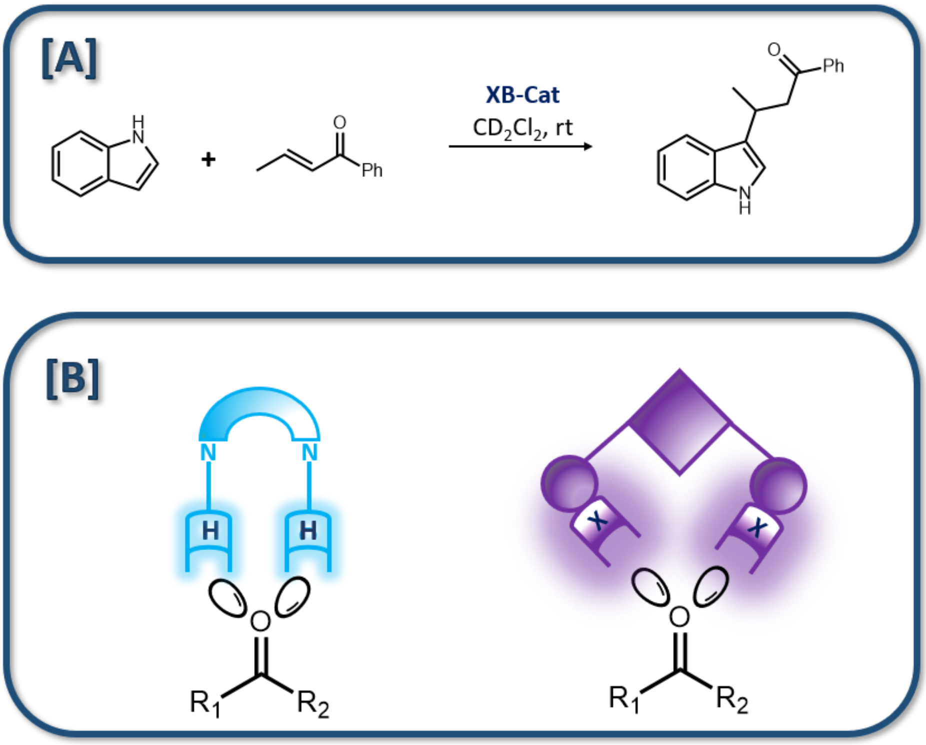

Figure 1. [A] Reaction under study, Michael addition [B] Binding mode hydrogen bonding *vs* halogen bonding

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Physicochemical, Structural and Conformational study of FMN-containing miniSOG

PO48

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In recent experimental studies[1], it has been demonstrated that certain flavins (such as FMN) and flavoproteins (FMN containing proteins such as miniSOG) have the ability to activate Pt(IV) prodrug complexes under hypoxic conditions and in the presence of electron donor species as NADH, to form therapeutically active Pt(II) complexes. Furthermore, selected mutations at the position 103 at the binding pocket and position 50 at outside of miniSOG modulate this catalytic activity[2]. In this work, molecular dynamic simulations (MD) are used in order to analyze the structure of Wild Type (WT) and mutated miniSOG during the photoreduction process, and the role the flavin binding pocket might have in the latter. It is observed that these mutations alter the coordination of the flavin to the flavoprotein, also hindering the entrance channel to the FMN in some cases.

Furthermore, the influence of the flavin coordination to the different miniSOG mutations in the reactivity of the flavin is studied by means of Density Functional Theory (DFT). In particular it is observed that (i) the photoexcitation of the oxidized flavin and (ii) electrophilicity of the excited flavin change with the mutations, unveiling the physicochemical fundamentals of the experimental outcome.

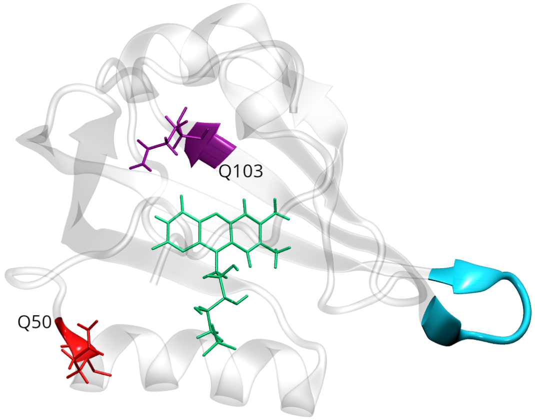

Figure 1. miniSOG's structural model. The backbone of miniSOG is shown in silver, FMN in green, and the amino acids in the mutation positions in red (Q50) and purple (Q103). Moreover, a mobile loop's residues are shown in cyan.

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Dicyanomethylene-Based Quinoidal π-systems: Theoretical Prediction of the Diradical Character

PO49

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Diradicals have arouse the scientific interest due to their unique electrical, optical and magnetic properties and their potential for numerous advanced technological applications[1]. Owing to their stability remains the major obstacle, the object of many experimental and theoretical studies is the design and synthesis of stable ground-state open-shell molecules. A very efficient strategy to stabilize the diradical species is the insertion of terminal electron-withdrawing dicyanomethylene (DCM) groups in a π-conjugated skeleton. An interesting family of π-conjugated systems with diradical character is formed by quinoidal oligothiophenes (QTs) with terminal DCM groups[2]. These QTs behave as organic semiconductors and they have been successfully implemented as active components in organic field-effect transistors (OFETs).

From a theoretical standpoint, the description and characterization of the electronic structure of organic diradicals (or polyradicals) is a difficult task that generally requires the use of accurate but computationally-demanding multiconfigurational methods due to their unpaired electrons. A new multiconfigurational approach to treat medium-large diradical organic systems with an affordable computational cost is the Density Matrix Renormalization Group Pair-Density Functional Theory (DMRG-PDFT)[3]. Herein, a series of conjugated quinoidal π-systems that combine thiophene and benzene rings with end-capping dicyanomethylene groups (Figure 1) is evaluated by means of DMRG-PDFT method to predict accurate singlet-triplet energy gaps, which is important for the design of new diradical compounds.

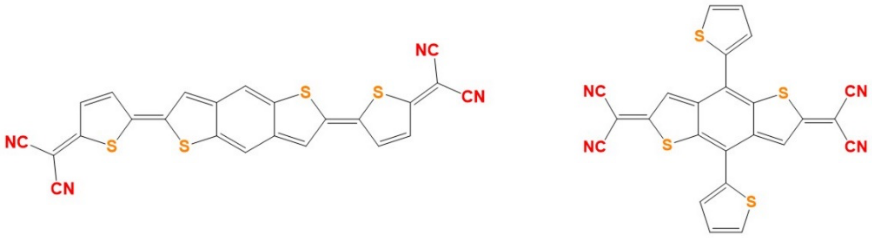

Figure 1. Chemical structures of the π-conjugated systems studied.

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Theoretical study of triazole-containing pesticides and their protonated forms

PO50

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We present a systematic study of the structure and chemical properties of a family of pesticides, in particular several DeMethylation Inhibitors, containing a triazole ring in their structure. The compounds selected are: Azaconazole, difenoconazole, diniconazole, fenbuconazole, metconazole, penconazole, tebuconazole, triadimefon, triadimenole and triticonazole and their protonated forms.

We have use CREST and CENSO programmes [1] to determine in a systematic way the most stable conformations for both the neutral and protonated forms, and we have considered the molecules in gas phase and water and octanol environments. Final properties are obtained at the B3LYP-D3/6-311+G(d,p) level.

Our results allow us to better understand chemical properties that can be related with the environmental impact of these pesticides[2]. We have also identified the most stable protonation sites inside each molecule and discuss the different effects observed: proton transfer mechanism, formation of internal bonds or lose of aromaticity.

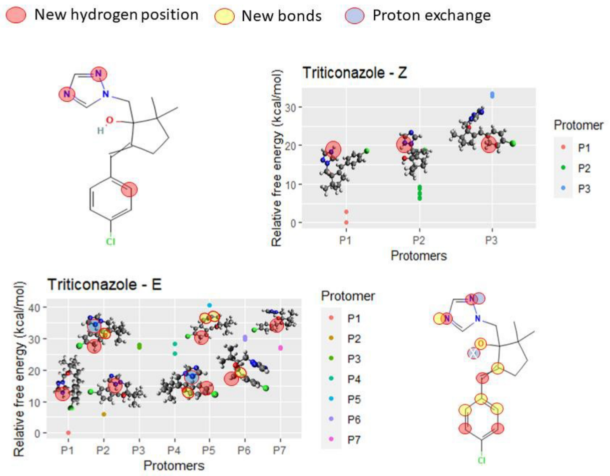

Figure 1. Relative free energies of the most stable protomers of two different isomers of Triticonazole pesticide.

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Non-covalent interactions and enthalpy-entropy compensation on regioselective iridium-catalyzed borylation of aromatic amides

PO51

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Selective functionalization of aromatic C-H bonds is a paramount synthetic challenge as it requires exclusive targeting of the desired bond amidst others with similar steric and/or electronic features [1]. Among the possible modifications, borylation is attractive because of the wide range of reactivities accessible to the organoboron products [2]. Benzamides are interesting targets for selective C-H functionalization as they are the core of a variety of compounds with biological or agrochemical properties (Figure 1) [3]. In this contribution, we present a new synthetic approach to the borylation of aromatic amides with a 5-substituted bipyridine iridium complex that allows complete regioselectivity towards the sterically hindered *ortho* position – the most challenging for this type of reaction so far – along with a detailed computational study that uncovers the reaction mechanism and the origin of regioselectivity.

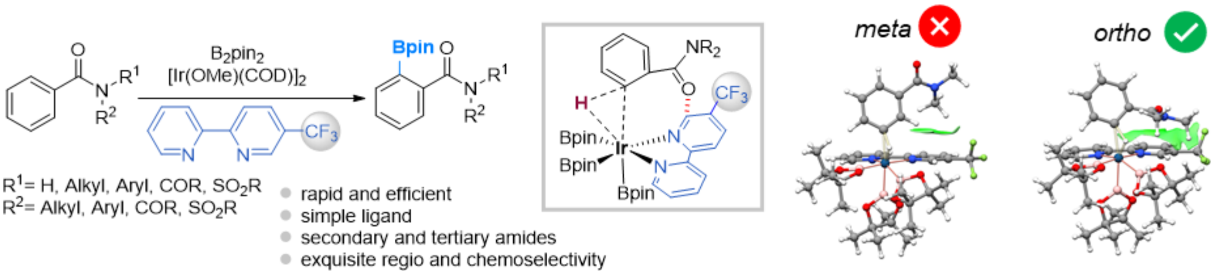

Figure 1. Secondary and tertiary aromatic amides ortho-borylation strategy with indication of the key non-covalent interaction for determining regioselectivity.

We ascribe the *ortho* selectivity to unconventional attractive outer-sphere non-covalent interactions between the amide group of the substrate and the substituted bipyridine, which overcome the larger expected steric hindrance at this position. We analyze the extent of these non-polar interactions at the TS of the rate limiting oxidative addition step for the *ortho* and *meta* pathways, revealing a larger interaction surface for the preferred *ortho* attack. Analysis of the computed relative activation free energies for differently substituted bipyridines shows a novel enthalpy-entropy compensation phenomenon in both the *ortho* and *meta* pathways. Kinetic and isotopic labelling studies corroborate the proposed mechanism and confirm that the observed regioselectivity is the result of a delicate interplay between enthalpic and entropic effects in the transition states.

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Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules

PO52

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Ever since the first models of organic solar cells were proposed more than 40 years ago, the search for new materials with the ability to produce a charge separation, necessary for photovoltaic applications, has kept drawing the scientific community's attention. Organic photovoltaic devices usually achieve charge photogeneration by using charge transfer complexes, which act as an intermediate step between exciton dissociation and charge extraction.

In order to capture the real time evolution of such electronic process, which takes place in the time range between tens of attoseconds to a few femtoseconds, a sub-femtosecond time resolution is required. Therefore, in this work we propose the use of a pump-probe scheme employing ultrafast laser sources to track the charge transfer process using as target a typical donnor-acceptor molecule in the gas phase. In particular, we investigate the ultrafast dynamics following the excitation of para-nitroaniline (PNA), which has been extensively studied in a solvent, both theoretically [1-3] and experimentally [1, 4, 5, 6], while scarcer works have been performed in gas phase to date.

We thus propose the use of a pump-probe scheme, using a few-fs UV pulse to excite the target. The ensuying electron-nuclear dynamics will be later probed by a time-delayed attosecond XUV pulse which will ionize the molecule. The time-varying ionization yields are expected to capture the complex dynamics triggered in the excited molecule.

In a first approach, using the fixed nuclei approximation, we retrieve the time evolution of the excited wave packet by analyzing the electron density variation, computed through a transition density matrix formalism. The imprint of these dynamics is later retrieved into the cation with the time-delayed absorption of the probe pulse.

We later explored how these electron dynamics evolved when coupled with the nuclear degrees of freedom, when non-adiabatic couplings come into play. The coupled electron-nuclear motion is described by means of a surface-hopping method, i.e. within a semi-classical picture. In short, the time-dependent wave function is retrieved at each time step, computing the electronic structure on-the-fly by means of a quantum mechanical description, while the nuclear dynamics follows the classical equations of motion.

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PO53

Experimental and Theoretical Analysis of $Ag/AgVO_3/Ag_3VO_4$ composite

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Silver orthovanadate, Ag_3VO_4, is a p-type semiconductor and presents three reversible polymorphs[1,2]. Its peculiar physicochemical properties of this class of materials, the vanadates, have attracted important attention for practical applications such as electrochemical cells, bactericidal agents, and photocatalysis [3-5]. In this work, we have combined the experimental and theoretical techniques in order to evaluate the formation of the $Ag/AgVO_3/Ag_3VO_4$ composite and to confirm the presence of the three materials.

Ag_3VO_4 powder was prepared by microwave-assisted hydrothermal method route varying the synthesis time at 120 °C. Then, from this powder, the composite has been synthesized via femtosecond pulsed laser irradiation so whose laser emitted pulses with a temporal width of 150 fs (FWHM - full width at half maximum), with a central wavelength of 775 nm at a repetition rate of 1 kHz and energy per pulse of up to 400 µJ. The theoretical calculations were made with CRYSTAL program [6], applying DFT with B3LYP and all-electron basis sets. After the optimization of α-Ag_3VO_4 and β-$AgVO_3$, the electronic properties, the frequencies, and Raman spectra were obtained.

The initial analysis of X-ray diffraction and the Raman spectrum showed the formation of Ag and $AgVO_3$ phases with the presence of Ag_3VO_4 in the system. The morphology of the particles does not show significant changes in their shape, size, and level of agglomeration in relation to the original single-phase Ag_3VO_4 particles. The structural and electronic properties of the optimized theoretical structures of Ag_3VO_4 and $AgVO_3$ are in good agreement with the experimental data. In the progress, The active modes, as well as the theoretical Raman spectra obtained, will be compared with the experimental ones. These analyses will help to understand not only the formation of the composite $Ag/AgVO_3/Ag_3VO_4$, but also the influence of each material on its final properties.

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Spin-crossover complexes in interaction with the substrate

PO54

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Iron (II) spin crossover (SCO) complexes belong to the family of bistable molecules, in which the ligand field around the Fe ion influences the electron configuration in such a way that the molecule has two different spin states, low spin (LS) and high spin (HS). The spin state can be manipulated by external stimuli such as a variation in light, temperature, pressure, electronic field, or magnetic field [1]. The use of spin crossover (SCO) complexes in spintronic devices would need connecting a single molecule with surfaces.

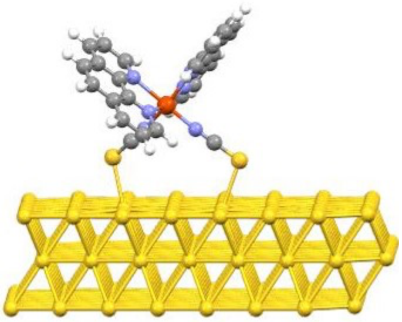

Figure 1. The complex on the surface of Au (1 1 1).

In this work, we show an overview on the spin crossover behavior of $Fe(phen)_2(NCS)_2$ complex adsorbed on Au (111) and Cu (111) surfaces from periodic density functional theory (DFT) calculations [2]. The complex has been deposited on Au (111) and Cu (111) with the −NCS ligands pointing to the surface, and several adsorption sites have been explored (Figure 1).

In the LS state, the sulfur atoms are on top positions on both surfaces. On the other hand, in the HS state, iron atoms are at fcc position on Au, and on hcp positions on Cu surface. Adsorption energies are larger for the complex adsorbed on Cu (111), what means a larger interaction with this metal surface. Finally, we have analyzed the spin-polarized density of states (DOS) projected on Fe, NCS groups, and phen groups of the Fe phen free complex and we have simulated STM images to visualize the molecules on the surfaces.

Our results show that the HS-LS energy difference of isolated complex is 32.3 kJ/mol. This value increases to 45.6 and 51.6 kJ/mol when the complex is adsorbed on Au (111) and Cu (111) respectively. This result is in line with previous experimental works, which show a suppression of SCO properties once $Fe(phen)_2(NCS)_2$ is adsorbed on metallic surfaces [3].

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New Ideas for Understanding the Structure and Magnetism in AgF_2: Prediction of Ferroelasticity

PO55

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Since the discovery of high-temperature (high-T_C) superconductivity in 1911, many efforts have been made to observe superconducting states at increasing temperatures. In the 1970s, superconductivity was found in some Nb-based metallic systems at temperatures above 20 K. However, the breakthrough came in 1986 with the discovery of superconductivity in copper oxides at about 92 K. In these compounds, high-T_C superconductivity seems to be driven by three main ingredients: (1) layered crystal structure, (2) the presence of elongated CuO_6 complexes and (3) strong antiferromagnetic (AFM) coupling in the Cu layer [1].

Superconductivity in cuprates arises from the strong interaction among d^9 electrons, localized on the metal planes. Along this line, in the last two decades superconductivity has been sought in materials containing Ag^{2+} ions, whose electronic configuration is $4d^9$ [2]. In particular, it has been proposed that the fluoroargentate AgF_2 can reach a superconducting state, due to the apparent similarities with the high-T_C superconductor La_2CuO_4, namely, layered structure and a charge-transfer insulating state with intraplanar AFM order [3]. In this work, we have focused on this fluoroargentate, performing a first principles analysis of its crystalline and magnetic structure in order to understand the underlying relationship between them.

To determine the origin of the AgF_2 structure, its *parent high-symmetry phase* has been optimized. Our results show that this parent phase is cubic and thus lacks a layered structure. Furthermore, in the parent phase Ag^{2+} ions are placed in trigonal lattice sites (local D_{3d} symmetry) and therefore the AFM order is geometrically frustrated. Under these conditions, the ground state of the sixfold coordinated AgF_6 complexes is orbitally twofold degenerate, allowing the existence of a Jahn-Teller (JT) effect, which lifts the degeneracy and lowers the energy. Cooperative JT effect leads to the observed orthorhombic crystal structure and the AFM coupling in the layers, as magnetic frustration is broken with deformation. By contrast to La_2CuO_4, where the origin of layers is chemical, in AgF_2 JT distortion causes the softening of two Ag-F bonds, but this effect is far from destroying the interlayer interaction [4]. On the other hand, one of the main consequences of cooperative JT effect is ferroelasticity, since the magnetic order of AgF_2 is controlled by the distortion. This fact is tightly related with the existence of multiple equivalent minima in the potential energy surface of a cubic system.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/ 10.13039/501100011033 and by "ERDF A way of making Europe", by the European Union.

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Exploring the conformational space within phase transfer catalysts: computational methods benchmarking

PO56

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In this study, a complete exploration of the conformational space of different type of phase transfer catalysts by means of computational methods benchmarking is presented. For this particular research work, only the most applied conformational analysis software (Balloon [1], RDKIT [2], wSterimol [3] and CREST [4]) have been chosen to characterise different Cinchona alkaloid-based phase transfer catalysts. This particular benchmarking study aims to rigorously compare the performance of different conformational methods, determining the strengths of each method and providing recommendations regarding suitable choices of methods for an analysis.

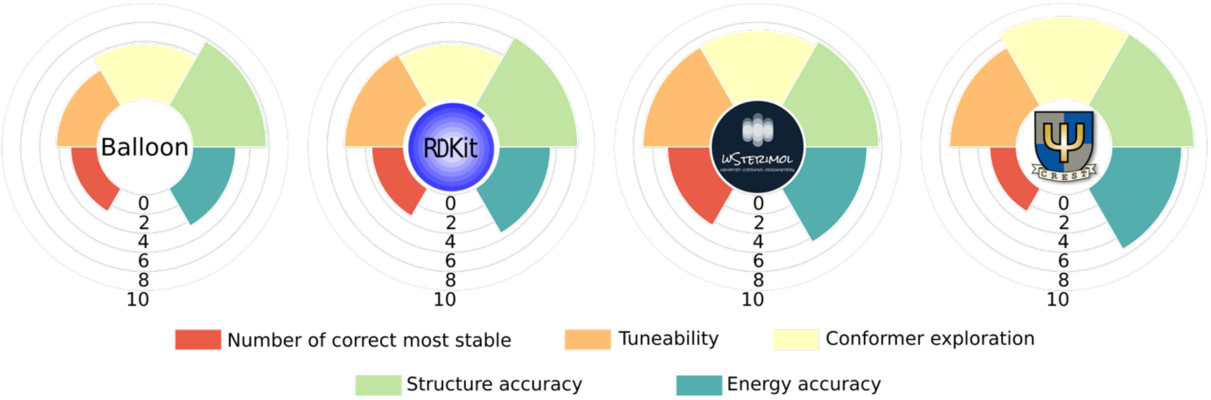

Figure 1. Grades obtained by each program using 5 different criteria

Five different criteria were analysed and quantified to determine the efficiency of each program. Being these criteria: 1) the number of catalyst in which the most stable conformer predicted by the software under study and the most stable conformer at the DFT level coincides, 2) the number of features that can be modified in each program to match the required conditions for a certain system, 3) how many of the clusters that were found were explored by each program, 4) the accuracy of a conformer predicted by each program compared with the DFT optimized structure (using RMSD and re-mapped from 0 to 10) and 5) the accuracy between the predicted energy of a conformer compared with the energy at the DFT level (using RMSE and re-mapped from 0 to 10).

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PO57

What's behind spectral shapes?

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Electronic spectroscopies stand as ubiquitous techniques to characterize photoactive systems. The position and shape of the bands bring detailed insight into the photoactive species and their interaction with the environment, which can only be unveiled resorting to models able to account for most of the physics involved.

In this contribution, we shall examine some of the main factors responsible for broadening spectral bands, including molecular vibrations of the dye, fluctuations of the environment or potential couplings among the electronic states involved. We will discuss effective ways to account for them, eventually introducing a computational protocol to simulate spectral band shapes for emission and absorption using no phenomenological parameters. This method, named Adiabatic MD generalized Vertical Hessian (AdMD|gVH), has been recently introduced in our group [1] and relies on a mixed quantum-classical approach. Namely, the stiff degrees of freedom of the pigment are treated quantum-mechanically, adopting harmonics potentials. At the same time, flexible modes and the fluctuation of the environment are described by a classical sampling conducted with Molecular Dynamics (MD), adopting accurate Quantum-Mechanically derived Force Fields for ground and excited states.

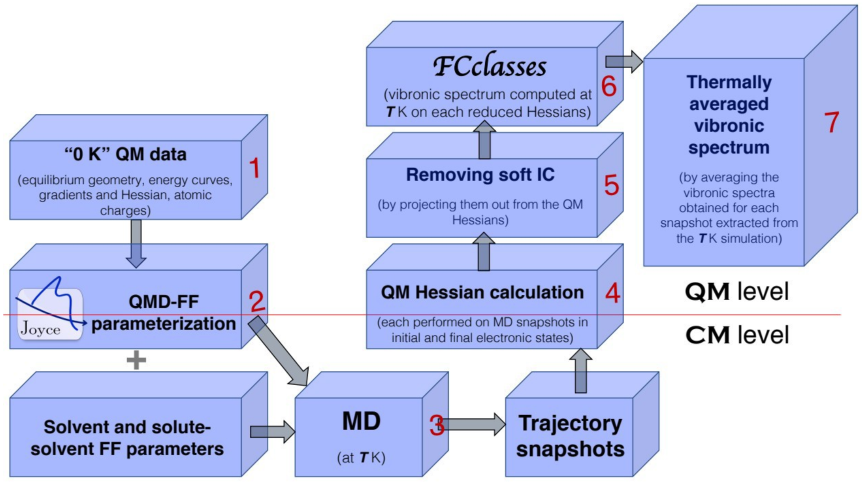

Figure 1. schematic representation of the different steps involved in the AdMD|gVH method.

We will show successful applications of the method to systems comprising flexible dyes within homogeneous solvents [2], which enables its extension to simulate complex biological environments, such as photoactive proteins. Moreover, it has also been adapted to deal with systems where non-adiabatic effects are explicitly accounted for through multi-state Quantum Dynamics propagations [3], thus opening the door to complex multichromophoric systems.

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Exciton dynamics in a N-heterotriangulene based supramolecular polymer: Do charge transfer states matter?

PO58

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Energy transport is one of the key processes for the efficiency of optoelectronic devices based on molecular materials [1]. This process can be explained as the transition from an initial state where an excitation is localized in one molecule to a final state where the excitation resides in the other molecule. Usually, only the Columbic component of the coupling between Frenkel-type states is generally computed, neglecting short-range interactions and contributions from other states as charge-transfer (CT) states. However, in the last years, has been demonstrated that going beyond the Coulombic coupling is essential for a correct description of the properties of molecular assemblies [2].

In this contribution, we present how charge-transfer states can play a key role in the exciton dynamics through a simple linear vibronic coupling model Hamiltonian parametrized from DFT calculations. Likewise, we will show how these CT states can be tuned by the molecular environment; in particular, by the self-assembly of a supramolecular polymer that gives rise to an increasing dipole moment with the length and its impact on the final exciton diffusion lengths. This situation may occur in systems like N-Heterotriangulenes, which have been reported to be excellent molecular systems for an efficient exciton transport [3].

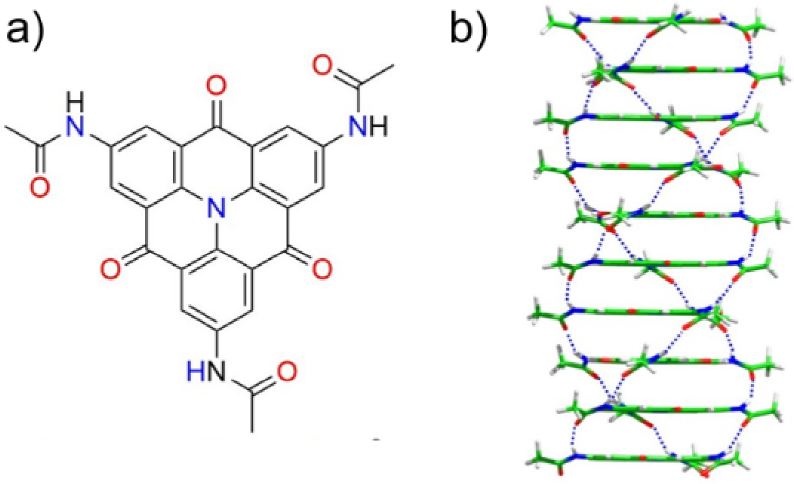

Figure 1. Chemical structure of the N-Heterotriangulene. b) Representation of an helicoidal supramolecular polymer of N-Heterotriangulene

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Bromine intercalation in carbon nanotubes: structure, stability and properties

PO59

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Substituting the copper wire currently used for Electric power transmission with ultra efficient and lightweight new materials would make long-distance transmission more economical which in turn could allow for the incorporation of more renewable sources to the energy mix. In this regard, carbon nanotubes (CNTs) as highly aligned fibres have shown their exceptionally high charge mobility and tensile mechanical properties in macroscopic structures[1], which makes them interesting candidates for power transmission. Moreover, it has been shown that the different compounds within the nanotubes can act as dopant agents and modify their structure[2]. The present work uses Density Functional Theory (DFT) to study the structure, stability and electric properties of ultra-aligned fibres of single and double-walled CNTs (SWCNTs and DWCNTs, respectively) intercalated with bromine, an electron acceptor and air-stable dopant. Our DFT calculations show the intercalation of bromine between the nanotubes is a thermodynamically favored process. Moreover, the simulations predict the arrangement of the Br atoms in linear triads, that can be identified with the the tribromide anion. Finally, our calculations predict the removing of electrons from the carbon nanotube by the bromine, which constitutes *p-type* doping and reproduces the available experimental data as well as previous studies on iodine intercalation[2].

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A systematic QM/MM study for predicting ^{31}P NMR chemical shifts for nucleotides in solution and protein environment

PO60

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NMR spectroscopy is a powerful tool to obtain rich structural information on extended biological systems and protein dynamics. In order to allow for reliable assignments of experimental spectra, theoretical calculations are often crucial. However, the computation of chemical shifts is very sensitive with regards to structural changes and heavily requires to account for ensemble averages. Therefore, careful selection of representative input structures is essential. With a nuclear spin of 1⁄2 and 100% natural isotopic abundance, ^{31}P is an easily observable NMR nucleus. Because of its presence in nucleic acids and other biological systems, quantum-chemical computations of ^{31}P NMR shielding tensors have proven to be of major importance. As an example of a biologically relevant system is the p97 ATPase, where point mutations lead to degenerative diseases in humans. By computing high quality ^{31}P NMR chemical shifts inside the binding pocket of p97 ATPase, as well as for ADP and ATP nucleotides in solution, we aim to make a relevant contribution for understanding the mechanochemical cycle[1] of the protein.

Our methodology is based on MM-MD sampling, followed by QM/MM calculations of NMR chemical shifts.[2,3] To account for conformational diversity and different interactions with the solvent, we compute the NMR shieldings as averages over the MM trajectory. Evenly spaced snapshots were extracted from the resulting trajectories and QM/MM NMR calculations were carried out at the B97-2/pcSseg-2[4,5] level of theory.

The quantum-chemically computed shieldings form broad distributions due to the structural ensemble diversity, however, due to deficiencies in the underlying MM structures, reliable assignments and links to the experiment are not possible. An intermediate step of refining the nucleotide geometries by QM/MM optimization before the NMR shift calculations leads to reasonable agreement between computation and measurement, and is therefore crucial. We applied the outlined protocol to p97 and carried out calculations inside the binding pocket. The first results show similar trends to what we have seen in solution and our results are in good agreement with the experimentally measured values.

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Influence of Zn(II) cations in the conformational dynamics of amyloid-β from multiscale molecular modelling and quantum mechanics calculations

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Amyloid fibrils are stable forms of misfolded proteins associated with numerous neurodegenerative diseases[1]. Among these, Alzheimer's disease may be the most prevalent, with over 55 million dementia cases reported by the World Health Organization in 2021[2]. The molecular origin of Alzheimer's is linked to amyloid fibril formation by misfolded Aβ-peptide (Aβ). These fibrils form aggregates that are stabilized by the presence of Zn(II) cations[3]. Nevertheless, the specific interactions governing Aβ-Zn(II) coordination are still largely unknown. Many possible Aβ-Zn(II) structures have been proposed experimentally (see figure 1) where Zn(II) adopts different coordinations [4]. In order to understand the intricate Aβ-Zn(II) interactions and conformational dynamics of Aβ, it is essential to obtain a good representation of the metal centres Aβ-Zn(II) system display. Standard Zn(II) models employed by classical force fields, i.e., nonbonded models, tend to fail[5]. These models heavily favour octahedral coordination although it has been reported that tetrahedral coordination is favoured in protein environment[6]. In this work, we will employ bonded models to accurately capture Aβ-Zn(II) coordination and extract precise conformational dynamics of the systems.

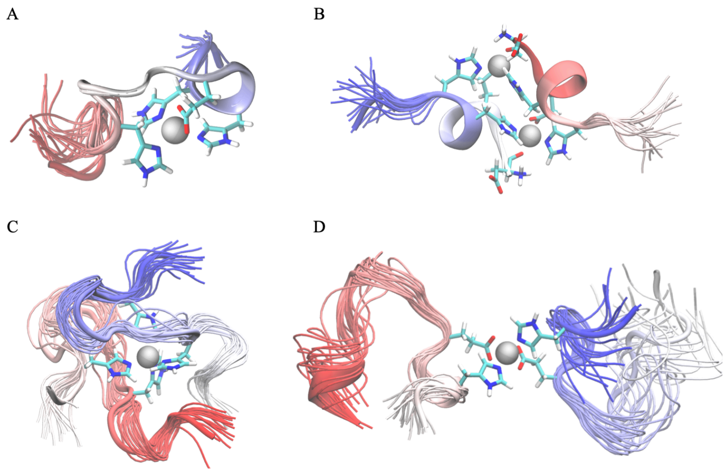

Figure 1. Various Aβ-Zn(II) experimental structures. PDB ID: 1ZE9 (A), 5LFY (B), 2LI9 (C) and 2MGT (D).

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A Quantum Chemical and Microkinetic Study to Combine Theory and Experiment in Catalysis

PO62

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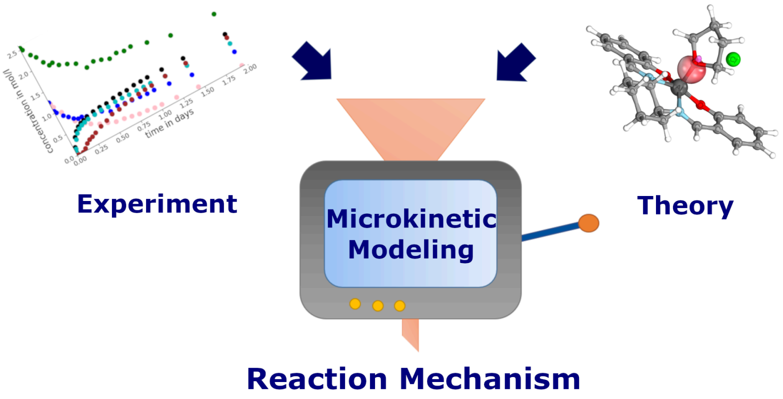
In our work[1], we combined microkinetic modelling to extract reaction barriers from experimental kinetics data and quantum chemical calculations to investigate the hydroboration of acetophenone with a highly active cooperative Lewis acid-ammonium salt catalyst. We have shown that such an approach allows combining theory and experiment, revealing detailed insight into the elementary steps of the reaction mechanism. We found that the counterion of the ammonium salt of the catalyst facilitates the hydride transfer step of the cycle. Chloride replacing iodide speeds up the main reaction but simultaneously has the same effect on a side reaction that consumes the product. With this mechanism we gained consistent free enthalpy barriers for the quantum chemical and kinetic model. Further, a microkinetic sensitivity analysis was used to determine the rate-limiting steps to discuss the states that are relevant for enantioselectivity.



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PO63

Time-optimal quantum driving in a time-dependent drift Hamiltonian

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Time-efficient control schemes for manipulating quantum systems are of great importance in quantum technologies, where external forces from the environment rapidly degrade the quality of states over time[1]. We derive an approach to time-optimal control that circumvents the boundary-value problem that plagues the quantum brachistochrone equation[2] at the expense of unlocking the form of the control Hamiltonian. In this setting, a coupled system of equations, one for the control Hamiltonian and another one for the duration of the protocol, realize a `no prior-guess' approach to quantum control theory. As an example, we show how external time-dependent forces, in the form of a Landau-Zener type Hamiltonian, can be maneuvered to speed-up a given state transformation[3,4] (see Fig. 1) without implying significant deviations from the adiabatic path (see Fig. 2). These results have implications in the field of quantum information processing by providing a scheme to manage background interactions.

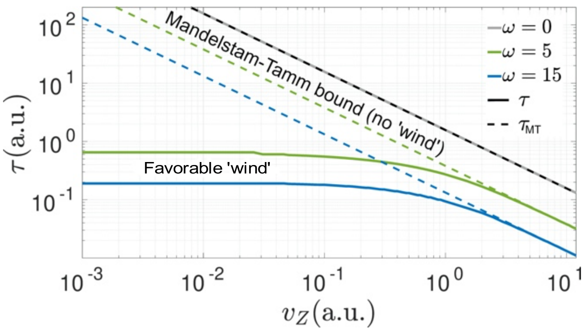

Figure 1. Time of the evolution as a function of the energy disposal of the control.

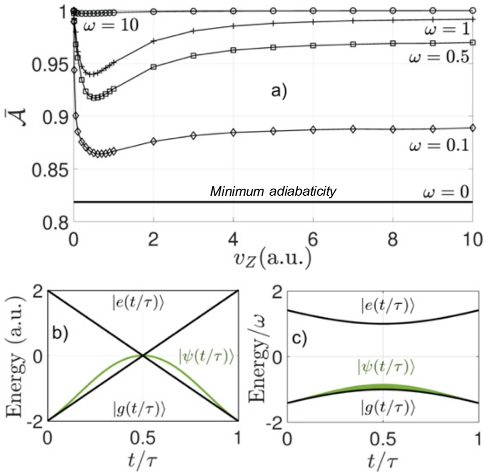

Figure 2. Mean adiabaticity of the evolution.

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Chemistry in Confined Spaces

PO64

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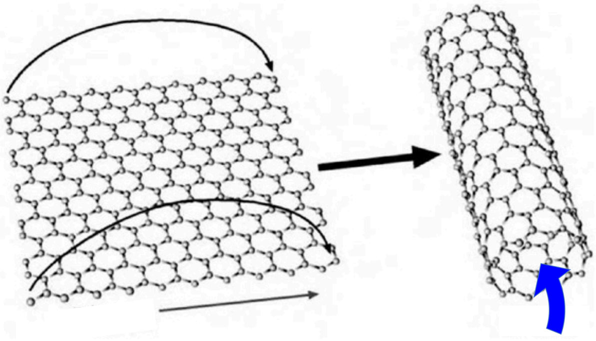
Spatial and chemical confinement can have a dramatic influence on the kinetics and thermodynamics of certain chemical reactions. In fact, the presence of a close molecular environment might result in inhibition or catalysis of reactions by changing the relative stability of the chemical reactive species or even by modifying the reaction mechanism.

We have analysed the behaviour of the prototype Menshutkin S_N2 type of reaction between ammonia and methyl chloride when it occurs in the interior of carbon nanotubes.[1] The main goal was to perform a systematic study to assess the effect of several factors, namely the diameter, chirality and B/N doping of carbon nanotubes, on the features of this specific reaction.



$$NH_{3\,(g)} + CH_3Cl_{(g)} \rightarrow CH_3NH_3^+{}_{(g)} + Cl^-{}_{(g)}$$

The theoretical predictions, obtained at the M06-2X/6-31++G(d,p)/3-21G level of Density Functional Theory, have shown that pristine carbon nanotubes are able to lower considerably the activation energy when compared to the gas phase. Moreover, the magnitude of the effect depends on the diameter of the nanotube and on its chirality, e.g. armchair, zigzag or chiral. For example, inside the chiral (6,4) nanotube, which has a diameter of 6.8 Å, the energy barrier of the reaction decreases 17.5 kcal.mol^{-1} as compared to the gas phase.[2] When the diameter of the nanotubes increases, regardless its chirality, the values converge to 28 kcal.mol^{-1} which corresponds to the reaction occurring over the surface of a graphene sheet.

By using B and N atoms as dopants, we were able to alter the electronic structure of the carbon nanotubes and graphene sheets, which represents an extra degree of freedom to control the chemical reaction. As an illustrative example, this Menshutkin reaction becomes even exothermic inside the doped (9,0) zigzag carbon nanotube with BNC4 stoichiometry, and its energy barrier decreased 10 kcal.mol^{-1} when compared with the corresponding pristine nanotube.

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FCT- Portuguese Foundation for Science and Technology: PTDC/QUI-QFI/29914/2017.

PO65

Oxidation of alkyl glyceryl monoethers catalysed by glycerol dehydrogenase

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Researchers are interested in finding new and inexpensive techniques to metabolize excess glycerol or derivatives that come from the production of biodiesel. One of the enzymes being investigated for this purpose is glycerol dehydrogenase, which catalyzes the selective oxidation of glycerol to dihydroxyketone (DHA)[1] with the consequent reduction of the cofactor NAD^+ to NADH.

In this work, a glycerol dehydrogenase from Bacillus stearothermophilus (BsGlyDH) has been engineered and immobilised to accept a battery of alkyl/aryl glyceryl monoethers and catalyse their enantioselective oxidation to yield the corresponding 3-alkoxy/aryloxy-1-hydroxyacetones. QM/MM computational studies decipher the key role of D123 in the oxidation catalytic mechanism, and reveal that this enzyme is highly enantioselective towards S-isomers. Through structure-guided site-selective mutagenesis, we find that the mutation L252A sculpts the active site to accommodate a productive configuration of 3-monoalkyl glycerols. This mutation enhances the k_{cat} 163-fold towards 3-ethoxypropan-1,2-diol, resulting in a specific activity similar to the one found for the wild-type towards glycerol [2]. Other mutations such as L252C and L252S are being also studied.

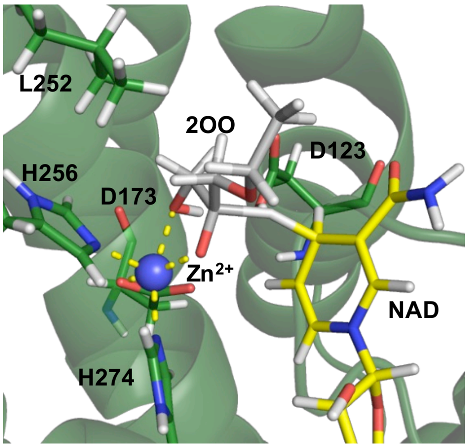

Figure 1. Transition state structure for the hydride transfer from 3-ethoxypropan-1,2-diol to NAD^+ in the wild-type.

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Computations on a semiconducting iodine-doped perylene-based Metal-Organic Framework

PO66

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Metal-organic frameworks (MOFs) are crystalline porous materials built from organic ligands and metallic nodes, which have experimented exponential scientific interest in the last decade due to their extraordinary chemical and structural versatility [1]. In addition to their exploitation in classical applications such as gas separation/storage and catalysis, electrically conductive MOFs have appeared in the recent years as promising materials for next-generation applications in the fields of optoelectronics, energy storage and conversion, among others [2,3]. One of the most common strategies employed in the design of conductive MOFs consist in the use of electroactive organic ligands and their partial oxidation/reduction to increase charge carrier concentration [4]. Most perylene-based MOFs have been studied towards gas sorption and sensing applications due to the remarkable luminescence properties of perylene [5]. However, despite being reported as the first molecular conductors [3], perylene units have been scarcely considered as building blocks for conductive MOFs.

Herein, we present a theoretical study on the electronic, conducting, and optical properties of a perylene-based MOF (**Per-MOF**) (Figure 1), formed by a herringbone packing of 3,4,9,10-perylenetetracarboxylate (PTC) ligands with potassium ions. Encouraged by the experimental evidence, DFT-level calculations were performed on the undoped and I_2-doped **Per-MOF** to shed light on the conductivity enhancement exhibited by the material upon iodine inclusion. This increase in the charge transport properties upon I_2-doping is rationalized by the spontaneous formation of PTC radical cation, which results from the oxidation of the perylene motif by I_2 and leads to the formation of I_3^- species. The charge transport in the semiconducting I_2-doped **Per-MOF** is described in terms of a through-space hopping mechanism along the herringbone PTC packing, where the communication between perylene units is boosted by the electronic participation of I_2/I_3^-.

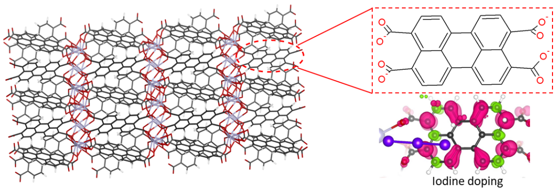

Figure 1. Herringbone arrangement of the PTC linkers (left), PTC ligand (upper right) and spin density after iodine doping (lower right). Grey, red, violet, and purple colours represent carbon, oxygen, potassium, and iodine atoms, respectively.

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DFT Approximations for the Description of $YSr_2Cu_2FeO_{7+\delta}$ ($0< \delta <1$) oxides: performance of the GGA, GGA+U, SCAN and SCAN+U

PO67

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Nowadays, electronic-structure computational calculations based on the density functional theory (DFT) are extensively applied to successfully predict and design materials with particular properties. However, the overestimation of electron delocalization and metallic character is a known failure of DFT methods for systems with localized and strongly interacting *d* and *f*-electrons. This is the case of numerous functional oxides based on partially filled 3*d* transition metal ions, such as the perovskite-type ABO_3 (B=transition metal) compounds. The investigation of perovskites and related oxides was, until recently, constricted by the development of exchange-correlation (XC) functionals able to describe strongly correlated electronic systems. The DFT + U approach [1] and the development of the strongly constrained and appropriately normed (SCAN) meta-GGA functionals [2] have emerged as a fair solution, that allows shedding light on some interesting phenomena observed in these kinds of systems e.g., insulating to metallic transitions [3] or the effects of hole and electron doping [4]. In addition, it has been demonstrated that the introduction of a Hubbard term in the SCAN approach can significantly improve the reproduction of ground-state properties in binary 3*d* transition metals oxides [5, 6].

In this work, we have chosen the complex perovskite family $YSr_2Cu_2FeO_{7+\delta}$ ($0< \delta <1$) as a case study to assess the performance of four DFT approximations i.e., GGA, SCAN, GGA + U, and SCAN + U. In the tittle family of compounds, the evolution from the metallic superconducting phase (δ~1) to the antiferromagnetic insulating phase (δ~0) truly constitute a challenge for DFT approximations. Moreover, the treatment of two different transition metals (Fe and Cu) within the DFT + U and SCAN + U approaches entails undoubtedly a major complexity.

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PO68

Understanding the acid-base behavior of disiloxane

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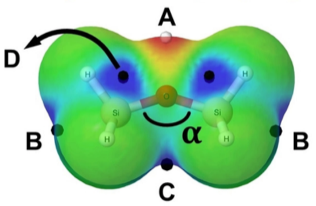
Disiloxane, the simplest silicone possible, is a paradigmatic system often used as a model for more complex systems containing a Si-O-Si moiety. It is well known that this molecule is less basic than the corresponding carbon counterpart, dimethyl ether, although reported results indicating that the oxygen atom in Si-O-Si linkages is more negatively charged than in analogous C-O-C systems seem to be in contradiction with this behavior [1]. Even more, oxygen becomes more negative at larger Si-O-Si angles [2,3], although the observations indicate that smaller angles lead to a more basic behavior. This could mean that electrostatic forces might not be enough to explain the non covalent interactions taking place when disiloxane acts as a Lewis base.



MEP critical points:

A minimum
B, **C**, **D** maxima

Different acid-base complexes

90º < α < 180º

Figure 1. Molecular electrostatic potential (MEP) stationary points for isolated disiloxane.

In previous works, we studied the disiloxane behavior towards Lewis acids and Lewis bases using topological tools and analysing the strength of the interactions the system is able to form [4,5]. In this study carried out at the MP2/aug'-cc-pVTZ level of theory [6], we monitor a simple and well known old magnitude such as the molecular electrostatic potential (MEP) in the different binding sites to provide an explanation to the abovementioned contradictions. The MEP and binding energies are obtained at different Si-O-Si angles for the isolated system, binary complexes with Lewis acids or Lewis bases, and ternary complexes using both acidic and basic sites. Observing the trends, not only electrostatics works perfectly well for explaining the acid-base properties of disiloxane, but is also able to correctly predict changes according to the Si-O-Si angle and even cooperativity effects. These results are a further evidence of the role of electrostatics in non covalent interactions and a reminder of the difficulties underlying the atomic charge concept.

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An initio simulation of tandem mass (MS^2) spectra

PO69

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Mass spectrometry (MS) is a key technology for the identification of small molecules [1]. It can be used in tandem (MS/MS or MS^2) yielding a fragmentation spectrum of the molecule. Collision-induced dissociation (CID). MS^2 is used for compound identification in a wide range of fields such as environmental analysis, drug screening, lipid analysis and metabolomics[1-3].

The main bottleneck in the use of this technique is the difficulty to interpret the fragmentation spectra. Today, the identification of metabolites from MS relies on the comparison with standard compounds or reference spectra[2]. MS^2 spectral databases (DB) cover less than 1% of the compound space that is covered in general purpose DB as Chemspider or PubChem (50 to 90 million compounds, respectively)[4]. The result is a very small percentage of molecules identified per sample (~2%)[5]. To tackle this problem several *in silico* software have been developed to identify unknown compounds by comparing with *in silicio* MS^2 spectra from target structures to experimental MS^2 spectra[6]. Identification rates have increased but still remain low (~25% using only in silico fragmentation tools)[4]. A common drawback of these approaches is that they rely in predefined fragmentation rules extracted from available experimental spectra which currently are quite scarce.

Chemical dynamics simulations can be employed to simulate unimolecular dissociation with the advantage that they only need the starting molecular structure as input. Furthermore, they also provide mechanistic insights. In particular, we used chemical dynamics to successfully explain fragmentation of different classes of molecules: peptides, saccharides, nucleosides, steroids[7] Recently, Grimme reported a QC-based approach to predict CID Mass Spectra using molecular dynamics[8].

In the present study we examine the fragmentation patterns of 19 AAs using chemical dynamics simulations to model the collision-induced dissociation (CID) typically employed in the experimental studies. We compare the simulated spectra with the experimentally obtained spectra. Additionally, the fragmentation mechanisms for selected fragments are discussed. Thus, a clearer picture of the fragmentation dynamics of these important molecules is provided.

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Morphology map of β-Li_3PS_4 nanocrystal by Wulff theory

PO70

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β-Li_3PS_4 is very applied as a solid electrolyte in lithium batteries, it is excellent ionic conductivity and is stable with a metallic lithium anode.[1] Many are studies dedicated to obtaining ideal characteristics for this material. However, as far as we know, there are no theoretical works that discuss the changes in the morphology of the β-Li_3PS_4 and its possible crystal shapes, achieved through the modifications and stabilization of its surfaces. MODALIS^2 is a multicountry European research program that aims to investigate new materials into next-generation lithium-ion batteries to integrate electric vehicles. In this sense, supported by MODALIS^2, this study proposes a morphology map of all crystal shapes possibilities for β-Li_3PS_4, by applying the Wulff classical theory.

The theoretical calculations were made with CRYSTAL program, applying DFT with PBE0 and all-electron basis sets. After the optimization of β-Li_3PS_4 bulk, the surfaces were obtained, taking to account 8 units of Li_3PS_4 in each surface. The surface energies (E_{surf}) were calculated for the optimized surfaces, and the morphology map was made (see Figure 1).

According to E_{surf} and Figure 1, the most stable and exposed surface is the (100), followed by (011), and (010). The surfaces (001) and (111) have a small contribution to the ideal crystal shape, due to their high surface energies. Hood and co-authors[2] obtained ultrathin nanoplates of Li_3PS_4.2ACN (where ACN is anhydrous acetonitrile), and according to our results, this nanostructure is formed by the stabilization of both (100) and (011). These results showed a good prediction of the different possibilities of Li_3PS_4 nanocrystals and were able to show the process of surface stabilization.

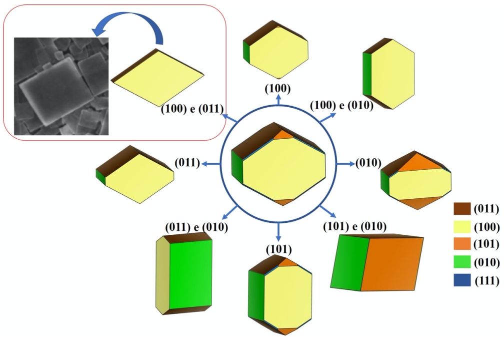

Figure 1. Morphology map of β-Li_3PS_4. In the center, is the ideal crystal. Each arrow indicates the direction of stabilization of one or two surfaces by decreasing the E_{surf}. On the left, is the SEM of β-Li_3PS_4 obtained by Hood and co-authors[2].

Acknowledgments

Acknowledgements: The financial support by the MODALIS2 project, grant agreement No 875193 of the European Union’s Horizon 2020 research and innovation program, is gratefully acknowledged

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PO71

Mechanochemical improvement of Norbornadiene-based molecular solar-thermal systems performance

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The development of large-scale renewable energy technologies is the main goal for the sustainability of the world society. The direct conversion from solar energy to stored chemical energy has the advantage that both harvesting and stored functions are combined in a single process. Molecular solar-thermal systems (MOST) offer a promising alternative to store and release solar energy, compared to more conventional solar cells[1]. Especially, the norbornadiene-based system was found to be, until now, the most efficient organic-based MOST offering, when opportunely substituted, several promising candidates that could lead to a commercial use. Nevertheless, all carried out experimental attempts largely lack a proper design, hence finding difficulties in improving selected MOST properties. In this work, a novel theoretical approach is described and applied to the norbornadiene-quadricyclane system, with the goal to study the effect of applied mechanical external forces, see the figure, that can be traduced into a steric substitution effect. Moreover, we show that optimal complex forces, resulting from a combination of different contributions, could be suitably converted into substitution patterns and allow further improvements of the MOST properties[2]. Moreover, it will be discussed the norbornadiene photochemistry, in particulat, the role of the Rydberg states and the electronic dynamic correlation.

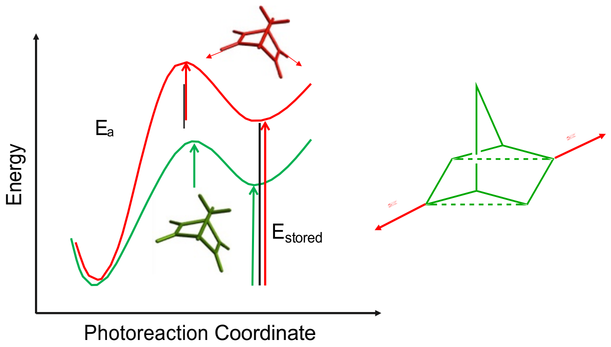

Figure 1. Schematic PES profile for (green) the photoisomerization reaction without applied external forces and (red) when the reaction is altered by an external costant force, and the corresponding variation of activation (E_a) and stored (E_{stored}) energies.[1]

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Spin-orbit couplings in open-shell systems with RASCI

PO72

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In non-relativistic Quantum Chemistry, the interaction between states with different spin vanishes. As a consequence, it cannot be used to describe a variety of phenomena, such as non-radiative transitions, i.e., intersystem crossing [1], or phosphorescence [2]. Such processes require taking into consideration relativistic effects, like spin-orbit coupling (SOC) [3]. In diradical systems, SOC is dominated by several factors as for example, the spatial localization of the unpaired electrons, or the ionic character of the state wave functions [4], making SOC a tuneable phenomenon that can be enhanced or suppressed depending upon system's attributes.

In this work we use the non-relativistic wave functions described by the restricted active space configuration interaction (RASCI) method [5], in conjunction with a recent implementation of the calculation of SOCs [6]. Using this approach, we investigate the role of SOC in three different model systems: (i) the trimethylene biradical (TM), (ii) the ethylene molecule, and (iii) the ethylene-oxygen non-bonded dimer. In all three examples, we explore the induced changes in the computed SOCs with respect to different molecular distortions as illustrated in Fig. 1, where we depict the SOCC profile for TM**.** The obtained results are in good agreement with previous theoretical works [7], and allow us to establish a deep understanding of the key parameters controlling SOC interactions in diradical species. Moreover, the model systems considered in this study represent special situations infrequently discussed in the literature.

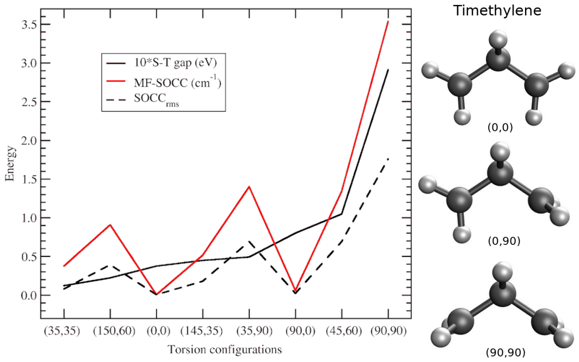

Figure 1. SOCC profile (in cm^{-1}) and vertical T-S gaps (in units of 10^{-1} eV) for TM at different torsions of the adjacent CH_2 fragments.

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PO73

Characterizing drug binding through Förster Resonance Energy Transfer

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The Förster resonance energy transfer (FRET) technique is an important tool in structural biology, due to its ability to monitor and measure distances in biological systems [1]. Albeit FRET is widely used to measure distances in fluorophore-tagged proteins, intrinsic FRET processes in protein-ligand complexes prevent straightforward application of Förster theory due to the lack of rotational freedom of the Trp and ligands involved and their relatively short separations. In this contribution, we aim at developing a novel technique to discover binding sites and characterize ligand binding modes in proteins by combining fluorescence spectroscopy with a novel multiscale computational methodology. Our methodology combines classical molecular dynamics (MD) simulations of predicted binding modes with polarizable quantum/molecular mechanical (QM/MM) calculations of FRET properties beyond Förster dipole and dielectric screening approximations[1,2]. We apply this approach to study the binding of several ligands to Human Serum Albumin (HSA), which presents several advantages to assess the novel methodology, like the presence of multiple binding sites, a single Trp residue, and binding FRET data reported for multiple ligands[2,3]. The ultimate objective of the project is to assess the ability of FRET simulations to characterize allosteric and cryptic binding sites and ligand binding modes for drug discovery targets.

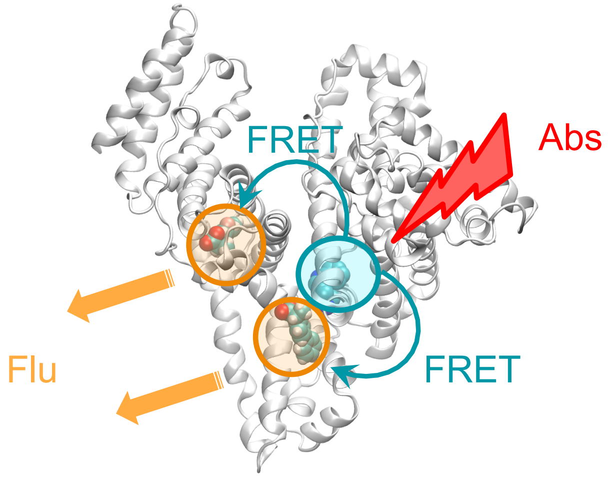

Figure 1. Schematic representation of Trp-to-ligand FRET process in HSA.

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Stability, Aromaticity and Infrared Spectra of Hydrogenated Polycyclic Aromatic Hydrocarbons

PO74

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Polycyclic Aromatic Hydrocarbons (PAHs) are molecules formed by multiple fused aromatic rings that are key in astrochemistry.[1] They are thought to participate in the energetic processes and reactions that occur in space and are candidates to catalyse the formation of molecular hydrogen via hydrogenation/dehydrogenation processes. Thus, the study of hydrogenated PAHs is of great interest.

However, studying hydrogenated PAHs is not trivial since there are different hydrogenation sites available that can produce billions of different possible structures. Here is where theoretical calculations play an important role in identifying and rationalizing the most stable structures. In addition, the computation of the infrared spectra can help us in the identification of the carriers of the aromatic infrared bands [1].

We present a systematic study on hydrogenated PAHs of different sizes using our simple model previously developed for fullerenes [2-4]. Results show that the most stable hydrogenated PAHs are those who preserve the maximum number of aromatic rings [5]. The computation of the infrared spectra has also helped us to rationalize the infrared features that appear in astronomical objects [6].

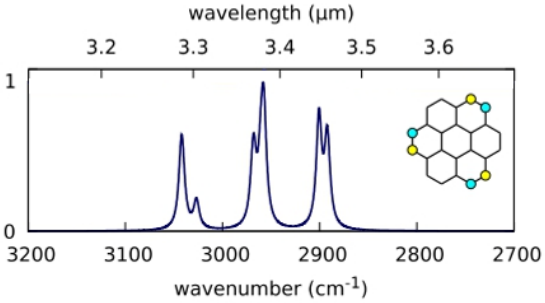

Figure 1. Infrared spectrum of the most stable isomer of coronene with 6 additional H atoms.

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PO75

Cosymlib: a Python library for continuous symmetry measures

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Cosymlib [1] is an open-source python library for computing continuous symmetry & shape measures (CSM & CShM) [2-3]. Its main aim is to provide simple and ready-to-use tools for the analysis of the symmetry & shape of molecules. Many of the procedures contained in **Cosymlib** can be easily applied to any finite geometrical object defined by a set of vertices or a by mass distribution function. Besides purely geometrical objects, **Cosymlib** can be also used to compute the symmetry content of more complex objects of interest in quantum chemistry such as electron densities, wave functions, and molecular orbitals [4]. The basic features included in the current version of **Cosymlib** are:

1. **Molecular structure analysis**
    - Continuous Shape Measures (CShM)
    - Continuous Symmetry Measures (CSM)
    - Continuous Chirality Measures (CCM)
2. **Electronic structure analysis**
    - Pseudosymmetry analysis of molecular orbitals & wavefunctions
    - CSMs & CCM for the molecular electron density

In this communication we give a general overview of the main features of **Cosymlib**, discussing some examples of the use of CSMs and CShMs in structural chemistry as well as in analyzing the electronic structure of molecules.

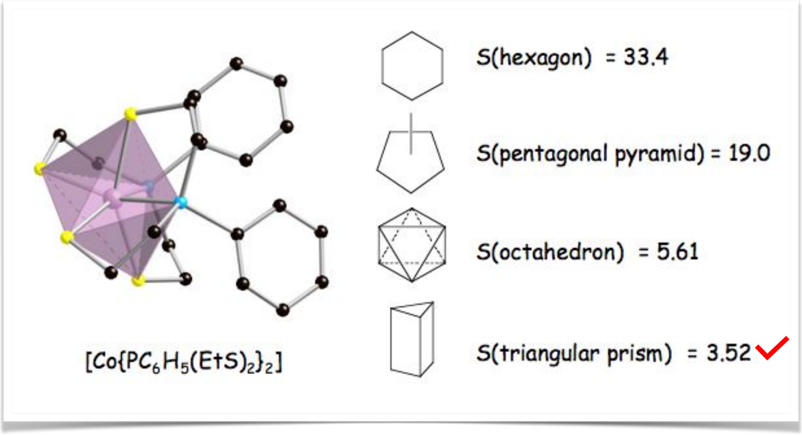

Figure 1. Continuous Shape Measures for the coordination environment of Co in a coordination complex.

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Characterization of hydroxy-azirine: a possible interstellar prebiotic molecule

PO76

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Today, more than 260 molecules have been detected in the interstellar medium or circumstellar shells. Among them a relevant role being played by the so-called interstellar complex organic molecules (iCOMs) (organic molecules containing more than six atoms). These molecules can evolve to more complex prebiotic systems.

In this work we present a theoretical study of one possible interstellar species, hydroxy-azirine (C_2H_3NO). This molecule is an isomer of the detected methyl isocyanate, CH_3NCO [1], and imino acetaldehyde, a possible interstellar molecule [2]. On the other hand, hydroxy-azirine is a derivative of the azirine (C_2H_3N), a nitrogen-containing three-membered cyclic molecule, which despite being searched for in the interstellar medium no conclusive detection has been reported. The different isomers and conformers of hydroxy-azirine have been characterized and their isomerization processes analysed. We also provide the relevant spectroscopic parameters for rotational and infrared spectroscopy for the most stable species, which are mandatory to guide an eventual laboratory or interstellar detection.

A protonated derivative of hydroxy azirine has been shown to be a possible product from the reaction HNO with $CH_2CHOH_2^+$ in the interstellar conditions [2]. The proton affinities of the characterized structures of hydroxy-azirine are computed to provide some insights into the protonation behaviour of the species under study. In addition, we also analyse the possible formation processes in space of hydroxy-azirine from azirine.

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Floating functions method to correct the out-of-plane bending frequencies issue

PO77

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In the late eighties, two groups independently identified a problem in calculating the out-of-plane bending (OPB) vibrational frequencies in ethylene and acetylene[1]. In both cases, it was found that the bending harmonic frequencies were too low when computed using correlated electronic structure methods. Furthermore, the modes showing the anomalous behaviour were extremely sensitive to the specific one-particle basis set used. Later on, Martin[2] and co-workers showed that this problem also happened in benzene and Moran[3] and co-workers showed that benzene would become non-planar at the MP2 and CISD levels of theory with basis sets that were commonly used and had vibrational modes that yielded imaginary frequencies. More importantly, they also showed this problem extended to a range of other arene type systems, including naphthalene or pyridine.

The main features of this problem can be summarized in four points: (a) the OPB issue appears for ab initio correlated wavefunction methods no matter what level of theory one uses (CC, CI or MPn), (b) when a system presents the OPB problem, the modes affected are extremely sensitive to the specific one-particle basis set, (c) it has been proven that it is not a numerical issue because the peculiar frequencies and geometries are reproduced with different computers, operating systems, and program packages even when high numerical precision is demanded and (d) the molecules which exhibit the OPB issue are not exclusively purely hydrocarbon systems which point out the problem is not directly linked to the molecule's symmetry.

Our work analyses the Hellmann-Feynman theorem's (HFT) nonfulfillment role as a possible mechanism behind the OPB issue. The HFT states that the derivative of the total energy with respect to a parameter is equal to the expectation value of the derivative of the Hamiltonian with respect to that same parameter. The HFT is satisfied on the proviso that the wave function is exact or fully variational. The latest cannot always be guaranteed, and therefore it should be taken into account in calculating the energy derivatives.

On the ground of the HFT fulfilment[4], we propose an *ab initio* method to correct the spurious frequencies effectively while keeping the computational resources demand at the same level as a standard calculation. It relies on adding a ghost atom in a molecule's point with a high symmetry, which gives the system enough flexibility to achieve a correct vibrational behaviour.

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A multiscale study of some nickel-based catalysts for CO_2 hydrogenation: Ni (111) vs. Ni clusters on TiC(001)

PO78

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Excessive anthropogenic CO_2 emissions are responsible of a devastating effect on the Earth's environment leading to the global warming. In order to overcome that problem, a lot of attention has been addressed in the last years towards the catalytic CO_2 chemical conversion.

Ni-based catalysts are commonly used for CO_2 hydrogenation reaction and depending on the support and metal structures the selectivity and conversion can be modified. In a recent theoretical study on CO_2 hydrogenation on Ni(111) [1], we have shown that the reverse water gas shift reaction (WGSR) dominates this reaction with no evidence of methane formation, which is opposite to what has been suggested in some earlier DFT and microkinetic studies based on some unreliable assumptions.

On the other hand, there are experimental evidences [2] on a highest activity for the catalytic hydrogenation of CO_2 on Ni clusters supported on titanium carbide (TiC) with respect to that on Cu and Au clusters supported on TiC(001) and the bare TiC(001) and Ni(111) surfaces. The highest activity is found for small two-dimensional particles, but the underlying chemistry is still unknown. For this reason, we have performed some theoretical investigations that have shown that 3D Ni clusters are more stable and easier to form than 2D Ni clusters, while the latest present a highest electronic polarization [3], which could relate to a highest activity for these systems. Indeed, this is confirmed in a latter study of the CO_2 and H_2 dissociation reactions over different 2D and 3D Ni clusters supported over TiC(001) [4], in which the highest adsorptions and dissociations are associated with the 2D Ni clusters.

In order to understand the molecular origin of the highest activity of the Ni/TiC surface with respect to the bare TiC(001) surface, a multiscale approach coupling DFT calculations with kinetic Monte Carlo simulations are in progress, following a similar procedure as in our previous study of Au nanoparticles on δ-MoC(001), which explained the high experimental WGSR activity due to a synergistic effect between bare MoC regions and Au adclusters. In the present study both TiC(001) and Ni_4/TiC models are considered to show as well the possible synergistic effect in the catalytic activity. In that sense, the molecular reaction mechanisms over the two different surfaces will be analysed and compared too with previous results on the bare Ni(111) surface [1]. The last results will be presented and discussed at the meeting.

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A Multi-technique Approach To Describe Radioactive Actinyl Cations in Water: EXAFS + Molecular Dynamics

PO79

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In this communication we present recent results on the physicochemical properties of the monovalent actinyl cations, PuO_2^+ and NpO_2^+, species involved in the treatment of waste nuclear fuel and its recycling. Due to their chemical stability, their hazardous handling and low concentrations, their physicochemical characterization is poor. Structural characterization of actinyl cations in water has been performed by both experimental and theoretical techniques. Among the experimental ones, the technique giving a more direct information is the X-ray absorption spectroscopy (XAS), in particular the extended X-ray absorption fine structure (EXAFS)[1]. This technique supplies short-range structural information around an specific atom, the absorbing atom, with a structural precision of one hundredth of angstrom for the first coordination shell distance and one unit in the coordination number[2]. From theoretical techniques, quantum-mechanical and computer simulations have also provided valuable information. The combination of XAS spectroscopy and MD simulations has been revealed as a useful strategy[3] to refine the structural properties of solutions where the standard fitting of the experimental spectra is clouded by different factors such as low concentrations, spectroscopical phenomena as multi-excitations or low signal/noise ratio. We have shown that the good reproduction of a spectrum by means of the use of information derived from a statistical simulation has a double consequence[4]. On one hand, it allows the access to a direct EXAFS-structure assignment provided by the atomistic picture of the statistical trajectory. On the other hand, it shows the ability of the interaction potentials employed in the statistical simulation when using classical force fields to describe properly the system [5,6].

A specific set of cation-water intermolecular potentials based on ab initio potential energy surfaces has been built for $AnO_2^{2+/+}$. Given the paramagnetic character of these actinyls, the cation-water interaction energies were computed from highly correlated wavefunctions using the NEVPT2 method. NVT and NPT MD simulations have been conducted. Several structural, dynamical, and energetic properties of the aqueous solutions have been obtained and analysed. Structural RDF analysis gives an An-O_{yl} distance of 1.82 and 1.84 Å and an An-O(water) distance of 2.51 and 2.53 Å for PuO_2^+ and NpO_2^+ in water, respectively. Experimental EXAFS spectra from dilute aqueous solutions of PuO_2^+ and NpO_2^+, have been revisited and analysed, assuming tetra- and penta-hydration of the actinyl cations. Simulated EXAFS spectra have been computed from the snapshots of the MD simulations. A good agreement with the experimental information available is found. The global analysis leads us to conclude that monovalent actinyl cations in water are stable pentahydrated aqua ion.

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Computational assessment of lipase LipA thermostability

PO80

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Stability is a crucial property of proteins, related with their resistance to changes in protein structure and thus function as a response to variations in the environment such as temperature fluctuations, different salinity, presence of cosolvents, denaturing agents, etc. Very often, dramatic changes in protein stability occur upon mutation, which can have serious detrimental effects on their biological function and metabolic regulation ultimately causing a disease. On the other hand, there is a sustained effort to enhance the stability of enzymes with industrial application in biocatalysis through protein engineering (either rational design or directed evolution). Protein stability is a multifaceted property that encompasses both kinetic (i.e. the rate of denaturation and/or aggregation) and thermodynamic stability (i.e. the free energy difference between the folded and unfolded states). Lysosomal acid lipase/cholesteryl ester hydrolase (LipA) is an enzyme which catalyzes the deacylation of triacylglyceryl and cholesteryl ester core lipids of endocytosed low-density lipoproteins to generate free fatty acids and cholesterol. Numerous efforts have been directed towards improving the stability of this enzyme, both kinetically and thermodynamically, particularly by saturation mutagenesis and directed evolution [1,2].

In the present work, we test an in-house developed computational protocol to assess the role of mutations in two lineages of laboratory LipA variants to improve its thermostability (Figure 1). To this aim, the physics-based Rosetta suite is used in combination with deep learning-based AlphaFold program to deconvolute the impact of amino acid substitutions in both the secondary structure and selected biophysical parameters along LipA directed evolution. Of note, the two evolutionary pathways increase the enzyme's stability through totally different mechanisms, revealing a non-trivial effect of surface mutations beyond textbook assumptions.

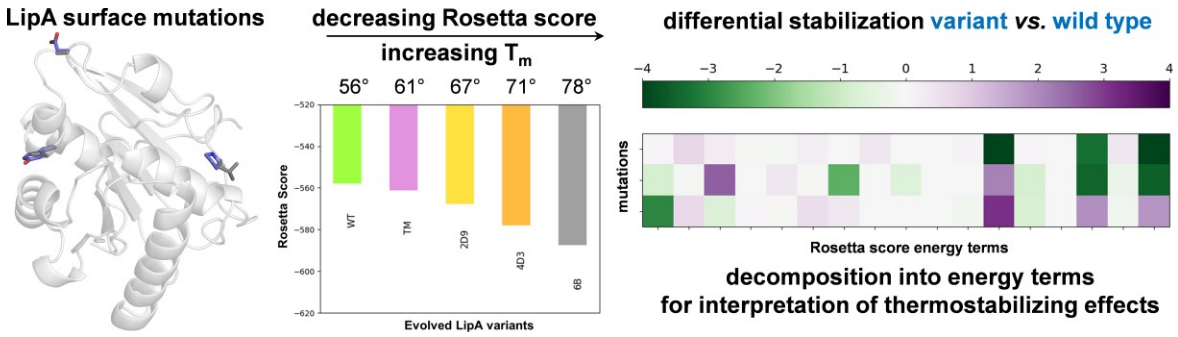

Figure 1. Schematic representation of the computational protocol (left to right): modelling of mutations, thermostability evaluation with Rosetta, and decomposition of per-residue score differences into energy terms.

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Understanding the influence of carbocations in natural and engineered terpenes synthases

PO81

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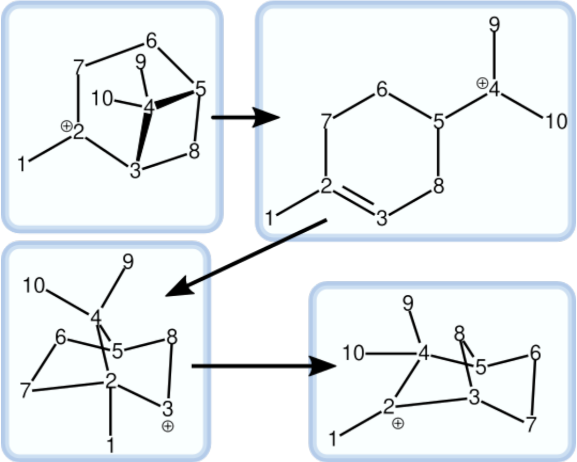
Monoterpenes are widely used compounds in industry as flavors, fragrances or, interestedly, in medical applications. However, the main source of these molecules is from natural origins. From the synthetic point of view, different monoterpenes can be interconverted with acidic media but the intermediate carbocations produced during the reaction produces a mixture of products hardly separable and unproductive, wasting money and valuable products. On the other hand, Nature produces monoterpenes by the use of enzymes, monoterpene synthases. Enzymes are usually selective and provide the desired single product in high yields. However, enzymes can be promiscuous, providing additional side-products, since it is an evolution advantage having the possibility of generating new products without changing the complete pathway. Many terpene cyclases are promiscuous, and have been experimentally engineered using extensive active site mutagenesis to improve the yield and selectivity of certain industrially-relevant products [1,2]. This is the case of squalene-hopene cyclases, that, after different rounds of mutations can selectively synthesize different products [3].

In this study, a rationale for the experimentally observed selectivity of some engineered squalene-hopene cyclases towards the production of different industrially-relevant monoterpenes such as camphene, pinene or iso-borneol is provided. In particular, we calculate the free energy of the different carbocations and the pathways that interconnect them in gas phase and inside the active site of the different engineered squalene-hopene variants to unveil the main causes of such mutation-induced differences in selectivity and yield. The free energy surfaces are calculated using first principle metadynamics and QM/MM metadynamics.



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PO82

Crystal Packing of Long Aliphatic Chains

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Bulk crystals of long-chain normal alkanes and Langmuir monolayers of alkane derivates show similar phase diagrams, including rotator phases and low-temperature herringbone-type structures [1-5]. By varying the temperature, the interactions between neighboring chains will be altered due to the increase in atomic movement, thus modifying the structure in which the chains pack. In this communication we will report on a crystallochemical study based on searches for structural information in the Cambridge Structural Database and molecular mechanics as well as *ab initio* DFT-based calculations for crystals of the C_nH_{2n+2} normal alkanes with $6 \leqq n \leqq 36$. Once the cell parameters and atomic positions have been obtained for different compounds, a geometric analysis based on continuous symmetry measures [6] has been performed in order to obtain the packing modes of the chains and to describe their changes during phase transitions.

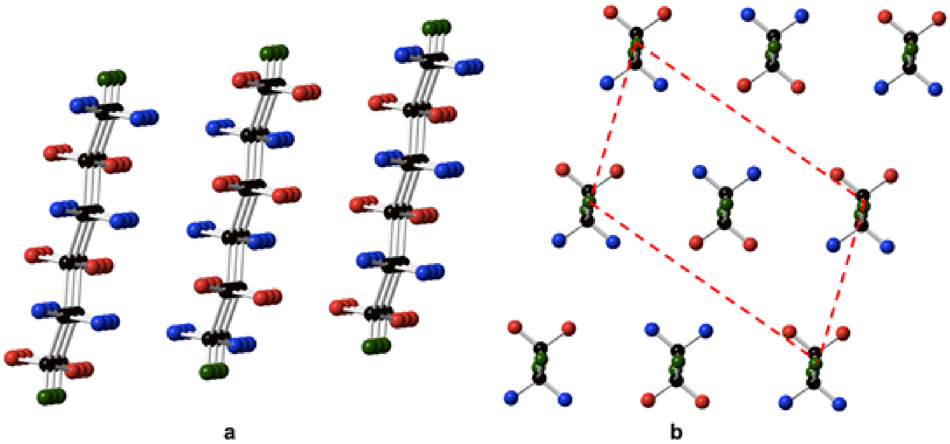

Figure 1. Layer of C_6H_{14} chains in the triclinic polymorph in a) a lateral view and b) a view along the direction of the chains.

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The effect of Feschbach resonances on the different vibrational states of N_2 in a RABBIT experiment.

PO83

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Due to the high photon energy of attosecond light sources, the theoretical description of attosecond experiments requires a proper representation of the ionization continuum. For polyelectronic molecules, the description of the ionization process requires the use of electronically correlated wave functions for the molecular bound states as well as the system's ionization continuum. Despite the huge success of state-of-the-art Quantum Chemistry Packages (QCP) for describing molecular bound states, the combination with their ionization continuum at the same level of theory is still challenging.

The XCHEM code, recently developed in our group, overcomes these difficulties by using a hybrid Gaussian-B-Spline (GABS) basis interfaced with existing QCPs via close-coupling scattering methods [1, 2]. The XCHEM approach has produced excellent results in different atomic and molecular systems [2-8].

By solving the time-dependent Schrödinger equation one can simulate attosecond experiments in which combinations of several pulses lead to complex interferometric patterns in the ionization continuum. We have extendeded the TD-XCHEM code to include both electronic and nuclear degrees of freedom.

We have employed this new method to simulate a Reconstruction of Attosecond Beating By Interference of Two photon Transitions (RABBIT) experiment of N_2 in an energy region that contains Feshbach resonances converging to $A^2\Pi_u$ and $B^2\Sigma_u^+$ states. Due to the inclusion of nuclear movement and to the capability of the XCHEM code to describe the electronic correlation, this simulation is able to consider the population of Feshbach resonances by different vibrational states.

In this work, we present the results obtained, which have an excellent agreement with experimental data [9] and allow to understand different unexplored features.

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PO84

Unravelling the Interaction of Octahedral Metal Complexes with DNA G-quadruplexes by means of Near Linear-Scaling Density Functional Studies of Non-Canonical DNA Model Structures Including ~1000 Atoms

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We have used near linear-scaling density functional theory (LS-DFT) methods including dispersion, for the first time[1], to study the interaction of two isomers, equatorial (Eq) and axial (Ax), of the $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Br(CO)_2(phen)}]$ metal complex with the DNA G-quadruplexes (GQ) to gain insight on its cytotoxicity[2]. The LMKLL/DZDP level of calculation[3,4], which includes van der Waals contributions, with the SIESTA software[5] was used to treat by means of first-principles computations the whole biological studied model system with ~1000 atoms. Computed formation energies point to systems containing the Ax isomer as the most stable although the nearest system in energy containing the Eq isomer is only 7.5 kcal mol^{-1} above. On the other hand, the energy decomposition analysis (EDA) favours interaction energies for the systems containing the Eq isomer. However, when solvent effects are taken into account the systems corresponding to the Ax isomer are again the most stable. This Ax isomer was found interacting by means of end-stacking with the GQ and surprisingly totally inside the non-canonical secondary structure, where all the ligands of the metal complex produce several weak interactions with the DNA structure. On the other hand, the Eq isomer prefers to interact from outside by means of intercalation in which the ancillary ligands have also some role in the interaction. Such features and comparison with the results regarding the interaction of the $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Br(CO)_2(phen)}]$ metal complex with duplex DNA suggest that the $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Br(CO)_2(phen)}]$ would have higher affinity and eventual selectivity for non-canonical DNA GQ structures. This selectivity GQ vs. duplex DNA is of current interest in the bibliography [6,7] and we hope our studies will shed some light on the topic.

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PO85

Computational modelling of squaramide-based supramolecular polymers

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The surging interest in adaptive materials for myriad applications, from biomedicine to electronics, has promoted the development of functional materials. Supramolecular polymers (SPs) have emerged as promising candidates to build novel functional materials due to its dynamic character originated by the reversibility of the noncovalent interactions that hold together the supramolecular structure [1]. Squaramide (SQ) units, which are conformationally rigid cyclobutenedione rings (Figure 1a), hold donor and acceptor hydrogen bonding units (two strong N–H hydrogen bond donors and two C=O hydrogen bond acceptors) promoting an optimal supramolecular growth. SQs present Z-E double bond isomerization (Figure 1b) that can give rise to different supramolecular assemblies (Figure 1c and 1d) with different optical properties [2].

Here, we present a quantum-chemical characterization of the structural, electronic, and optical properties of novel SQ-based derivatives and their possible supramolecular aggregates. Furthermore, we have analyzed the strong effect of the supramolecular structure on optical properties through a simple extended Kasha model Hamiltonian.

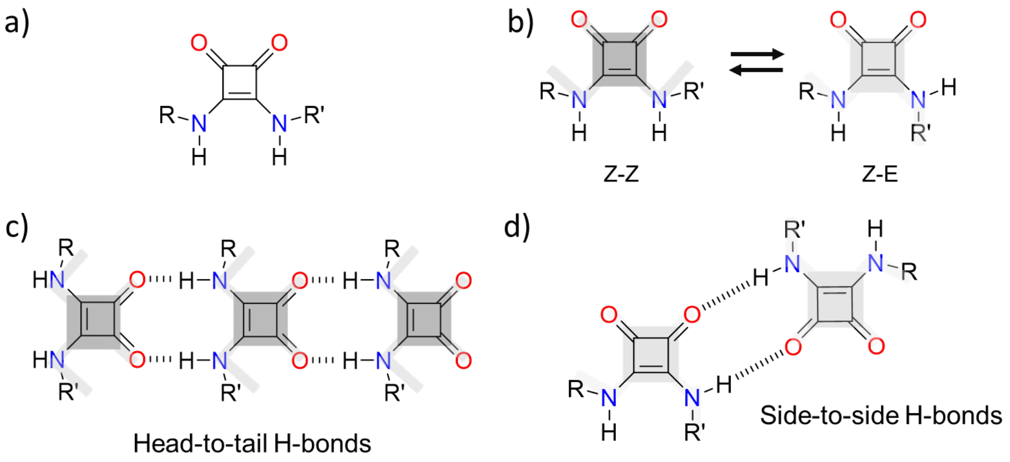

Figure 1. Chemical structure of a simple squaramide derivative (a). Scheme of the geometrical Z/E isomerism in disecondary SQs (b). Head-to-tail (c) and side-to-side (d) patterns for the supramolecular growth of SQ-based derivatives.

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Assessment of the Properties of Potential Drugs of Photodynamic Therapy

PO86

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Photodynamic therapy (PDT) is a promising cancer treatement in which a light with a specific wavelength activates a photosensitizer drug molecule. This photosensitization creates reactive oxygen species (ROS) causing the apoptosis. Compared to other traditional treatment protocols, such as surgery, chemotherapy, and radiotherapy, PDT has a non-invasive nature and extensive number of potential applications because ROS damage a wide range cells including blood vessels feeding cancer cells and it can be combined with conventional treatments. That is why it has become an important research topic over the past few decades [1].

Despite its advantages over the conventional ones, PDT still suffers from some challenges mainly based on the chemical nature of photosensitizer, small radius of action (<20 nm) and extremely short half-life of ROS (<40ns) [2]. For this reason, the delivery of therapeutic agents to specific cells is desired to have efficient photodynamic effect. Some targeted therapeutic agents with structural variations can accumulate in the plasma membrane, mitochondria, lysosomes, nucleus, and endoplasmic reticulum[3]. And the ultimate location of a PS within the living being plays an important role in cell destroy to have high efficiency during the treatment.

In this study, we aimed to propose new design strategies of PS agents to be used efficiently in the deep tissue tumours and to rationalize the effects of the modification on the PS within the biological environment. For this reason, the PS agents will be encapsulated with commonly used drug delivery agents and advanced molecular dynamics techniques will be used to investigate the pharmacodynamic properties of these complex systems in different environments.

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Design of photoactive cages for the encapsulation/delivery of antibiotics

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PO87

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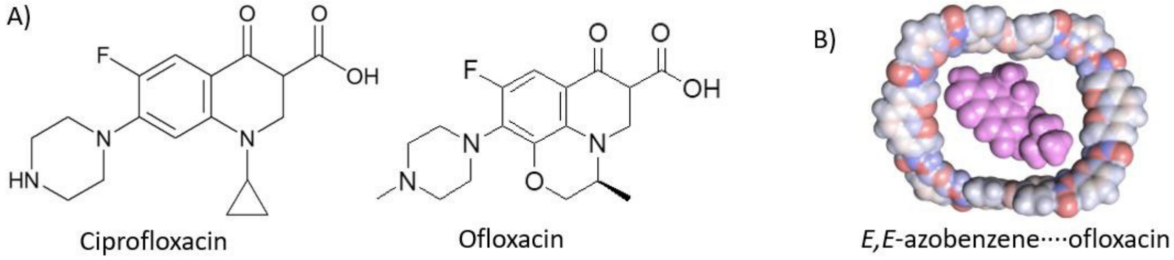
Antibiotics are considered as essential emerging contaminants due to their presence in water-waste. In some cases, the sewage treatment for antibiotics elimination is not quantitative [1]. Hence, the treated water, used for further domestic used or irrigation, has a significant content on antibiotics and a direct impact on human's health (antibiotic's resistance). For this reason, we propose the photodriven encapsulation/delivery of antibiotics by photocages to enhance their elimination from waterwaste. The aim is to design, from a computational point of view, photocages able to encapsulate the antibiotic through non-covalent interactions. Then, upon light irradiation, their macrocyclic shape would change drastically forcing the drug delivery. In particular, we selected, ciprofloxacin and ofloxacin, due to their spread used in pharmaceutics, large amount in waterwaste and huge human's resistance. Regarding the photocages, macrocycles formed of molecular photoswitches and phenanthroline are proposed. Photoswitches are molecules that can be reversibly interconverted by light irradiation between two states [2].

Regarding the design, we have first proposed cages of different sizes to evaluate their compatibility to encapsulate the antibiotics under study and their three-dimension cage-like size. For this aim, each photocage has been optimized considering the different photoswitch states at the DFT level. The most promising photocages have been selected and their photophysical and photochemical properties have been computed at the TD-DFT level. After, the cage complexation with the antibiotics through non-covalent interactions has been evaluated by molecular docking. The most stable cage-drug poses have been retrieved from this calculation and optimized at the DFT level. At this stage, we compare the cage-drug interactions for each photocage, considering the different molecular switch state. This information let us discern if upon light irradiation the cage-drug complex is disrupted, as desired, or if both switch states lead to stable complexes. Finally, the dynamic stability of the proposed cage-drug complexes has been studied through molecular dynamic simulations.



Ciprofloxacin

Ofloxacin

E,*E*-azobenzene····ofloxacin

Figure 1. A) Chemical structure of ciprofloxacin and ofloxacin. B) Schematic representation of a selected cage-drug complex.

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The possible role of photoionized CO_2 clusters in the origin of O_2^+ at the Martian atmosphere

PO88

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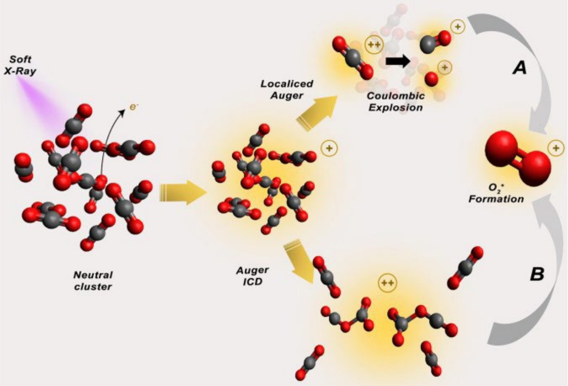

Cluster chemistry has been traditionally understood as the bridge between macroscopic chemistry and pure element chemistry or single-molecule chemistry. Thus, different physicochemical properties are to be expected as we increase the cluster size from free molecules to bulk-like and even periodic systems. These features are particularly interesting for astrochemistry and atmospheric chemistry studies, since molecular clusters are expected to act as precursors to larger particles like aerosols or clouds [1,2] and their interaction with solar radiation are fundamental for the understanding of climate related processes. Molecular O_2^+ is the dominant ionic species in the lower Martian ionosphere [3] and its primarily believed to be formed via photodissociation of CO_2 single molecules. However, as reported by Lo et al. [4], this mechanism significantly underestimates the production of molecular oxygen when compared with direct measurements at these altitudes and therefore, additional sources should be found. Here we present an alternative (or complementary) origin for the formation of O_2^+ molecules, from core-ionized CO2 clusters after interaction with soft X-Ray photons. Theoretical calculations were performed taking into consideration two possible Auger decay mechanisms after photoionization leading to different dicationic states. When analyzing the stability of dicationic $(CO_2)_m^{2+}$ clusters after ICD, we have identified an interesting type of covalently bound structures stabilized via polarization and solvation effects stable only for $m < 12$ CO_2 molecules. The chemistry of these doubly-charged clusters have turn out to be extremely interesting, and different mechanisms were obtained for the formation of the targeted O_2^+ ion [5]. Ab Initio Molecular Dynamics simulations for $(CO_2)_m^{2+}$ clusters provide complementary information, such as the kinetics of the processes as well as the yields of the main channels. All these calculations have been employed to infer the measurements obtained with state-of-the-art experimental techniques: 3-D momentum coincidence imaging of fragments produced in clusters ionized using soft X-Rays (320 eV) at the MAX-lab synchrotron in Sweden.

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Natural range separation of the Coulomb hole

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TIn this work, a natural range separation of the Coulomb hole into two components, one of them being predominant at long inter-electronic separations (hc_I) and the other at short distances (hc_{II}), is exhaustively analyzed throughout various examples that put forward the most relevant features of this approach and how they can be used to develop efficient ways to capture electron correlation [1]. We show that hc_I [2-4], which only depends on the first-order reduced density matrix, can be used to identify molecules with a predominant nondynamic correlation regime and differentiate between two types of nondynamic correlation, types A and B. Through the asymptotic properties of the hole components, we explain how hc_I can retrieve the long-range part of electron correlation. We perform an exhaustive analysis of the hydrogen molecule in a minimal basis set, dissecting the hole contributions into spin components. We also analyze the simplest molecule presenting a dispersion interaction and how hc_{II} helps identify it. The study of several atoms in different spin states reveals that the Coulomb hole components distinguish correlation regimes that are not apparent from the entire hole.

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Intramolecular charge migration in betaine by impact of fast atomic ions

PO90

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Electron dynamics governs the fragmentation dynamics occurring at long timescales. Experimentally, it is possible to observe this can be observed using diferent experimental schemes: On the one hand, it is possible to obtain the time-resolved dynamics by using pump-probe schemes, for example with high harmonic generation or free electron lasers [1]. Alternatively, it is possible to clock the electronic dynamics using Coulomb explosion or electron emission after photoionization. On the other hand, electronic dynamics can also be induced with low-energy ion collisions that are characterized by a sub-fs interaction time where one can expect a “sudden" ionization. In this regime, resonant electron captures dominate and are associated with large cross sections, thus low target excitation are expected. The main disadvantage is that currently it is not possible to perform pump-probe experiments at the fs timescale with ion beams and ion collisions are not selective.

Betaine is a zwitterion molecule, i.e. with one end positively charged ($N(CD_3)_3$ group) and the other one negatively charged (CO_2 group) while the whole molecular system remains neutral. During the collision with 3 keV/amu O^{6+}, two electrons are removed from the CO_2 side leading to the formation of a dication with two holes localized at both sides. Beside the expected direct Coulomb explosion giving the pair CO^{+2} /$(CD_2)N(CD_3)^{+2}$, we observe a competitive channel following intramolecular charge migration (ICM) and giving the pair $CD^{+3}/(CD_2)N(CD_3)^{+2}$. These two channels are rationalized by simulating the dynamics with surface hopping semi-classical methodology where the electronic states are represented via perturbation theory based in multireference wavefunctions [2].

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Strategies to boost electrical conductivity in porous materials: a theoretical framework

PO91

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The design of materials combining electrical conductivity and porosity is an interesting but challenging topic that has gained exponential attention in recent years for exploitation in next-generation applications [1]. Despite being traditionally considered as insulators, (metal)-organic frameworks are porous crystalline structures that have proved to be efficient for the transport of electrical charge upon suitable chemical design [2]. Among the most promising strategies to infuse charge conductivity in porous crystals, we emphasize the π-π stacking of electroactive ligands, the incorporation of guest molecules within the pores, or the exploitation of mixed valency in chemically available metal redox pairs.

Herein, we showcase the theoretical modelling of novel porous materials that take advantage of each of these chemical strategies to boost charge conductivity. First, the charge transport of a series of purely organic porous frameworks based on H-bonding (HOFs) is described in terms of a through-space hopping of charge carriers between stacked electroactive TTF-based ligands in a zwitterionic form (Figure 1a). Second, one of the first examples of perylene-based MOFs with semiconductivity is presented based on the partial oxidation of the ligand upon inclusion of I_2 dopant, and promoted by a herringbone CH···π perylene-perylene stacking (Figure 1b). Last, the record 3D conducting MOF based on Fe(II)/Fe(III) redox pair and tetrazole ligand **$Fe_2(BDT)_3$** (Figure 1c) [3] is characterized theoretically, and compared with its polymorphs and other related pyrazole-based conducting MOF. In this case, the effect of protonation distribution and mixed-valence redox pair formation on the charge transport properties is described.

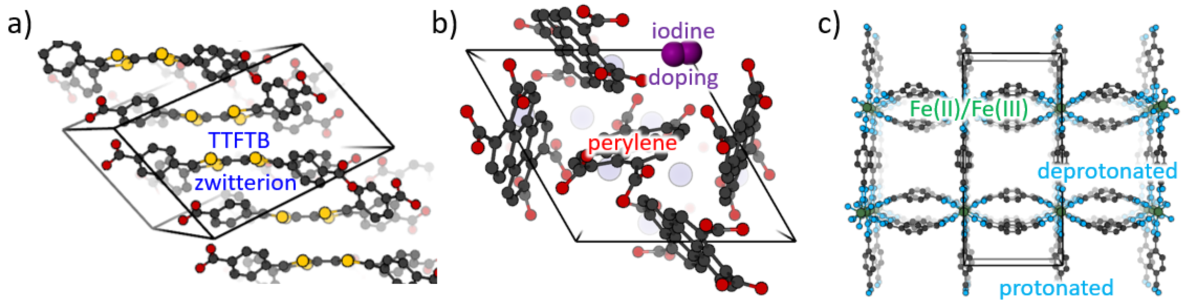

Figure 1. Crystal structure of a) TTF-based **MUV-20a**, b) perylene-based **Per-MOF**, and c) tetrazole-based **$Fe_2(BDT)_3$** frameworks.

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Exploring non-classical reaction pathways in selective catalytic hydrosilylation reactions

PO92

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The synthesis of vinylsilanes, *i.e.* organic derivatives with C=C-Si bonds, via catalytic reduction of alkynes with hydrosilanes is a topic of upmost importance in current chemical research due to their low toxicity and easiness to functionalize. Nonetheless, this reaction generally suffers from lack of selectivity and several isomers are afforded (Figure 1a). Traditionally, the selectivity of inner sphere catalysts for the hydrosililation of terminal alkynes has been explained by the Chalk-Harrod and modified Chalk-Harrod mechanisms (Figure 1b). However, this framework has many shortcomings, and the recent development of new catalysts with uncommon selectivity has revealed the need for exploring new mechanistic pathways [1].

In this context, we have explored from a theoretical perspective – by using state-of-the-art DFT methodology – the reaction mechanism of a series of highly selective and active Rh- and Ir-based catalysts that bear non-innocent ligands and proceed via non-classical reaction mechanisms, such as that depicted in Figure 1c [2]. A summary of the studied systems and results will be shown, in conjunction with an in-depth analysis of the factors that determine the reactions activity and selectivity.

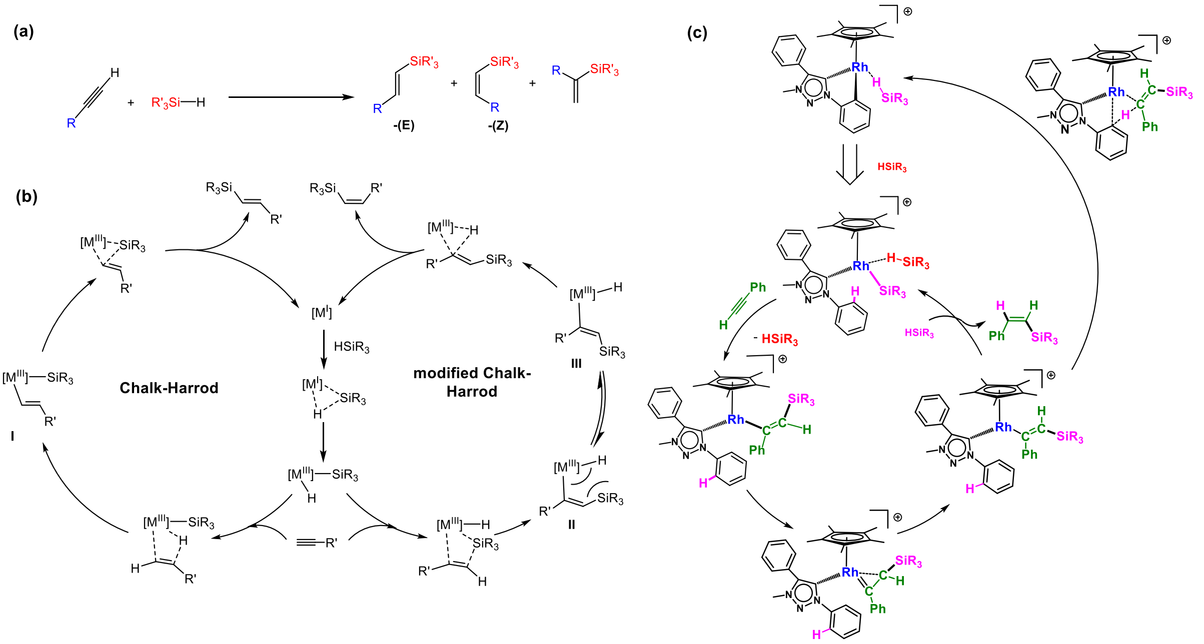

Figure 1. (a) Possible hydrosilylation products. (b) Schematic representation of the Chalk-Harrod and modified Chalk-Harrod classical mechanisms. (c) Example of a non-classical hydrosilylation reaction mechanism.

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Classification of biomolecular structures by invariant shape and deformation parameters

PO93

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The classification of biomolecules according to structural similarities is an relevant issue in biochemistry [1], recently attracting an increasing interest boosted by the upcoming big data era. Proper choices of parameters, containing invariant structural information, could possibly induce, upon systematic exploration, convenient mapping and grouping of structures depending on predominant structural motifs or also individual amino acid geometry and connectivity properties. Here, we give a summary of the theoretical background of parameter derivation from many-body hyperspherical coordinates and extend a previous work based on the use of shape parameters and deformation indexes. Such parameters are derived from "symmetric" hyperspherical coordinates and applied to a large set of protein structures each represented as a network of nodes. Different choices for the network nodes are also investigated.

Acknowledgements: This work is supported by a grant from Fondazione Cassa di Risparmio di Perugia n.# 220.0513 to C.E.

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New Re-BODIPY complexes as dyes for dye sensitized solar cells

PO94

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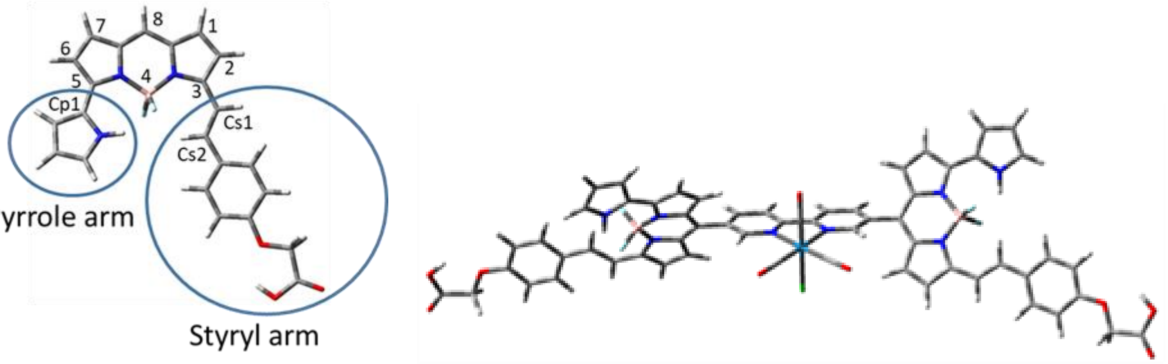
Dye sensitized solar cells are one of the promising types of solar cells designed to generate energy from the renewable solar light [1]. The selection of adequate dyes is an essential topic in this field and theoretical calculations can help by analysing the photophysical properties of different potential dyes.

In this work, a BODIPY with a styryl arm and a pyrrole at the 3 and 5 positions, respectively, is considered (see Figure 1.a). Then, one and two BODIPY units are linked to bipyridine in different positions. Finally, the substituted bipyridine is included as a bidentate ligand in a tricabonyl Re(I) complex (see Figure1.b).



(a) (b)

Figure 1. BODIPY (a) and [ReCl(CO)$_3$(BBb55)]) complex (b) as potential dyes for solar cells.

According to our DFT and TD-DFT study all the systems considered display absorption bands in the Vis and near IR region, which is one of the desired features of a dye. Besides, the energy of the frontier molecular orbitals of these systems fulfils the needed requirements: the LUMO energy is larger than that of the conduction band of TiO$_2$ semiconductor and the HOMO energy is smaller than the redox potential of the usual redox mediator [2]. However, as the system increases in size, these properties improve, with the Re complexes substituted at positions 4 and 5 of the bipyridine being the species with the best photophysical properties.

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Characterization of interactions between dioxins and lipid membranes by QM/MM energy decomposition analysis

PO95

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Dioxins and dibenzofurans are aromatic substances with a special toxicological interest in their tetrachlorinated derivatives. Particularly interesting are 2,3,7,8-tetrachloro-p-dibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) because of their carcinogenic and mutagenic effects in living organisms. Their bioaccumulation in lipids is well-known, however, their mechanisms of toxicity leading to harmful effects in biological cells are not fully clarified.

In this work, we try to shed more light on the permeation process of these compounds across lipid membranes by means of umbrella sampling classical molecular dynamic simulations, using a model composed by 128 1,2-dioleoyl-sn-glycero-3-phosphocholine lipids (DOPC). The computation and analysis of its free-energy profile from dynamic study allow selecting along the diffusion process those regions of special interest for the analysis of the intermolecular interactions between TCDD/TCDF and lipid bilayers. Thus, the characterization of pollutant-membrane interactions was performed by combining quantum mechanics/molecular mechanics (QM/MM) calculations and energy decomposition analysis (EDA) [1]. In this way, a deeper knowledge is possible from the study of these interactions, as well as the weight of the different contributions: electrostatic, exchange, repulsion and polarization, which unveil the permeation mechanisms [2,3].

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An automated method for graph-based chemical space exploration and transition state finding

PO96

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Applications of algorithms that automatically explore the chemical space have been limited to chemical systems with a low number of atoms due to expensive involved quantum calculations. Nonetheless, it is possible to explore large regions of the chemical space with low-cost graph theory techniques, to later apply quantum calculations on relevant reaction paths.

The method described here tackles the problem of chemical exploration by generating reaction networks with heuristics based on chemical theory. This is done by defining molecular graph transformations that represent elementary reactions in a graph theory approach. Such transformations act upon functional groups in molecules that fulfil the Lewis Structure, which are represented in terms of bond order matrices. This way, a study showing computational time and method's performance in five different chemical systems is presented with a concise chemical representation of graphs, to finally apply an efficient combination of quantum chemical calculations on the reaction paths.

XCHEM beyond diatomics: photoionization of the water molecule

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The XCHEM [1] code considers the effect of electron correlation in the configuration interaction picture and takes into account the coupling between different continua. Thus it is especially convenient for the study of low energy ionization, when the electron still feels the ionic core and electron correlation plays an important role. The XCHEM methodology has been successfully applied to atomic and diatomic systems, such as neon [2], nitrogen [3], and carbon monoxide [4]. In this communication we present for the first time results for a triatomic system, the water molecule.

The XCHEM methodology uses a hybrid Gaussian-Bspline basis (GABS) [5] composed of a set of monocentric gaussians (MC) located at the centre of mass of the molecule and a set of Bsplines that ranges from a selected distance to the centre of mass R_0 to a sufficiently far distance R_∞. Bsplines are highly oscillating functions that are better suited than Gaussians to represent the properties of the continuum. XCHEM couples this basis with the polycentric Gaussian basis (PC) that comes from a standard quantum chemistry calculation. The R_0 distance is chosen so that the overlap between PC and Bsplines is negligible. The MC basis serves as a bridge that communicates Bsplines and PC.

The XCHEM wavefunction is built by augmenting with a single electron in both the GABS basis and the PC Gaussians for each of the considered parent ions. Thus, only a single electron is allowed to go into the continuum.

In this communication we show the calculated photoionization cross sections and asymmetry parameter and their comparison to experimental results [6–8]. We will show also the resonance series that appear at low kinetic energies of the electron in the photoionization spectra and the effect these resonances have in the photoelectron angular distributions.

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Non-orthogonal Configuration Interaction applications

PO98

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Non-Orthogonal Configuration Interaction method has proved to be a great tool to shed light on relevant molecular properties that were hidden for the classic Electronic Structure Methods. It allows every state to be expressed in its own set of optimal atomic orbitals, leading to an easy interpretation of chemical bonding that is analogous to that offered by Valence Bond Theory.

One specific area or research that can benefit from this method is singlet-fission, in which we want to measure the spin-coupling between two chromophores in order to identify new candidates. As we express each single molecule state in its own set of optimal orbitals, we can properly estimate the non-adiabatic coupling between molecular states, which greatly influences the singlet-fission process.

NOCI also leads to a more appropriate estimation of relevant magnitudes such as transition dipole moment, determining dark and bright states. In this poster we show an example of its estimation and detail how they can help when performing a screening of singlet-fission candidates.

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Shining Light on the Atomistic Mechanisms Involved in Battery Operations

PO99

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In the last decade, Li-ion batteries (LIB) have clearly emerged as the dominant battery technology. Density functional simulations have been crucial in the improvement and design of novel better-performing battery components, understanding the atomistic factors driving voltage, thermal stability, degradation mechanisms, and Li-ion diffusion [1,2].

Flammability, toxicity, and cost are only a few drawbacks to the use of LIBs due to the presence of organic liquid electrolytes. Working using aqueous electrolytes would be extremely beneficial especially to lower production cost, higher safety, and lower toxicity. Nevertheless, the use of water opens the possibility of proton co-insertion, electrode degradation, and the possible oxygen and hydrogen evolution reactions. But are protons able to intercalate in the electrodes? and if the answer is affirmative, which is the effect of proton intercalation on the battery performance? Is the oxygen evolution reaction preventable?

In this work, we use periodic and molecular density functional computations to investigate the mechanisms of the lithium/proton exchange and the oxygen evolution reaction in well-known cathode materials like $LiCoO_2$ and $LiMn_2O_4$. The analysis of the proton insertion mechanism has been carried out in the bulk and surfaces of these materials to demonstrate which specific chemical and structural features lead to electrochemically stable materials for aqueous batteries. Thanks to the simulations, we were able to contradict one of the most extended hypotheses about the use of layered structures as electrode materials using aqueous electrolytes. This study provides fundamental investigations about the performance of aqueous battery operations and shows how computations can be involved on the design of efficient LIBs.

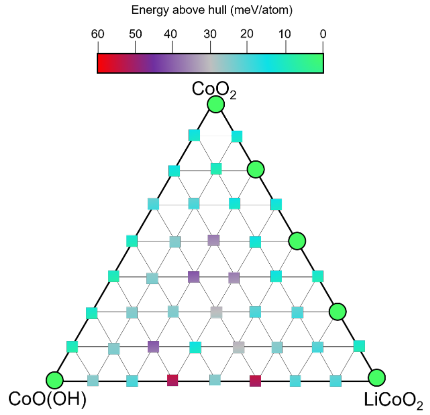

Figure 1. Phase diagram (0K) of $H_yLi_xCoO_2$ ($x+y \leq 1$) structures. Circles indicate the stable compositions, while squares represent structures with energies above hull [3].

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cell2mol: Encoding Chemistry to Interpret Crystallographic Data

PO100

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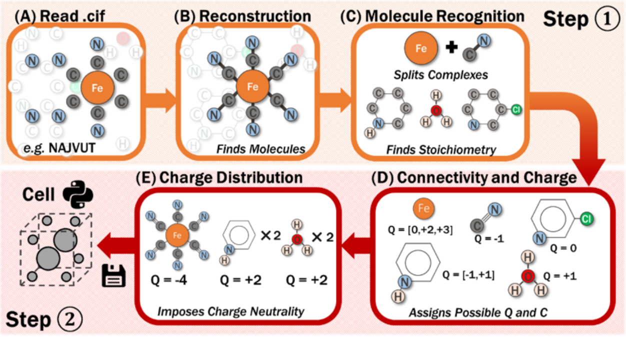
Data is nowadays a most valuable resource in the application of artificial intelligence and screening techniques to the discovery of new molecules and materials[1]. Yet, obtaining enough reliable and chemically-diverse data to explore the chemical space is often a challenging task. While crystallographic data repositories (*e.g.* the Cambridge Structural Database, CSD) are the best potential source of diversity to that purpose, the information contained therein is insufficient to set up a quantum chemistry computation of the individual molecules because their number of electrons, a requisite to define their electronic states, is not known. This problem is even worse when transition-metal complexes (TMC) are involved, due to their variable number of electrons (or oxidation state) and intricated structure. Thus, the exploration of TMCs in materials design is particularly difficult despite the large collection of available crystallographic data [2].

To solve this shortcoming, we present and make public the software *cell2mol*, a program that deconstructs molecular crystals, and univocally determines the bond connectivity and charge of all molecules contained therein. Our code only reads the structural information contained in its crystallography file (*i.e.* the cif), and exploits common chemical concepts and rules to interpret molecules, similarly to what chemists do when looking at a crystal structure. To demonstrate its performance, we constructed QML-ready datasets of TM complexes based on eight selected metals: Cr, Mn, Fe, Co, Ni, Cu, Ru, and Re. cell2mol successfully interprets about 75% of the 41,750 tested CSD entries with mono-metallic complexes, with a reliability of 95%. We will demonstrate that these metrics surpass other popular parametrized (BVS) and machine-learning (ML) approaches dedicated to the assignment of metal OS [3,4], with *cell2mol* being much more versatile. As a result, *cell2mol* enables the user to exploit the incomparable chemical diversity contained in crystallographic data repositories to generate fully customizable databases that are ready for quantum chemistry computations.



Scheme 1. Representation of the *cell2mol* pipeline to interpret a unit cell (refcode NAJVUT). From reading the structural information in the input .cif file, to the creation of the cell python object, with all the unit cell information, including the total and atomic charge distribution and the bond network.

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Second Principles Time Dependent Simulations of Electric Transport in Graphene

PO101

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The study of transport properties is a very important field of research due to its importance from the fundamental point of view and its many practical applications. The phenomena associated with these properties is immensely varied going from common conducting materials copper wires or lithium anodes of batteries, to novel and exotic structures as topological materials. Microscopically, the origin of resistivity resides in the collapse of translational symmetry occurring with the presence of impurities or the distortion of the lattice created by phonons. The global effect is strongly dependent on the temperature. A broad solution of transport problems from a computational perspective using *ab initio* techniques is still an open problem.

In the last decades, the advances of first principles methods such as Density Functional Theory (DFT) have allowed gaining a deeper knowledge of the electronic structure of materials. However, transport, like other properties that are strongly temperature-dependent or involve states beyond the ground state still represents a very important challenge for first-principles simulations. This fact motivates the development of a new family of methods, known as Second Principles (SP) [1], based on DFT. They allow large-scale materials simulations including both atomic and electronic degrees of freedom, at a very modest computational cost. The method is based on the construction of models written in localized Wannier functions [2] and includes the capacity to describe the changes in the electronic state induced by the application of electric fields, variations in the geometry (including electron-phonon coupling) and the electron density itself (electron-electron scattering).

In this work, we present both our novel technique to generate general SP models including the above characteristics (implemented in the code modelmaker and based on SIESTA [3] calculations) and the development of real-time time-dependent second-principles simulations to carry out transport simulations and their application to graphene.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/ 10.13039/501100011033 and “ERDF A way of making Europe”, by the European Union. T.F.R. Acknowledge financial support from Grant PRE2019-089054 funded by MCIN/AEI/10.13039/501100011033 and by ESF Investing in your future.

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PO102

Application of QM/MM Methods to Understand the Role Played by Different Amino Acid Residues in the Catalytic Mechanism of Plastic PET degrading Enzymes

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Plastic accumulation is one of the main environmental issues of our time. In 2016, two enzymes capable of degrading polyethylene terephthalate (PET), one of the most common plastic polymers, were discovered. PETase and MHETase from *Ideonella sakaiensis* (*Is*PETase and *Is*MHETase, respectively) work sequentially to degrade PET to its constituent monomers. PETase catalyzes the cleavage of PET repetitive units ((mono-(2-hydroxyethyl)terephthalic acid (MHET)), whereas MHETase hydrolyses MHET into terephthalic acid (TPA) and ethylene glycol (EG). In this work, the catalytic mechanism of *Is*PETase was studied by QM/MM [1].

The reaction was found to progress in four distinct steps, divided into two major events: formation of the first transition intermediate and hydrolysis of the adduct. The transition state and respective reactant and product of each step were fully characterized and described. The rate-limiting step was found to be step 3, with an activation barrier of 12.5 kcal mol^{-1}. Furthermore, in this study, we have shown the critical role of a triad of residues composed by Ser207, Ile208, and Ala209 in stabilizing the catalytic Asp206 residue. This finding confirms the importance of using a larger QM region since our results disclose some important differences when compared with previous computational studies of the same mechanism. These results provide valuable insights into the catalytic mechanism of *Is*PETase that can contribute to the rational development of more efficient engineered enzymes.

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Acknowledgments: This research was supported by national funds from the Portuguese Foundation for Science and Technology (FCT) under the scope of the strategic funding UIDP/04378/2020 and UIDB/04378/2020. The author acknowledges FCT by funding 2020.01423.CEECIND/CP1596/CT0003.

Molecular design for catalytic activities of helical chiral oligoureas

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Aliphatic N,N'-linked oligoureas that fold with high fidelity (foldamers) have recently be shown, together with peptides, as robust alternatives to achieve challenging asymmetric transformations. Specifically, it has been observed that short foldamers combined with achiral Brønsted bases act as H-bond donors, and are able to catalyze challenging C-C bond forming reactions with high enantioselectivity, and loadings as low as 1:10000 chiral catalyst/substrates molar ratios. In this investigation we used DFT computations to rationalize the influence of the aforementioned foldamers on the conjugate addition of diethylmalonate to (1E)-3-methyl-1-nitrobut-1-ene (see Figure 1). In the first place, a Global Optimization procedure was developed, which revealed the most probable position of the substrates on the catalyst surface: the nitroalkene occupies the second site, while the malonate ester is on the first. Furthermore, we found that the sites 1 and 2 of the foldamer are the only H-bond donor ureas which are capable to accommodate the substrates and stabilize the system through a set of interactions, predominantly with an electrostatic nature, because the rest of ureas are used in the folding process. The presence of the monomer (2 ureas) foldamer significantly decreases the frontier orbitals energy difference between the substrates, but the subsequent increase of foldamer's size does not influences this gap. Finally, we have observed that the R configuration is close in energy to the S configuration from monomer to tetramer, whilst it is strongly favored from pentamer to nonamer, what is in agreement with the experimental observations. This study reveals information at the atomistic level that is fundamental for further developments of foldamers as highly efficient catalyst.

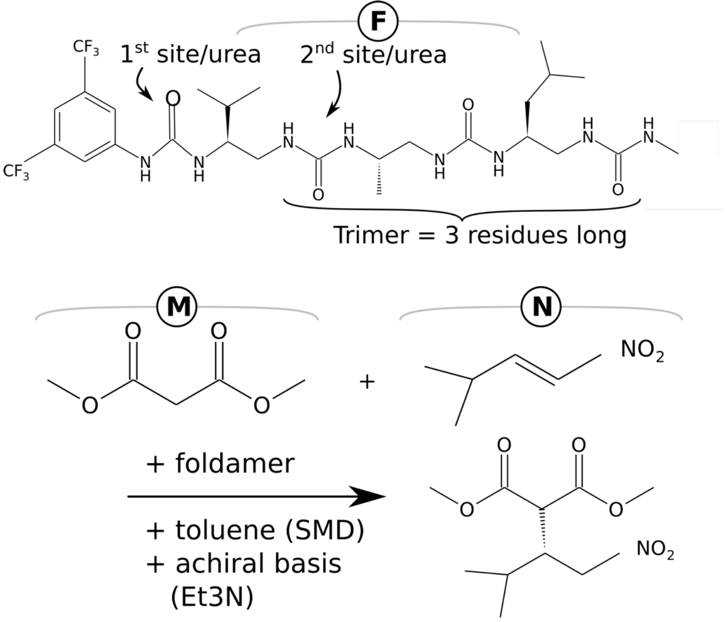

Figure 1. Foldamer (F) presentation and description, along with the diethylmalonate (M) – (1E)-3-methyl-1-nitrobut-1-ene nitroalkene (N) C-C bond forming reaction under study in our investigation.

A Molecular Model for Hydrated Silicate Ionic Liquids: Towards a Better Understanding of Zeolite Formation

PO104

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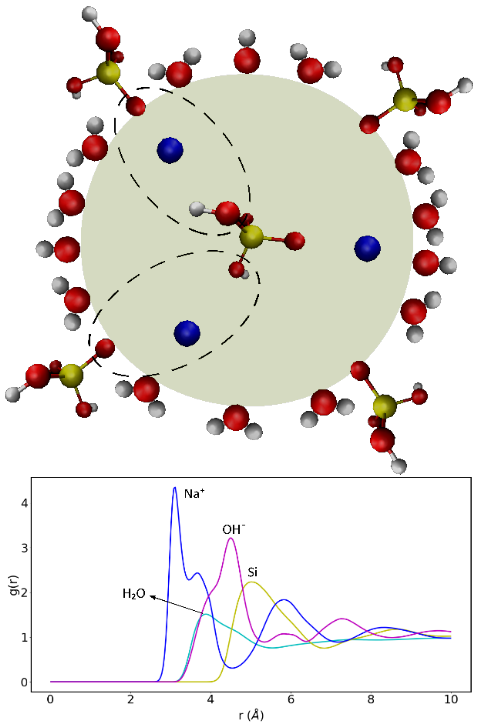

Figure 1. (top) 2D-intuitive representation of the local silicon environment in HSIL, showing the role of the cation and (bottom) corresponding RDF

Although zeolites are very important for many chemical industries, their formation process is not fully understood as their typical formation conditions are difficult to characterize experimentally. Theoretical models, on the other hand, have been hampered by a poor description of the hydrogen bond network present in the crucial water solvent. Recently, a new synthesis route was proposed involving hydrated silicate ionic liquids (HSILs), whereby the main problems (pressure build-up and gel-formation) for direct experimental observation and characterization are evaded [1]. Indeed, HSILs are fully clear, contain no particles or gel-phases and only a very limited number of water molecules. Furthermore, it was found that zeolite formation only occurs upon aluminium addition, allowing a very controlled propagation of the formation process. Since then, HSILs have been under intense experimental investigation in order to characterize the ionic liquid, asses the role of aluminium and construct a generally valid model for zeolite crystallization.

Given the low amount of water, the presence of only small molecular (alumino)silica species (monomers, dimers, 3- and 4-rings) and the fact that the formation only starts upon in introduction of (low amounts of) aluminium, accurate molecular modelling of these systems also becomes feasible. This is important as it is accepted that zeolite topology is solvent-governed and thus depends directly on the liquid structure of the growth liquid. As such, accurate modelling of HSILs gives important insights into the structure directing effects of the synthesis conditions and growth liquid composition towards the final zeolite topology. In this work, molecular dynamics simulations were used to characterize the ionic liquid and the behaviour of its cations in close collaboration with experimental results.

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Natural-orbital based multireference diagnostic for wavefunction methods

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The treatment of electron correlation is always a challenge in theoretical chemistry computations and simulations. The popular Single Reference (SR) correlated wavefunction methods (MP2, CCSD, etc.,) and Kohn-Sham DFT are good at capturing dynamic correlation, but poorly describe nondynamic correlation. When running a calculation, a diagnostic tool can help users decide whether to choose SR methods or Multi-Reference (MR) methods (CASSCF, DMRG,etc.,), the latter is usually more complicated and expensive.

Although a series of diagnostics exist currently, a recent work of Kulik and coworkers[1] have reported the disagreement between different diagnostic criteria, so it is still hard to use these diagnostics to evaluate dynamic or nondynamic correlation. In recent years, our group proposed the dynamic and nondynamic indices I_{D} and I_{ND} in terms of natural spin-orbital occupancies[2,3]. Later, Martin and coworkers[4] have pointed out that our I_{ND} is not size-intensive as it scales with system size. Hence, in this work, we firstly propose the following normalization factor to ensure our indices are size-intensive, we also suggest a new index $I_{\mathrm{ND}}^{\max}$ for measuring non-dynamic correlation,

$$I_{\mathrm{D,norm}} = \sqrt{\frac{8}{M\,N}}\left(\frac{1}{4}\sum_{\sigma,i}[n_i^\sigma(1-n_i^\sigma)]^{1/2} - \frac{1}{2}\sum_{\sigma,i} n_i^\sigma(1-n_i^\sigma)\right) \tag{1}$$

$$I_{\mathrm{ND,norm}} = \frac{1}{N}\sum_{\sigma,i} n_i^\sigma(1-n_i^\sigma) \tag{2}$$

$$I_{\mathrm{ND}}^{\max} = \max\{n_i^\sigma(1-n_i^\sigma)\} \tag{3}$$

M being number of molecular orbitals, N the total electron number and n_i^σ the natural spin-orbital occupancies. We analyze the performance of over 20 diagnostics in an extensive dataset using CCSD and MP2 wavefunctions. We determine the agreement between each pair diagnostics, and classify according to their ability to identify the non-dynamic correlation. We find that our new index $I_{\mathrm{ND}}^{\max}$ can indicate the same information of MR character compared with D_2 diagnostic of CCSD and MP2, and the $I_{\mathrm{ND}}^{\max}$ can be obtained in a much easier and cheaper way.

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Exploring Co(III)-based fluorination reactions. A Density Functional Theory study

PO106

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Noble-metal catalysts, such as Ru, Pt, Rh and Ir, are well-known for their high catalytic activity in a wide number of chemical processes. However, the scarcity of these metals and subsequent high economical cost calls for their progressive replacement by first-row transition metals, which are far environmentally friendlier, as well as much more earth-abundant, and thus significantly less expensive. In this regard, cobalt-based complexes stand up as promising candidates for such important processes as the dehydrogenation of alcohols, C–H bond activation and fluorination reactions [1].

Within this context, we focused on fluorination reactions based on Co(III)-complexes bearing Cp* and phosphine ligands (see Figure 1). It should be noted that this kind of molecular architecture has recently been shown to be active in fluorination reactions[1b,2]. Nonetheless, the information on how the reaction proceeds at a molecular level is very limited, and mechanistic proposals are generally based just by relaying on chemical intuition. Namely, to the best of our knowledge, any in-depth DFT study of Co-based fluorination reactions has been performed.

This way, we have taken the system depicted in Figure 1 as a case study, and the relative energetics of the potential reaction pathways have been studied by means of Density Functional Theory. The calculations point towards the reaction proceeding via a Co-assisted nucleophilic addition of the reacting fluoride anion to the C atom, directly releasing the chloride moiety and the final product. The results have also been rationalized by means of several chemical bonding tools such as the ELF, NBO and IQA [3].

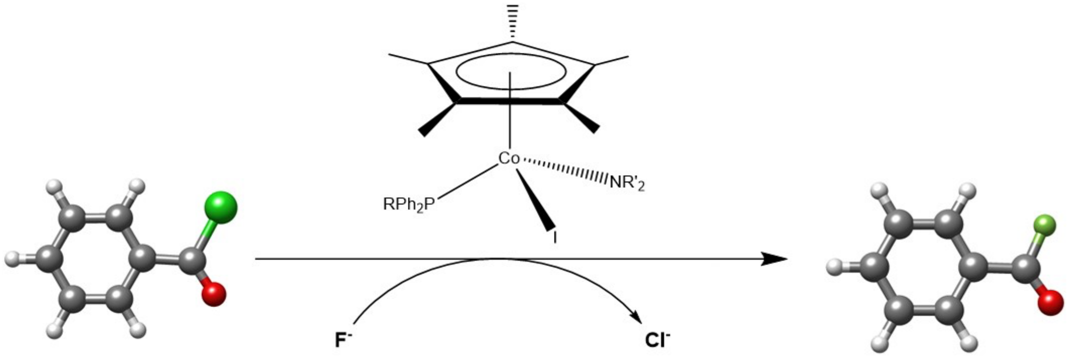

Figure 1. Fluorination reaction of benzoyl chloride catalyzed by the Co(III)-complex which bears a bidentate triazole-phosphine ligand, Cp* and yodide.

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Rationalizing the geometrical and electron density influence on the efficiency and emission energy of TADF derivatives

PO107

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Thermally activated delayed fluorescence (TADF) plays a key role in the design of highly efficient organic light-emitting diodes [1]. The mechanism of the process consists in both, direct fluorescence (25%) and delayed fluorescence produced after thermal transformation of triplet to singlet excited states (75%), known as reverse intersystem crossing (rISC). Achieving the triplet-singlet states energy degeneracy, hence facilitating the rISC, the efficiency of the system increases [2].

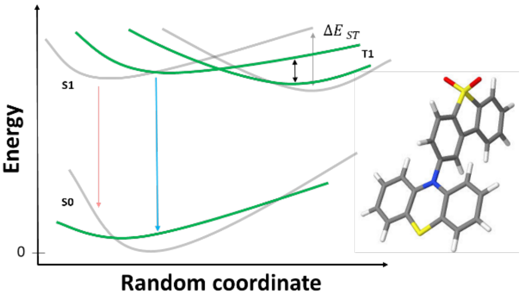

Figure 1. Description of the system

In this work we use the model system PTZ-DBTO2 (phenothiazine-dibenzothiophene-S,S-dioxide) to help us to understand the models proposed and how to modulate the electronic character of the adiabatic surfaces to achieve greater process efficiency (Figure 1) With the aim of rationalize the efficiency and emission energy modulation on TADF systems, we propose several derivatives differing on the electronic nature and position of the substituents. The effect of each substituent will be analysed by considering two components. On the one hand, it is analysed the influence of the variation in the geometry, with respect to the unsubstituted system, due to the variation of the energy minimum. On the other hand, we consider the effect that the substituent causes, for a given geometry, on the relative stability of the surfaces involved in the process, mainly driven by electron density variations. By analysing the results, we finally propose TADF derivatives with degenerated T_1-S_1 states, hence improving the rISC and the TADF system efficiency. Moreover, we have analysed the substituent effect on the emission energy for the most efficient candidates. It should be remarked that in general, an increase of the energy emission, that is a blue-shift of the emission spectrum is observed for them. Hence, this work get insight and would guide into the design of novel and efficient TADF systems.

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Topology of the Electron Density and its Laplacian from Periodic LCAO Calculation on f-Electron Materials

PO108

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The nature of the chemical bonding (CB) of f-electrons is as fascinating as still puzzling. Many aspects of this intricate phenomenon are widely studied since its full rationalization would have both fundamental and technological relevance. The main objective of our research work is the development of new methodologies for a better description of CB features for materials containing Lanthanides and Actinides. The most rigorous technique allowing for a description of multiple aspects of CB is Bader's quantum theory of atoms in molecules and crystals (QTAIMAC). At the core of this methodology is the topology of the electron density, and therefore, it can in principle be adopted both experimentally and theoretically, thus allowing for a mutual validation of the two approaches. In this context, we have extended the TOPOND library of the CRYSTAL code[1], which implements the QTAIMAC, to f- and g-type basis function. Then, we applied our new methodologies to systems that have already been experimentally studied in order to validate our approach. In particular, we considered the papers by Gianopoulos et al.[2] and by Zhurov et al.[3], which investigated, from an experimental point of view, uranium-containing compounds, respectively the $[PPh_4][UF_6]$ and the $Cs_2UO_2Cl_4$ crystals. On our side, we simulated these systems from the theoretical point of view and we got a really coherent description of many aspects of the chemical bond with experimental data[4,5]. Since a remarkable agreement represents a strong mutual validation of both approaches, we decided to work a common system, the UCl_4, along with the Toledo university and to try to understand if a union of the experimental and theoretical methodology could give us a further improvement.

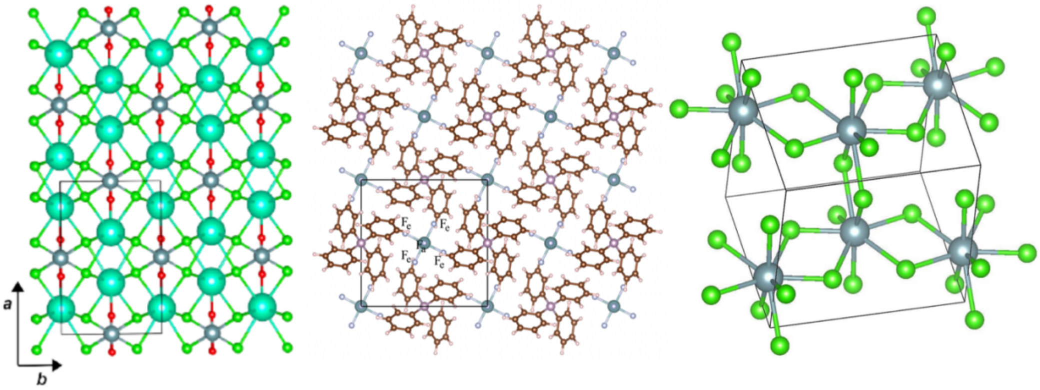

Figure 1. The three systems under investigation (from left to right: $Cs_2UO_2Cl_4$, $[PPh_4][UF_6]$, UCl_4)

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Ge as a promoter for the catalytic oxidation of CO by Pt clusters

PO109

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Carbon monoxide (CO) is one of the major pollutants in the chemical and automotive industry. Thus, the catalytic oxidation of CO plays an important role in the removal of CO from automobile exhausts, industrial emissions of incomplete combustions of hydrocarbons and hydrogen feedstock gas for fuel cells. CO oxidation is also used as a probe reaction to study more complex reaction such as the Fischer–Tropsch proccess[1-3]. Platinum group metals (PGM) are the most widely used catalyts[4]. Nonetheles, they present several drawbacks like high cost and low durability. The high afinity to CO is especially problematic as it can lead to the poisoning and degradation of the catalyst[5]. In this regard, bimetallic clusters have attracted widespread attention over the last decades as they offer several degrees of freedom to fine-tune the catalytic properties, such as size, composition and morphology[6]. In addition, more economical elements can be used and thus the PGM loading is reduced, making them more appealing for large-scale production. In this work, we have studied the effect of Ge doping small–size Pt clusters supported on MgO(100) on the oxidation of CO by means of a combination of density functional theory (DFT) and microkinetic modeling. To begin with, global minima search techniques were used to locate the most stable structures and adsorption sites for CO and O_2 molecules. Thereafter, a concise mechanistic study of the main reaction pathways was carried out, *viz.*: Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms.

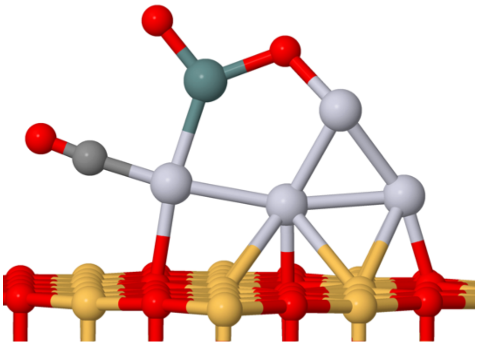

Figure 1. $Pt_4Ge/MgO(100)$ with co–adsorbed CO and O_2.

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Hydrogen bonds as controlling elements of preferential growth processes of ZnO structures: an integrated experimental-theoretical approach

PO110

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The multifunctional behaviour of ZnO material is determined in part by the electronic structure, which depends on the size, shape, and crystallographic facets of the particle surfaces. This study highlights the key role of a synergistic experimental-theoretical approach in providing deeper insight into the growth mechanism and photocatalytic behaviour of hierarchical ZnO structures [1]. The DFT calculations revealed that the preferential growth processes of ZnO structures are driven by O─H···O hydrogen bonds as controlling elements. The specific structural motif of the $(ZnO─H_2O)_{12}$ dodecamers with calculated negative $\Delta_rG^*_{INT}$ free release energy indicates that the formation of an anisotropic nanocrystalline ZnO with the *c*-axis as the primary growth direction is spontaneous and accelerated exclusively in "pure" aqueous solution, whereas it is an unfavourable endergonic process in aqueous NaOH solution ($\Delta_rG^*_{INT} > 0$; Fig 1). According to the X-ray absorption spectroscopy measurements, the ZnO particles obtained in "pure" aqueous solution show the highest photocatalytic activity, which is due to the presence of a larger amount of oxygen vacancies.

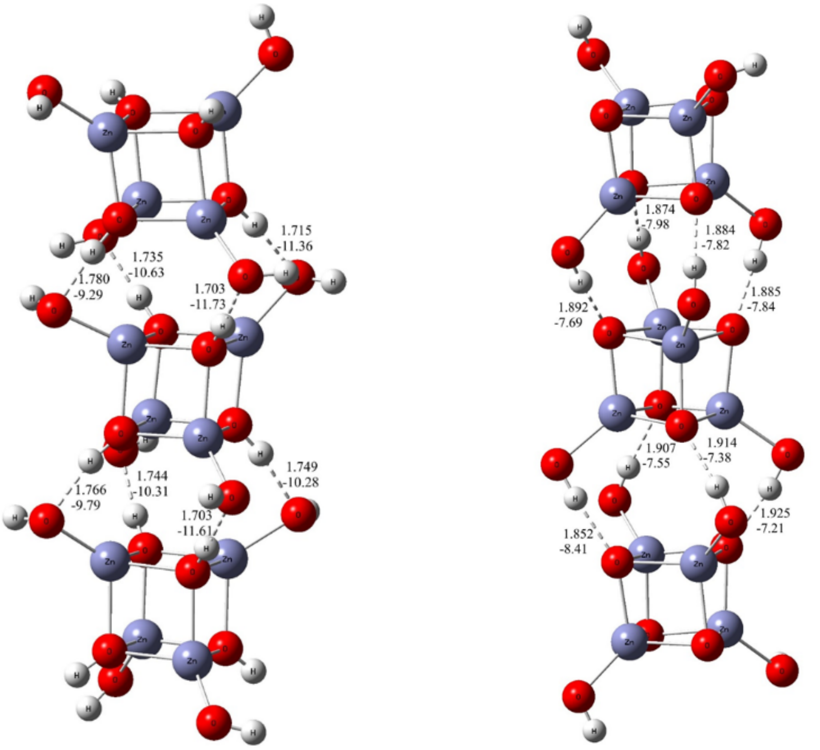

Figure 1. The most stable structures of the $(ZnO─H_2O)_{12}$ with $\mathbf{\Delta_rG^*/kcal\ mol^{-1} = -3.05}$ (left) and $(ZnO─OH^-)_{12}$ with $\mathbf{\Delta_rG^*/kcal\ mol^{-1} = 24.94}$ (right) (d/Å, $E_{O\cdots H}$ /kcal mol^{-1}).

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Does N–methylation protect amino acids against ionising radiation?

PO111

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We present a combined experimental and theoretical study of the possible protective effect caused by single and double N-methylation of glycine from ionising radiation[1]. For this purpose, the complex fragmentation dynamics of excited doubly ionised N-methylglycine (sarcosine) and N,N-Dimethylglycine (DMG) molecules in the gas phase have been the subject of our study. Ionisation, excitation, and subsequent fragmentation of the molecules are induced in low-energy (keV) collisions with O^{6+} particles. Multicoincidence mass spectrometry techniques and quantum chemistry simulations (ab initio molecular dynamics and density functional theory) allow us to characterize the produced fragments, and to obtain information on all possible exit channels, as well as their associated mechanisms. We focus on the doubly ionised species, where the coincidencemeasurements provide valuable insight in the fragmentation dynamics and pathways.

Interestingly, instead of a protection effect caused by the methyl groups, the reactivity following radiation is enriched; in particular a large number of possible fragmentation channels from molecular reorganisation are observed in the doubly ionised sarcosine. One of them shows a delayed fragmentation, appearing in the microsecond timescale; a complex pathway leading to this exit channel has been characterised, and explains the metastability of the parent doubly-charged ion with the presence of significantly high energetic barriers. As a general trend, we observe similar behaviour in the fragmentation of sarcosine with its isomeric linear amino acid β-alanine, and in the evolution of DMG in comparison with glycine. Thus, we conclude that N-methylation barely protect amino acids from ionising radiation.

A good understanding of the ionizing radiation effects in molecules could help us to correctly comprehend the mechanisms that lead to damage in biological tissues, proteins and DNA. Other amino acids like glycine [2], β-alanine [3] or Betaine [4] have been previously studied in the group.

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Computational study of the molecular packing in crystalline polyethylene using DFT-based methods with van der Waals functionals

PO112

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The rationalization of the packing modes of long aliphatic chains [1] is crucial in the development of molecular materials, since the addition of these chains can strongly modify the properties of a material with the same functional core. The simplest system to study supramolecular interactions between chains is polyethylene (PE). Since its first synthesis in 1898, polyethylene's properties have been broadly studied and its crystalline structure has been obtained by X-ray and neutron diffraction. For these reasons, PE is an excellent system to validate several methods to describe the weak interactions between chains [2] without the presence of other functional groups.

In this work, the interaction energy between PE chains has been determined considering the polymorphs obtained when the packing mode is changed [3]. Density functional theory (DFT) calculations have been carried out using van der Waals type functionals. Calculations using several force fields have also been made. Analysing the results we found the relative stability of the polymorphs, the relation between the different phases, and their interconversion energy. We used phonon calculations (Figure 1) to determine if a structure is mechanically stable. We also wanted to compare the accuracy and the limitations of using the most popular force fields used in computational modelling of polymers and molecular materials.

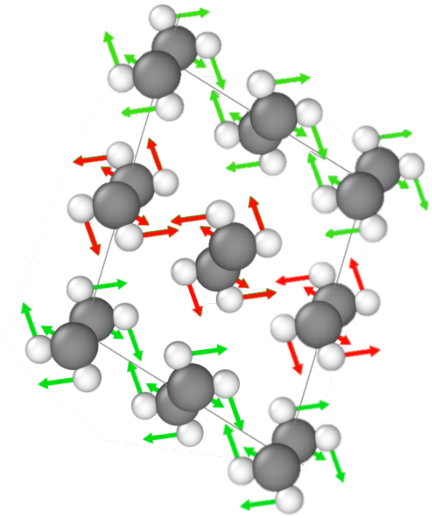

Figure 1. A concerted rotation of polymer chains in the monoclinic polymorph of polyethylene.

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Kinetics of the CH_3OH + H reaction. Theoretical calculations of thermal rate constants and kinetic isotope effects

PO113

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The kinetics of the abstraction reactions of hydrogen atoms with methanol have been studied using variational transition state theory with multidimensional tunnelling corrections (VTST/MT). This is an important reaction in combustion chemistry at very high temperatures and interstellar chemistry at very low temperatures. Two reaction channels are considered: hydrogen abstraction from the methyl group (R1) and hydrogen abstraction from the hydroxyl group (R2), R1 being much more likely to occur in the wide temperature range under study (250-2000 K), as expected from the lower barrier height and statistical factors. Results agree better with experiment [1] than most theoretical values, but in the intermediate temperature range, relevant to low-temperature combustion chemistry, theoretical rate constants tend to underestimate reactivity, suggesting that barrier heights could be overestimated despite the high *ab initio* calculation methods employed [2]. The importance of tunnelling, relevant to low temperature chemistry and astrochemistry, is discussed.

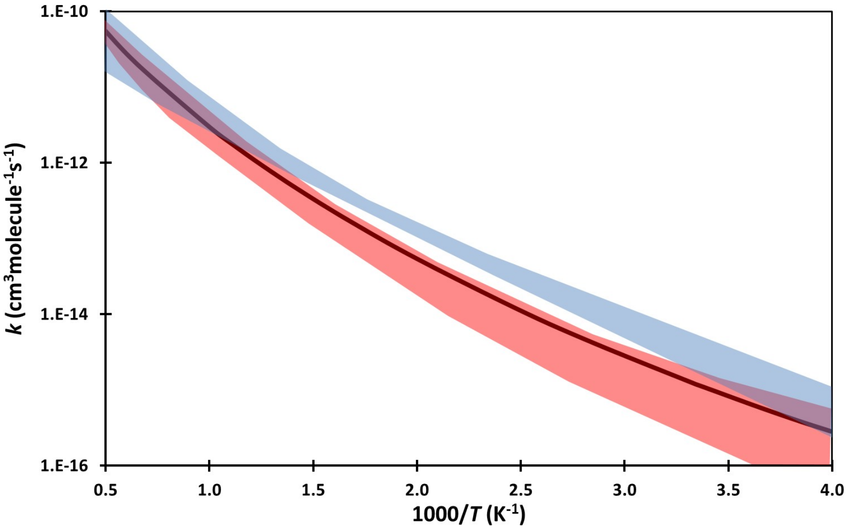

Figure 1. Arrhenius plot of the rate constants from the present work (solid line), experimental values [1] (blue shaded area), and previous theoretical values [2] (red shaded area)

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On Astrochemistry's Century-old Celestial Mystery

PO114

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More than 500 absorption lines exist in celestial spectra whose molecular sources are unknown; an unsolved astrochemistry mystery spanning a century. A key of our objectives is to facilitate the identification of the DIBs' chemical carriers. By identifying diffuse interstellar bands (DIBs) with correlated equivalent widths (EWs) and comparable dependencies on dust [1-3], interrelated DIBs may be subsequently compared with experimental or calculated spectra. To that end, observations from *The Apache Point Observatory Catalog of Optical DIBs* [4] were analysed, and high correlations were discovered. The highest correlations amongst 56893 DIB pairs are (in Å) 6284.05-6203.58, 6203.58-5780.64, 6993.12-6269.89, 6843.76-6792.51, 6203.58-5487.64, and 5061.50-4969.12. The highest correlations with optical reddening $E(B - V)$ were found for λ(Å)= 5236.27, 5793.24, 5797.18, 6449.27, 6795.26, 5948.87, 6113.22, 6860.02, 6059.34, 6520.74. We have begun an investigation to compare observational constraints with results from RASCALL (*Rapid Approximate Spectral Calculations for ALL* [5]).

METHODS: The *Apache Point Observatory Catalog of Optical DIBs* samples DIBs in the wavelength domain between 4000 and 9000 Å. A total of 25 sightlines were surveyed toward the stars that are primarily of an earlier type to reduce stellar line contamination. DIB wavelengths, EWs, EW uncertainties, and optical reddening $E(B - V)$ were adopted from Fan *et al*. [4]. Pearson correlations and their uncertainties were determined via Monte Carlo simulations.

RESULTS: The highest correlations for the resulting 56,893 DIB unique pairs are conveyed in **Table 1** (for a comprehensive listing see [3]). The highest EW–$E(B - V)$ correlations featuring $n > 15$ sightlines are displayed in **Table 2**. (For a full tabulation see [2]). Importantly, independent observations are desirable to support the findings.

Table 1

DIB_1 (Å)	DIB_2 (Å)	$r \pm \sigma_r$
6284.05	6203.58	0.990 ± 0.001
6203.58	5780.64	0.986 ± 0.001
6993.12	6269.89	0.984 ± 0.001
6843.76	6792.51	0.984 ± 0.005
6203.58	5487.64	0.983 ± 0.002

Table 2

DIB (Å)	n	$r \pm \sigma_r$
5793.24	19	0.916 ± 0.009
5797.18	23	0.915 ± 0.004
6449.27	21	0.912 ± 0.008
6795.26	18	0.910 ± 0.008
6113.22	18	0.897 ± 0.006

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Ab initio characterization of vanadium species at TiO_2 anatase surfaces through IR spectra simulation

PO115

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The selective catalytic reduction (SCR) of NO and NO_2 (NO_x) by NH_3 to N_2 and H_2O is a well-established technology to control the emission of NO_x formed during combustion in diesel engines, power plants and other pollution sources. This type of catalysis is heterogeneous and the most widely used catalyst for the SCR process in power plants is vanadium oxide (vanadia) dispersed on titania oxide (anatase) [1,2]. Although these systems have been studied extensively in the past, no clear conclusion about a catalytic mechanism, especially on the atomic level, has been made which demonstrates the complexity of the catalytic chemistry of the SCR process [1-3]. What is known is that in operando condition a vanadium +5/+4 redox cycle occurs. Vanadium +4 surface complexes are characterized by the presence of a single unpaired electron in the 3d orbitals and so Electronic Paramagnetic Resonance (EPR) is a useful technique to characterize these systems [4]. Infrared (IR) spectroscopy is also informative as it can monitor the TiO_2 coverage and evaluate the acidity of catalytic sites through the analysis of OH stretching bands [5].

In this work the CRYSTAL code [6] is used to characterize and investigate vanadyl complexes at TiO_2 surfaces. A great advantage in studying catalysts with CRYSTAL is the possibility of easily use hybrid functionals (mixture of the Hartree-Fock and Density Functional Theory approaches): the presence of an exact exchange term deriving from Hartree-Fock calculations allows to deal with electron correlation, something to take in account describing transition metals centres in which the electrons can be highly localized and correlated.

With CRYSTAL different vanadium complexes have been modelled considering monomers and dimers of V^{+4} and V^{+5} on (101) and (001) anatase surfaces. The goal of this study is to validate the proposed surface complexes and to establish an unambiguous correlation between structure and hyperfine couplings or IR frequencies. EPR parameters have been accurately predicted and compared with experimental data in a recent publication [4] while here IR stretching of different OH present on the surface will be evaluated and compared with experiment, see for example Figure 1. This analysis can allow to distinguish different catalytic sites present on the surface and to presume their acidity and reactivity towards NO_x and NH_3.

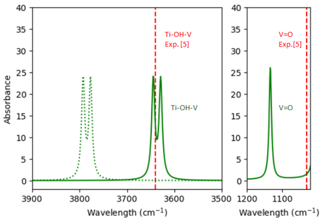

Figure 1. Computed IR spectra for a vanadyl monomer on anatase (001) surface (green dotted line for harmonic approximation, green thick line for anharmonic correction), red dashed line for experimental data from [5].

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Functionals benchmark for photophysical properties of pyranoflavylium derivatives

PO116

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In recent years, the search for new photosensitive molecules for various applications has increased e. g., photodynamic therapy (PDT) and dye-sensitized solar cells (DSSC). The environmental appeal directs this investigation towards molecules of natural origin and their analogues, since they are ecologically friendly and biologically compatible. In this context, chromophores analogous to pyranoanthocyanins present in red wine are potential photosensitizers for photodynamic processes, due to their spectroscopic properties [1,2]. Thus, it was carried out an in-depth study of the photophysical processes of a group of pyranoflavylium cations using density functional theory and its time-dependent variant. Furthermore, for the simulation of the excited states of these chromophores, the performance of several density functionals was evaluated and compared to wave function methodology and experimental data. Aspects such as molecular orbitals, excited state diagram, energy of photophysical processes and configuration weights were discussed and analyzed with emphasis on photodynamic therapy. The obtained errors revel that for singlet states processes the hybrids yield smaller errors than range-separated ones. In opposite direction, range-separate present smaller errors for triplet emission. Although there are many functional options, choosing the most suitable to photophysical processes could be a non-trivial task and it is often arbitrary.

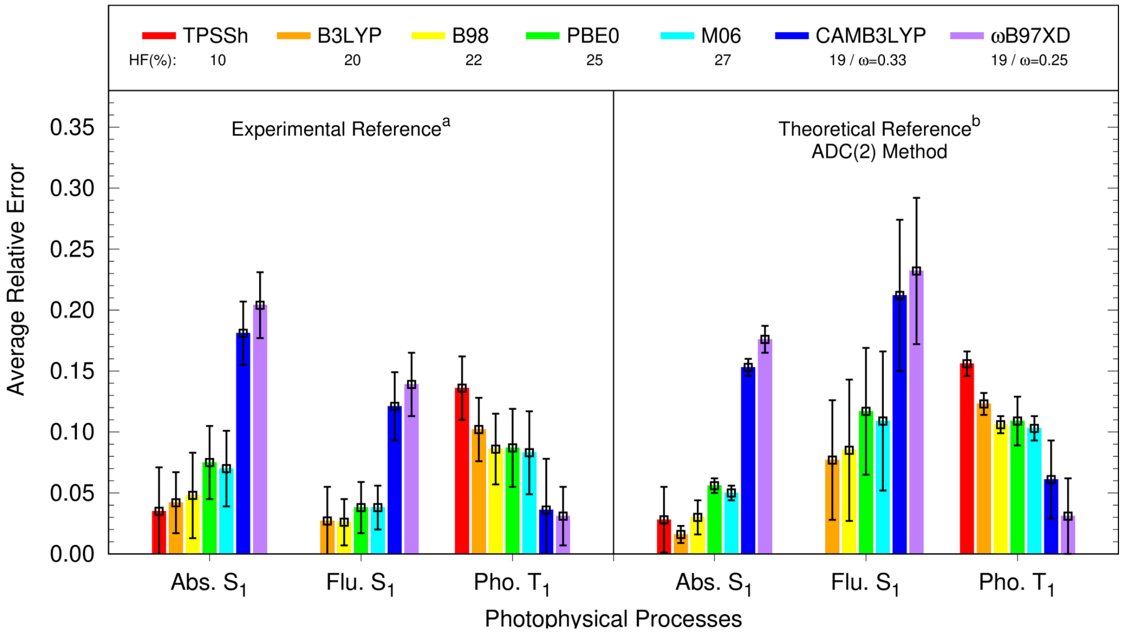

Figure 1. Average relative error of energy (eV) of the photophysical processes

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On the use of MC-PDFT and TD-DFT calculations to evaluate the inversion of the first singlet-triplet excited states

PO117

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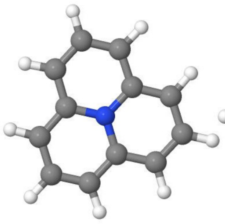
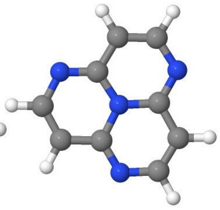
There is some uncertainty in the calculations of the first singlet (S1) and triplet (T1) excited states of unconventional conjugated organic chromophores, where the TD-DFT model does not seem to work correctly. Despite the multitude of exchange-correlation functionals used, other factors must be considered for their correct evaluation [1].

New data have recently emerged on the inversion between singlet-triplet states[2], leading to conside- ration of the solvent effect or extended character of an amorphous organic material [3], incorporating a polarized continuum model (PCM) [4].

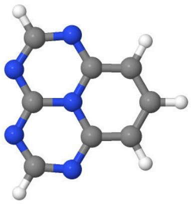
In this work we show the results for a set of molecules belonging to the azaphenalene family (mono- (MAP), tetra-(TAP), penta- (PAP) and hepta-azaphenalene (HAP)), for which a relative energy reversal of the first excited states S1 and T1 has been recently documented, giving rise to a negative energy difference (ΔEST) between them (See refs. of [1]).



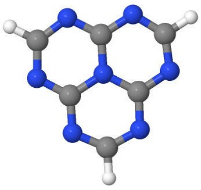
MAP



TAP



PAP



HAP

Along with the TD-DFT methods, we will employ a non-standard density functional method, Multi- Configurational Pair Density Functional Theory or MC-PDFT [5,6], where MC means a Complete Active Space Self-Consistent Field (CASSCF) wavefunction with an active space of N electrons housed in M orbitals, or simply (N,M), to incorporate non-dynamic (or static) correlation effects in a consistent way. All calculations have been performed using the def2-TZVP basis set [7] and the Gaussian16 [8] or GAMESS [9] calculation programs.

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Fast and Simple method to predict Oriented External Electric Field Induced Catalysis and Selectivity

PO118

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In the oriented external electric-field-driven catalysis, the reaction rates and the selectivity of chemical reactions can be tuned at will[1]. The activation barriers of chemical reactions within external electric fields of several strengths and directions can be computationally modelled. However, the calculation of all of the required field-dependent transition states and reactants is computationally demanding, especially for large systems. We have developed fast and accurate approach based on the Taylor expansion of the field-dependent energy of the reactants and transition states in terms of their field-free dipole moments and electrical (hyper)polarizabilities to predict the reactivity and selectivity induced by the presence of external electric fields[2]. This approach, called FDBβ, allows to easily generate one-dimensional (1D), two-dimensional (2D) (Figure 1), and three-dimensional (3D) representations of the activation energy barriers for any strength and direction of the external electric field. The calculation of the field-dependent FDBβ energy barriers has a computational cost several orders of magnitude lower than the explicit electric field optimizations, and the errors of the FDBβ barriers are within the range of only 1−2 kcal·mol^{-1}. The achieved accuracy is sufficient for using FDBβ as a fast-screening tool to study and predict the best orientation of the external electric field to achieved the desired catalysis, regioselectivity, and stereoselectivity. As illustrative examples, four cycloadditions (1,3-dipolar and Diels−Alder) were studied.

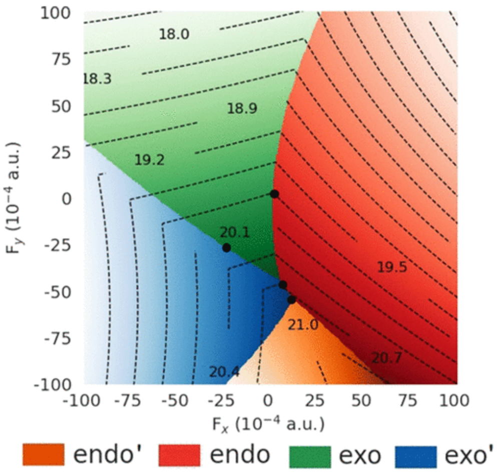

Figure 1. 2D representation of the FDB$_\beta$ barriers for the catalysis and selectivity of the (3 + 2) dipolar reaction between phenyl diazomethane and methoxyethene.

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PO119

How Aromatic Are Molecular Nanorings?

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Porphyrin nanorings are very attractive compounds because they offer a π-conjugated system with remarkable properties such as photophysics, which could lead to a variety of applications in the field of electronics [1], serving as light-harvesting antennas [2], or investigate energy transfer in biomimetic systems [3], among others. Thus, large conjugated rings with persistent currents are promising new structures in molecular-scale electronics. In this sense, a structure of six porphyrin nanorings was recently synthesized that allegedly sustained an aromatic ring current [4]. We provide here convincing evidence that this molecule is poorly aromatic, contrary to what was inferred from analysis of ^{1}H-NMR data and computational calculations that suffer from large delocalization errors. These results highlight the importance of choosing a suitable computational method to study conjugated large molecules and aromaticity descriptors. Furthermore, we show that indirect evidence of a ring current from experimental ^{1}H-NMR data is not definitive proof of aromaticity.

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Back to curly arrows representation by using BET: towards a deeper understanding of reaction mechanisms

PO120

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Detailed knowledge of how take place the bond formation/cleavage processes along the reaction progress is one of the central research topics of chemistry. This work seeks to solve one of the basic problems in chemistry learning: describing the molecular mechanism of chemical rearrangements by using the curly arrows representation based on detailed physical grounds. This concept is deeply embodied in the chemistry textbooks to rationalize how a chemical reaction occurs, i.e. how old bonds are broken and new bonds formed. Due to the experimental challenges, theory is far more advanced than experiment. To this end, the bonding evolution theory (BET), which combines the topological analysis of the electron localization function (ELF) and Thom's catastrophe theory (CT), has established to provide and visualize the bond breaking/forming evolution, i.e. the electron density flow. This has already facilitated remarkable improvements ~~of~~ about how the curly arrow notation is retrieved and allows a representation of the movements of electrons in the framework of quantum mechanics. Present findings lead to a more comprehensive foundation for chemical reactivity theory and covers highlights performed in our research group. The usefulness of BET will be notably illustrated on selected representative examples [1-4].

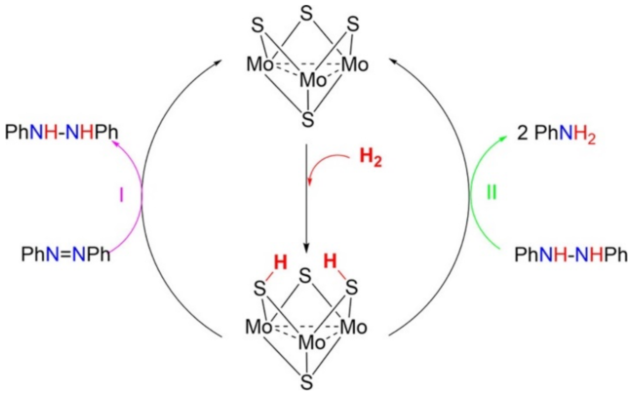

Figure 1. Mechanism proposed for the catalytic conversion of azobenzene into aniline. The figure illustrates the operation of two interconnected catalytic cycles, one for the hydrogenation of diazobenzene (cycle I) and another for the hydrogenation of 1,2 diphenylhydrazine (cycle II)

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Accelerated Screening of the Thermoelectric Efficiency of Skutterudites by Machine Learning

PO121

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When approximately 70 percent of energy produced by humans is wasted as heat, improving the efficiency of the grid is as important as using environmentally friendly energy sources. Thermoelectricity stands out as one of the best solutions to recycle that heat, producing electricity. The discovery or optimization of more efficient and less expensive thermoelectric materials cannot be seen as an easy task. During the last decades, significant resources have been dedicated to the improvement of the efficiency of these materials, measured by its figure of merit, *ZT*. The importance of computational material science in the discovery of new thermoelectric materials has run in parallel to the development of new frameworks and methodologies to compute the electron and thermal transport properties linked to *ZT*. A large set of methods, packages and frameworks have been developed during the last twenty years to predict the aforementioned properties [1,2]. The main disadvantage underneath all these options stems from the accuracy-computational cost trade-off. In the last years, new approaches have been developed to reduce the computational cost or the need of experimental data without compromising the accuracy of the results. The use of machine learning techniques in the calculation of interatomic force constants has drastically reduced one or two orders of magnitude the computational cost of predicting the lattice thermal conductivity of solids using the Boltzmann transport equation [3]. On the other hand, new efficient methods have been reported for calculating carrier scattering rates of semiconductors and insulators from first principles without any external parameter [4]. To the best of our knowledge, we combine these new strategies to compute ZT for first time. This approach does not only guarantee accurate values for ZT but also reduces the cost, giving the opportunity of studying larger sets of materials to understand the physical and chemical factors that govern thermoelectricity. In this work, the whole family of skutterudites MX_3 (M = Co, Rh, Ir; X= P, As, Sb), with high potential applications in thermoelectrics, is explored.

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Using Molecular Dynamics simulations with organic solvents/water mixtures to identify I2 binding sites

PO122

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The imidazoline receptors (IRs) are a group of pharmacologically characterized receptors involved in several physiological functions. Specifically, I2-IR are involved in a variety of human brain disorders, ranging from depression to Alzheimer’ s type dementia[1], to Parkinson’ s disease[2] and glial tumors. Indeed, selective I2 ligands have shown great potential as neuroprotective agents[3], however, to date efforts aimed at identifying the molecular structure of I2-IRs have been unsuccessful. A growing body of evidence suggests that at least some neuroprotective effects associated to I2 ligands may not be due to the interaction of I2 ligands with an unknown macromolecular receptor but could instead be related to their ability to bind to I2-sites located in different proteins. Specifically, Monoamino Oxidase B, Creatine Kinase and Nischarin have all been shown to bind I2 ligands [4,5]. Furthermore, preliminary results that combine proteomics and thermal shift assays have highlighted up to five additional proteins that display both altered expression patterns and relevant shifts in thermal stability in the presence of selective I2 ligand 2-(2-benzofuranyl)-2-imidazoline (2BFI).

In this work, we employed Molecular Dynamics simulations using solvation boxes of water/organic solvent mixtures[6] in order to characterize putative I2 sites within the structure of several proteins. Specific probes including ethanol, iso-propanol, pyridine, ammonium acetate and water are used to identify high-affinity interaction hotspots for molecular features present in I2-ligands, both on the interior and surface of the protein. Density analysis for the retained solvent molecules has provided useful insights for the identification of the binding sites able to accomodate I2 ligands.

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Hybrid core shell materials for OER by first principles calculations

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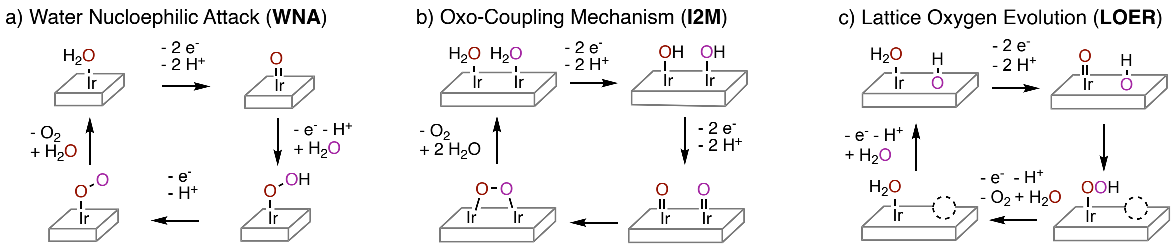
PO123

Extensive research is currently focused on H_2 production as sustainable sunlight storage source [1]. This takes place through water electrochemical splitting through the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), with the former being widely considered to be the rate-determining half reaction [1,2]. Many different catalysts have been developed for the OER and IrO_2 provides great efficiency in acidic media owing to its stability in the harsh acidic media and activity. Yet reaction upscaling remains limited by the costly iridium [3]. Thus, research naturally develops into mainly two different directions: i) reducing the kinetic overpotential may enhance the process' overall efficiency; and ii) advanced nanofabrication could provide an effective means to minimize metal loading on the catalyst without compromising its activity [4]. Hybrid core shell nanoparticles happen to conveniently merge both strategies: not only can their catalytic properties be tuned finely, but their composition may also be changed to perfectly suit the required noble metal ratio at the catalytic sites whilst minimizing its content elsewhere [4].



Scheme 1. Proposed reaction mechanisms for the oxygen evolution reaction [5].

In this contribution we will show our work on the catalytic activity for the oxygen evolution reaction of three hybrid core shell surface models: $RuO_2@IrO_2$; $Ir@IrO_2$ and $IrNi@IrO_2$. For each material, we will discuss, by means of DFT periodic calculations, the feasibility of the three most frequently described OER mechanisms, namely, the water nucleophilic attack (WNA), the oxo-coupling mechanism (I2M) and the lattice oxygen evolution reaction (LOER) (Scheme 1) [5]. Moreover, we will also analyze how the shell-to-core ratio influences the catalytic performance and report the most efficient systems, which ultimately will allow us to propose new potentially active materials.

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The impact of functionalization in the fluorescent properties of BODIPY derivatives

PO124

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During the past decades, the boost in biomedical research has called for the design of new tools for diagnosis and treatment of both animal and human medical conditions. Thus, the search for innocuous, efficient, and non-invasive tools for detection of diseases, being tumors one of the most desired targets, has become one of the hottest topics in multidisciplinary research. We have recently proposed a turn-on hypoxia sensor based on a BODIPY group coupled to an azo benzene moiety [1]. These non-emissive dyes are able to turn on their emission properties under chemical and biological reductive conditions and have opened the door to the rational design of new BODIPY derivatives with the desired photophysical properties.

Supported by state-of-the-art quantum chemical calculations, our aim is to understand the influence of the linker atom(s) connecting the BODIPY and aromatic chromophores in response to light upon irradiation. Our results reveal that both structural and electronic density rearrangement when reaching the excited state are key pieces to scrutinize the photophysical behavior of these systems following photon absorption.

Eventually, we aim at the rational design, and synthesis of highly efficient dual-fluorescent probes coupling two organic dyes through a specific linker that allows the electronic disconnection between the former, perpetuating their emissive properties.

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Lewis Structures from Open Quantum Systems Natural Orbitals: Real Space Adaptive Natural Density Partitioning

PO125

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Building chemical models from state-of-the-art electronic structure calculations is not an easy task, since the high-dimensional information contained in the wave function needs to be compressed and read in terms of the accepted chemical language. We have already shown in a previous work [1] how to access Lewis structures from general wave functions in real space by reformulating the adaptive natural density partitioning (AdNDP) method of by Zubarev and Boldyrev [2]. This provides intuitive Lewis descriptions from fully orbital invariant position space descriptors but depends on not immediately accessible from the output of electronic structure codes of higher order cumulant density matrices. By using an open quantum systems (OQS) perspective [3], we here show that the rigorously defined OQS fragment natural orbitals can be used to build a consistent real space adaptive natural density partitioning (rs-AdNDP) based only on spatial information and the system's one-particle density matrix. We show here that the rs-AdNDP approach is a cheap, efficient, and robust technique that immerses electron counting arguments fully in the real space realm. A simplified pseudocode flowchart of the present rs-AdNDP algorithm is given below.

```
1. Obtain the density matrix $\rho$ and the atomic overlap matrices (AOM)
2. n=1;  nloc=1;  $\rho_{deplet}=0$; $\rho^0_{deplet}=0$.
3. do while [(n≤maxcent)and (nloc ≤ N)]
4.     if (ncenter, 2 electron (nc,2e) bonds desired)
5.         for all ntuples(n)
6.             if [(n=1) and is hydrogen (H)  and  skip(H)] or
7.                 [(n=2) and (nlinks>maxlinks)]  or
8.                 [(n>2) and (all coordinations < 2)] go to 16
9.             $S \leftarrow \Sigma_A S^A$
10.            obtain $S^{1/2}$ and $S^{1/2}\rho S^{1/2}$
11.            diagonalize $S^{1/2}\rho S^{1/2} - \rho^0_{deplet} \rightarrow \lambda_i, v_i$
12.            for all $\lambda_i$ eigenvalues
13.                if ($\lambda_i \geq \varepsilon_n$) ===> [(nloc +1 $\leftarrow$ nloc) and (save $v_i$)]
14.            end for
15.            increase $\rho_{deplet}$ by $\Sigma_{\lambda i=1} \lambda_i v_i v_i^t$
16.        end for
17.    end if
18.    n+1 $\leftarrow$ n; $\rho^0_{deplet} \leftarrow \rho_{deplet}$
19. end do
```

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NNAIMQ: a combined ML/QTAIM approach for the fast prediction of electron populations

PO126

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The electron density (ρ) plays, undeniably, a crucial role in the chemistry realm, being a fundamental pillar for both theoretical and experimental perspectives. Similarly, the local values taken by ρ, as measured by partial or atomic charges, are key to the development of numerous chemical models and rules that constitute the chemical narrative. Among the many different schemes developed for the calculation of atomic charges, the Quantum Theory of Atoms in Molecules (QTAIM) [1] offers a particularly rigorous and solid alternative. However, the computational cost attributed to these, and other, real space based techniques has restrained their application to simple molecular systems of reduced complexity and size. In this work [2] we exploit the extraordinary inferring abilities brought by machine learning (ML) to develop a neural network (NN) model, NNAIMQ, for the computation of QTAIM atomic charges. NNAIMQ is a Python interfaced model gathering a collection of atomistic NN to reconstruct the partial charges of C, H, O or N containing systems relying solely on the atomic numbers and nuclear positions. The training was performed in a collection of more than 45.000 structures (~ 10^5 atomic environments for each element) of the equilibrium or near-equilibrium chemical space computed in the gas phase and at the DFT level of theory (M06-2X/def2-TZVP). The molecular environments were extracted from a combination of different data-bases to account for most commonly encountered functional groups in the CHON chemical universe. The performance of the NNs is put to the test in a variety of scenarios, including equilibrium geometries, molecular dynamic simulations and even chemical reactions. The results show that the NNAIMQ model is able to accurately predict the expected quantitative and qualitative trends in the electron populations even for high energy regions of the potential energy surface, well beyond the training interpolation regime. Altogether, we consider that this work constitutes a good starting point for the extension of expensive real-space techniques to the state-of-the-art chemical research, paving the way towards the calculation of large systems at feasible time-scales.

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PO127

Reactivity of the superhalogen/superalkali ion encapsulating C_{60} fullerene

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The Diels–Alder (DA) reaction rate of ion-encapsulated fullerene ($Li^+@C_{60}$) with cyclopentadiene was reported to be 3 orders of magnitude faster than empty C_{60} [1]. There are significant number of experimental and theoretical study suggesting that the reactivity of C_{60} fullerene is enhanced by encapsulation of cationic species [2]. Herein, we show a mechanistic study of the DA cycloaddition reaction between 1,3-cyclohexadiene and a series of C_{60} fullerenes with encapsulated superalkali (SA)/superhalogen (SH) species ($Li^+@C_{60}$, $Li_2F^+@C_{60}$, $Cl^-@C_{60}$, and $LiF_2^-@C_{60}$) by means of DFT calculations.[3] The reactivity of the ion encapsulating systems was compared to that of the parent C_{60} fullerene. Significant enhancement in reactivity was found for cation-encapsulating $Li^+/Li_2F^+@C_{60}$ complexes. The cycloadduct formed by $LiF_2^-@C_{60}$ was found to be the most thermodynamically favorable among the studied ones. In contrast, encapsulation of $Cl^–$ anions disfavors the cycloaddition reaction both kinetically and thermodynamically. Higher activation energy barrier and less stability of the reaction product in the case of $Cl^-@C_{60}$ were associated with the higher deformation energies of the fullerene cage and the lower interaction energy between the reactants in comparison with the other studied complexes.

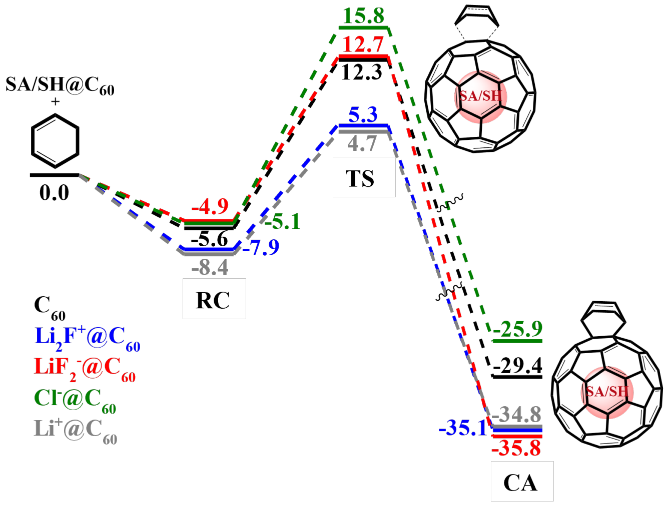

Figure 1. Computed reaction profiles for the DA reaction involving SA/SH encapsulated fullerene. Relative energies are given in Kcal mol^{-1}.

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Electron Transport in Peptide Based Molecular Junctions

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PO128

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The field of molecular electronics is coming along in the design of nanocomponents for its integration in molecular scale devices. However, nature has provided with efficient gears from biological systems with unique characteristics as they were not designed but evolved. This is why, in the last decades, a significant effort within the field has developed towards mimicking biological systems for integration into biocompatible electronics. This potentially could provide cleaner and cheaper chemical compounds also capable of selective reactivity, highly specific substrate recognition and binding, and efficient and directional electron tunnelling.

Herein, the analysis of a set of short peptides for its possible integration in single-molecule junctions is performed [1,2]. For these peptide chains, the effect of the length, the nature of the substituents and the anchoring group coupling is going to be evaluated and compared with equivalent alkyl and alkene chains. For this aim, the electron transport ability of different systems will be computed within the scope of the Electron Deformation Orbital (EDO) method [2]. This method allows for the discrimination of the electron transport channels from a molecular orbital perspective so that the process can potentially be understood in terms of the different amino acid or other molecular moieties contributions. In addition, the effect of length and conformational changes in the peptide chain will also be analyzed.

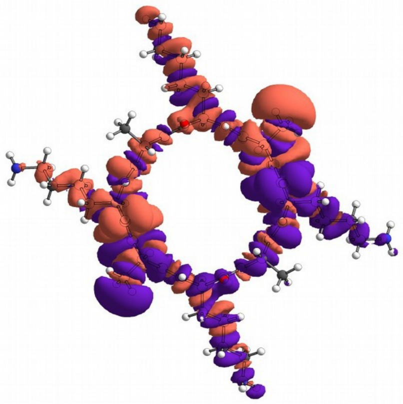

Figure 1. Electron transport channels responsible for the conductance in a cyclic peptide molecular junction.

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Photoreduction of gaseous oxidized mercury compounds: quantum chemical modelling and environmental implications

PO129

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Air pollution is considered to be the world's largest environmental health risk by the World Health Organization. The negative effects that atmospheric contaminants have on the environment and on human health reflect the urgent need to reduce their anthropogenic emissions. For that purpose, atmospheric models can be used to simulate the global dynamics of these contaminants and analyze their dispersion and accumulation around the globe. To obtain accurate simulations, a correct description of the thermal and photochemical reactivity that governs the atmospheric cycle of these species is mandatory. However, the photochemistry of atmospheric compounds is sometimes scarcely understood, leading to models and simulations that do not match field observations.

That is the case of mercury (Hg), a strong neurotoxin of global concern that is released into the atmosphere mainly in its elemental form Hg(0), which can then be further oxidized to reactive Hg(I) and Hg(II) derivatives. Due to the efficient deposition on Earth's surface shown by the latter, the chemical cycling between these species ultimately determines the fate of this contaminant in the atmosphere. Over the last few years, we have explored the response to irradiation of atmospheric Hg compounds and the impact of their photochemistry on the global cycle of this metal. By means of the SA-CASSCF and MS-CASPT2 methods, in conjunction with a nuclear-ensemble computational approach, theoretical absorption spectra were computed for a collection of atmospheric Hg(II) and Hg(I) derivatives of atmospheric interest [1,2]. In addition, the conversion mechanisms among Hg(II), Hg(I) and Hg(0) species were studied by means of *ab initio* non-adiabatic molecular dynamics (AINAMD) with the CASSCF method, obtaining the branching ratio of the different photodissociation channels for each compound [3]. Taking advantage of the computed cross sections and photolysis yields, photolysis rates and lifetimes were estimated for each compound using a global chemistry-climate model. Combining each photoproduct percentage and the photolysis rates, a quantitative kinetic model for the atmospheric photochemistry of the major Hg compounds was constructed, showing that the photoreduction of these species leads directly, or indirectly, to elemental mercury. These results suggest that gas-phase photolysis can dominate atmospheric Hg reduction. When evaluating the impact of this photoreduction in a state-of-the-art global chemical transport model, we observe that the photochemistry of Hg(I) and Hg(II) species leads to an unrealistically long Hg lifetime, implying that a key missing Hg(0) oxidation pathway is still unaccounted for in current atmospheric models [4].

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Water–Gas Shift Reaction on Cu/TiO_2 Surfaces Promoted by Potassium

PO130

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It is well-known that the activity and selectivity of a heterogeneous catalyst can be substantially affected by the addition of an alkali metal. The addition of potassium atoms to Cu(111) and Cu/TiO_2(110) surfaces significantly enhances the rate for water dissociation and the production of hydrogen through the water–gas shift reaction (WGS, CO + H_2O → H_2 + CO_2) [1,2]. In the range of temperatures investigated, 550–625 K, Cu/K/TiO_2(110) exhibits a WGS activity substantially higher than those of K/Cu(111), Cu(111), and Cu/ZnO(0001 systems used to model an industrial Cu/ZnO catalyst. The apparent activation energy for the WGS drops from 18 kcal/mol on Cu(111) to 12 kcal/mol on K/Cu(111) and 6 kcal/mol on Cu/K/TiO_2(110). The results of density functional calculations show that K adatoms favor the thermochemistry for water dissociation on Cu(111) and Cu/TiO_2 (110) with the cleavage of O–H bonds occurring at room temperature. Furthermore, at the Cu/K/TiO_2 interface, there is a synergy and this system has a unique ability to dissociate the water molecule and catalyze hydrogen production through the WGS process. In summary, addition of an alkali promoter on the metal–oxide interface appears to be essential in the optimization of multifunctional catalysts [3].

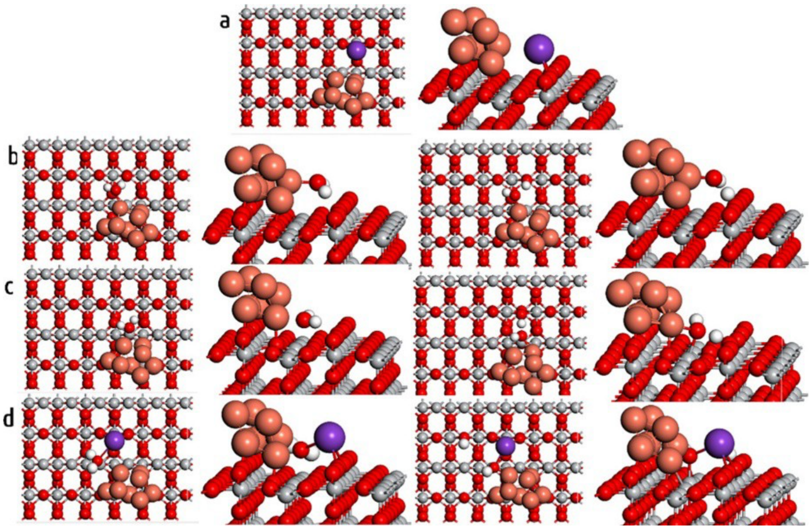

Figure 1. (a) Model for adsorption of K and Cu cluster on the TiO_2(110) surface. (b) Water adsorption on the Cu/TiO_2 interface: Cu cluster site. (c) Water adsorption on Cu/TiO_2: interface site. (d) Water adsorption on Cu/K/TiO_2 interface. Colors code: Cu (light brown), K (violet), O (red), and H (white).

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Solid-state effects on the singlet-triplet energy gaps of switchable biradicals

PO131

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Biradicals are not only important for understanding the nature of chemical bonding but also in materials chemistry because their unique electronic, optical, and magnetic properties show great potential for organic electronics and spintronics[1]. The key parameter that defines the physical properties of biradicals is the energy gap between the lowest singlet and triplet states. It has been shown that the singlet-triplet energy gap of biradicals based on bis(triarylamine) dications can be controlled in the solid state by means of changes in temperature[2,3]. In this contribution, the mechanisms behind the thermal control of the singlet-triplet energy gap will be explained. The solid-state DFT calculations combined with the first-principles molecular dynamics simulations that have been carried out to understand these mechanisms show the key role played by intermolecular interactions in the solid state in controlling the singlet-triplet energy gap of charged biradicals.

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Reaction force and reaction electronic flux profiles of alloxydim herbicide

PO132

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The food demand by a growing world population and the intensive agriculture, have led to the widespread use of pesticides to maximize crop yields. In this way, numerous legislations arise throughout the world in the last fifty years demanding to perform practical and pragmatic risk assessments of these compounds based on scientific data before their commercialization and use. Many times, obtaining these data has required performing studies on vertebrates. However, the growing animalist awareness in society is also beginning to be reflected in the regulations. In this regard, the Preamble 11 of the European Pesticide Regulation (EC) No. 1107/2009 notes that "*the development of non-animal test methods should be promoted in order to produce safety data relevant to humans and to replace animal studies currently in use*". In this sense, the search for new approaches to study the relationships between both quantum properties that can be studied at a computational level [1, 2] and ecotoxicological effects on target organisms is arousing great interest [3].

This work proposes a quantum chemistry methodology where the reaction force and the reaction electronic flux profiles were explored for the cyclohexanedione oxime herbicide alloxydim and some of its derivatives at B3LYP/6-311G(d,p) level of theory. The exploration was achieved by varying the dihedral angle located nearby the most reactive regions in order to understand the responses of the, for example oxime group (**Figure 1**), against this perturbation, highlighting the intrinsic structural and the electronic reorganization.

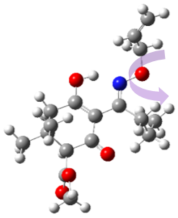

Figure 1. Alloxydim with arrow indicating the dihedral angle that was rotated, next to the oxime group.

The results showed that the rotation of the dihedral angle triggers the alloxydim to go through three transition states. The first step of the transformation begins by the cleavage of the hydrogen bond and is characterized by a pronounced structural reorganization. The electronic reorganization is more important to return to the same structure in the last step of the process. In between, N-O bond goes through different state of the reinforcement and weakening showing the ideal conformer where the oxime fragment might be dissociated.

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PO133

Electrostatic embedding of Machine Learning potentials

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Machine Learning (ML) potentials are rapidly gaining popularity as an affordable and precise alternative to quantum mechanical calculations. However, the computational cost of ML potentials is still prohibitive for large and heterogeneous condensed phase systems, such as biopolymers in explicit solvent. Therefore, hybrid "ML/MM" schemes, with ML only being employed for a small part of the system while the rest being described by a cheap molecular mechanics (MM) force field, would offer huge savings of computer time. Unfortunately, approaches used for embedding a QM region into an MM environment in state-of-the-art QM/MM are not applicable for ML. For instance, electrostatic embedding relies on the electronic density of QM part being polarized by the MM environment. ML potentials, generally, do not provide description of the electronic density, let alone it's response properties, rendering electrostatic embedding inapplicable.

In the present work we show how the interaction energy between QM and MM subsystems can be reproduced by physically motivated models of molecular electrostatics and polarizability combined with ML approaches for predicting atomic properties. Using only a small set of diverse molecules as the training data, it was possible to reproduce both the electrostatic potential and the polarizability of the entire QM7 dataset, consisting of 7165 molecules covering wide chemical space. This result opens the possibility of an ML/MM embedding scheme applicable to a wide range of problems in condensed phase simulations.

A theoretical study of the photophysical and photochemical behavior of two derivatives of 3-Hydroxyflavone

PO134

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In substituted flavones with electron-donor or electron-acceptor groups, electron transitions produce important charge fluxes; as a consequence, these compounds can display large hypsochromic and hypochromic shifts. Besides, flavonols can display Excited State Intramolecular Proton Transfer[1]. The frequency and intensity of the emission bands (from the excited initial state N* or from the excited tautomer T*) can be modeled by a suitable choice of substituents and solvents, being able in some cases to observe dual fluorescence[2]. Due to the different chemical nature of the absorption and emission structures, the Stokes shifts can be very large; because of this it has been proposed the use of these compounds as frequency shifters.

In this work, photophysical and photochemical properties of two flavones, 4’-diethylamino-3-hidroxyflavone and 4’-diethylamino-3-hidroxy-7-methoxyflavone, in protic and aprotic solvents are studied using implicit (Polarizable continuum model, PCM[3]) and explicit solvent (Averaged Solvent Electrostatic Potential from Molecular Dynamics calculations ASEP/MD[4]) models. Free energy differences between the critical points of the ground and excited state surface have been calculated. This analysis has consented to clarify the role played by the solvent in the relative stability of the two tautomers.

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A theoretical study of the photophysical properties of 3-hydroxyflavone

PO135

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The 3-hydroxyflavone and related compounds have received much attention [1] over the last few decades as they serve as model systems to study Excited State Intramolecular Proton Transfer (ESIPT)[2]. During the ESIPT reaction of a flavonol a proton is transferred in the excited state from the hydroxyl to the carbonyl group. The frequency and intensity of the emission bands (from the initial state N* or from the tautomer T*) can be modeled by a suitable choice of substituents and solvents, being able in some cases to observe dual fluorescence [3]. This characteristic joined to the large Stokes shift of flavonols explains the importance of these compounds as fluorescent probes, fluorescent sensor, organic light emitting diode, etc. [4].

Photophysical and photochemical properties of 3-hydroxyflavone in protic and aprotic solvents have been studied using implicit (Polarizable continuum model, PCM) and explicit solvent (Averaged Solvent Electrostatic Potential from Molecular Dynamics calculations ASEP/MD) models. The conformational equilibrium in the excited state between the Normal (N*) and Tautomer (T*) forms and their absorption and fluorescence spectra has been studied with Time-Dependent Density Functional Theory (TD-DFT) and three different functionals. The calculated transitions are in good agreement with the spectroscopic data. It was found that solvent effects on the absorption and fluorescence spectral bands are negligible but they can modify appreciable the relative stability of N* minimum with respect to the Franck-Condon position.

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Triplet Excitonic States Character Description in Perylenebismide Aggregates

PO136

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Perylene-3,4:9,10-bis(dicarboximide) (PDI) and its derivatives are well known visible organic chromophores with excellent optoelectronic properties for energy and charge transport [1]. Moreover, their molecular rigidity results in robust thermal and photochemical stabilities, and strong absorption capabilities of visible and near-infrared (NIR) light. Photophysical properties of PDI aggregates are of special interest as light-harvesting materials in organic photovoltaics [2].

While low-lying singlet excitations of PDI have been largely investigated, much less is known about their triplet states. Despite that the triplet manifold is not initially accessible through photoexcitation, recent studies have identified spin triplets as the final photoproduct states upon exciton decay processes in PDI covalent dimers [3] and in the crystal [4].

Recently, a simple diabatization procedure within a restricted orbital space has been used to analyze the Frenkel Exciton (FE) and Charge Transfer (CT) character of singlet adiabatic states of PDI aggregates [5]. By contrast, few investigations have been reported for the analysis of triplet states [6] of PDI dimers. In the present work, we aim to analyze the lowest excited triplet states of molecular dimers of PDI. To that end, we have computed the vertical adiabatic triplet excited states by means of the time-dependent (TDDFT) version of the Density Functional Theory (DFT) for a number of molecular configurations along the intermolecular longitudinal translation coordinate. We have then applied a simple diabatic approach [5] to analyze the CT/FE character of the triplet states and the interplay of inter-molecular interactions determining the adiabatic energy profiles of the lowest triplet exciton states.

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About the Correlation Between Structure and Solvent Effects in Absorption Spectra: Flavonols

PO137

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3-Hydroxyflavone (3-HF) is the base structure of a group of flavonoids called flavonols[1]. Many of these compounds have important photophysical and photochemical properties as they can undergo proton transfer in the excited state (ESIPT[2]) and, depending on the environment, they can give rise to one or two fluorescent signals; that is, they can exhibit dual fluorescence. The interesting photochemical properties of flavonols can be tuned in several ways: modifying the skeleton structure of the molecule, introducing electron donor or acceptor groups, changing the solvent, etc. Solvent effects on the UV-Vis spectrum of 3-hydroxyflavone and other three molecules structurally related (3-hydroxychromen-4-one, 3-hydroxy-4-pyrone and 4-pyrone) have been studied by combining Time Dependent Density Functional Theory (TDDFT) and the Polarizable Continuum Method (PCM[3]). The interesting photophysical and photochemical properties of 3-HF are related to the formation of an intramolecular hydrogen bond and to the π→π* character of the first transition. Among the first five excited states of the four considered molecules both n→π* and π→π* electronic sates are located. The stability of n→π* increases in solution and with the decreasing of the number of π orbitals, in such a way that the n→π* state become the first exited state both in 3-hydroxy-4-pyrone and 4-pyrone. Given that the photophysical and photochemical properties of 3-HF need a first excited state of π →π* nature, only the 3-hydroxychromen-4-one can be used as simplified model to study the photochemistry of 3-HF. The performance of corrected-Linear Response[4] and IBSF[5] versions of the Specific State PCM method in predicting the transition energies are compared.

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Hydrogen bonds and their binding modes

PO138

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Hydrogen bonds (HB) are one of the most important and abundant non-covalent interactions yet many aspects have still to be well described. Prevalent in the recognition of molecules between a substrate and a corresponding enzyme making it a crucial step in many biological processes[1]. A multitude of life essential processes rely on site specific binding, proving the significance of molecular recognition, and are highly established in the immune system and DNA replication that depend on the recognition of antigen–antibody and DNA–protein, respectively[2]. Furthermore, pharmaceutical drugs help achieve therapeutic effects by having structural complementarities with specific biological targets[2]. With this in mind, squaramide, thiourea and guanidinium systems, well reported to be highly effective in HB formation having the capability to form two HB with a reactant and offers linearity facilitating HB[3], were chosen for a DFT investigation to elucidate and provide insight on the preferential binding mode in biological systems.

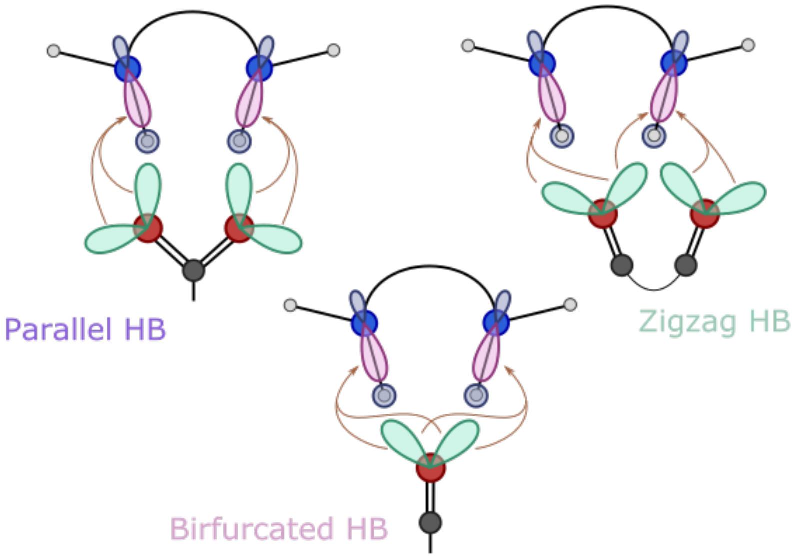

Figure 1. Three HB binding modes parallel (purple), bifurcated (pink) and zigzag (green)

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Shape-shifting molecules: disentangling the valence tautomerism phenomena in 1-substituted barbaralones

PO139

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The phenomena of valence tautomerism consists in a particular intramolecular process involving just one reactive species where a redistribution of bonding electrons gives rise to a different structure (see Figure 1). In this context, barbaralones are large fluxional molecules that are key to the understanding of the phenomena of valence tautomerism. They can go through low energy [3, 3]-sigmatropic process, where the number of valence tautomers rely on the presence and chemical nature of any possible substituent that induces isomerization constraints. Herein, we have interrogated an archetypal 1-phenyl barbaralone by means of high-resolution rotational spectroscopy coupled with laser ablation techniques. Guided by theoretical computations, the two valence tautomers of this bistable molecular system have been characterized in the isolation conditions granted by the supersonic jet [1]. This work provides definite experimental evidence of the [3,3]-rearrangement in barbaralones and highlights the use of rotational spectroscopy to analyze shape-shifting mixtures. Moreover, we have extended our investigation to two edge cases, 1-methyl-barbaralone and 1-tert-butyl-phenyl-barbaralone, to shed light on the effect of the 1-substituent. This observation opens the door towards the characterization of new fluxional systems under isolation conditions and should serve as a reference point in the general understanding of valence tautomerism.

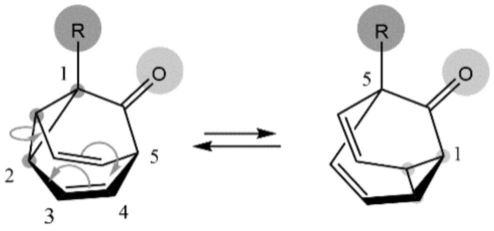

Figure 1. Valence tautomerism of 1-substituted barbaralones showing the σ-bond migratation and π-bond reorganization related to the sigmatropic equilibrium.

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Rate acceleration in water microdroplets: the case of the isoprene + OH reaction

PO140

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Recently, chemical reactivity in water microdroplets has attracted a lot of interest [1]. Reactions are very often accelerated in these microscaled aqueous systems, although the reasons for such catalytic effect remain elusive [2]. The phenomenon has strong implications, not only in environmental and atmospheric chemistry [3], but also for the development of environmentally friendly synthetic methods that reduce the need for organic solvents[4].

During the last years, we have developed a theoretical approach to study this phenomenon based on combined QM/MM molecular dynamics simulations, and several works have been devoted to assessing the role of cloud water droplets on the photochemical production of OH radicals in the atmosphere [5]. Our results have contributed to explain the difference existing between measured OH concentrations and concentrations predicted by current atmospheric models, which are mainly based on gas phase chemistry. The main conclusion of these studies is that many chemical reactions proceed significantly faster at the surface of water droplets (the air-water interface) than in bulk water solution. In this poster, we will present some results for the isoprene + OH thermal reaction, and will analyse the main factors determining interfacial catalysis [6].

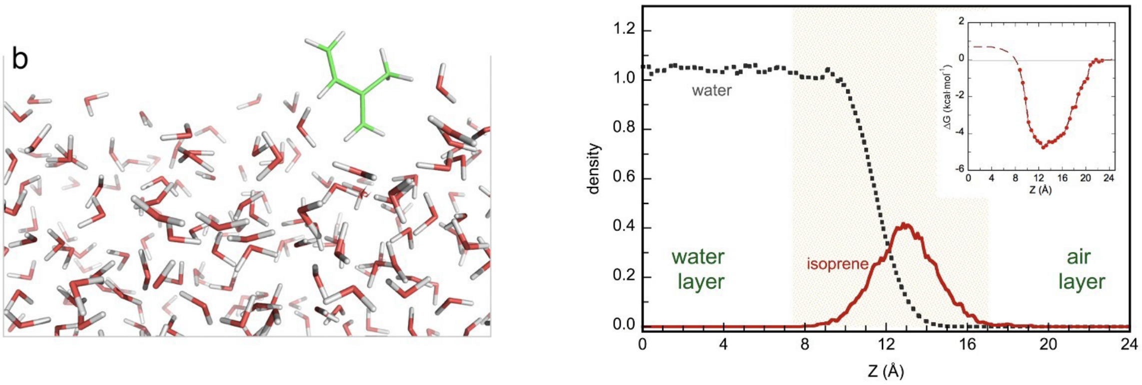

Figure1. Snapshot from QM/MM MD simulations of isoprene at the air-water interface and associated density profiles

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Assessment of Molecular Nanoreactor Simulations and Automated Reaction Network Construction

PO141

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In recent years, due to great improvements in terms of novel computational methods and computing resources, the automated computational exploration of chemical reaction space has gained more and more attention. A theoretical nanoreactor method was introduced by Wang *et al.* [1] and it uses *ab initio* molecular dynamics, along with an external potential to confine molecules to a periodically contracting sphere. This approach has already been applied to several test systems ranging from relevant organic molecules, including Miller–Urey type systems, to homogeneous systems resulting in the oligomerization of acetylene and the synthesis of graphene starting from a collection of ethylene molecules [1-3].

We present a comprehensive analysis of the parameters influencing the molecular nanoreactor outcome. In addition, an alternative form for the applied external potential is introduced, which has great importance for the variety of obtained species. Furthermore, we investigate the role of inert buffer atoms on homogeneous cyanhydric acid systems regarding the abundance of polymolecular reactions. An alternative, fully automated post-processing routine is outlined, based on RDKit, NetworkX, and PyVis, providing the user with a quantitative summary of the obtained species, a reaction database, and an interactive reaction network [4-5].

We apply this alternative nanoreactor concept on various homogeneous systems at the PBEh-3c/def2-mSVP level of theory, allowing for the comparison to results conducted with HF/3-21G and GFN2-xTB [6-8]. In addition, a collection of HCN molecules with buffer atoms, as well as the formose network are investigated focusing on the presence of primary and secondary precursors for the prebiotic synthesis of RNA.

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Prebiotic Thermodynamic “Selection of the Fittest” Anomers

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At a final analysis, both kinetics and thermodynamics must have played a dominant role in the evolutionary selection of life’s building blocks. Our calculations presented in this poster focuses on the latter control as a tool for “natural selection” of present-day known building blocks. The predominance of the β- over the α-anomers in nucleosides and nucleotides emerges from a thermodynamic analysis of their assembly from their components, i.e. bases, sugars, and a phosphate group. The calculations (DFT-B3LYP/6-31G(*d*,*p*)) suggest a slight but *consistent* thermodynamic advantage that favors the selection of the β- over the α-anomers. This is aligned with the concept of an evolutionary “energetic” selection of the fittest. Furthermore, the incorporation of uracil (U) into RNA and thymine (T) into DNA rather than the other way around is also predicted from the calculations. A comparison of the canonical (U-ribose, T-deoxyribose) vs. the non-canonical nucleotides of these two bases (U-deoxyribose, T-ribose) indicates an energetic advantage of the canonical pairs compared to the non-canonical pairs when gauged by the “sugar exchange reactions”. Furthermore, this thermodynamic advantage exists only for the β-anomers (10 kcal/mol) and vanishes in the case of the α-anomers. These results can be considered preliminary and will be refined at more accurate computational levels of theory.

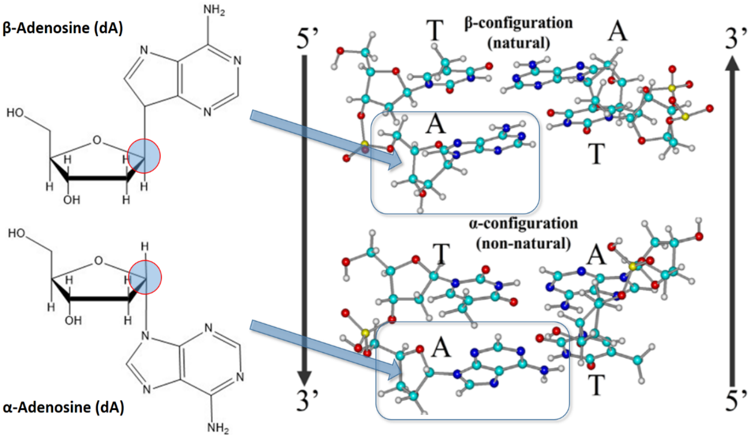

Fig. 1 Left: (*top*) An example of aβ-nucleoside (β-2'-deoxyadenosine), the form that predominates in present day nucleic acids, and **(*bottom*)** the corresponding α-isomer which is seldom observed. **Right: (*top*)** A representation of a present-day β-DNA Watson-Crick (WC) double-helix, and **(*bottom*)** a model constructed using molecular builders (*HyperChem / GaussView*) demonstrating the perfect *geometric* WC base pairing in the non-predominant form of α-DNA.

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Quantum Computational Chemistry. Current state and perspectives

PO143

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Quantum computing (QC) is an emerging paradigm exploiting quantum-mechanical phenomena, such as entanglement and superposition, to perform computation [1,2]. QC has the potential to offer computational capabilities beyond those of current, classical, supercomputers. Therefore, QC opens the door to dealing with many complex and computationally intractable problems in domains such as cryptography, data science, clean energy, quantum chemistry, and drug design, to name just a few. Specifically, in theoretical and computational chemistry, QC has gained increasing attention. This new approach, which we can call Quantum Computational Chemistry (QCC), seeks to develop, and apply, efficient QC algorithms for tackling theoretical chemistry problems (for detailed reviews of the primary, research, literature on the topic see [3,4]).

However, as in any emerging research field, there is a need in QCC to identify open challenges and future research directions. Here, the main problem is how to organize, analyze, and make sense of the large amount of scientific literature available. Beyond the traditional literature review, a new approach has emerged to extract information from the huge number of primary studies found in nowadays literature: the Systematic Mapping Study, SMS [5,6]. The SMS is especially well suited to identify research trends by analyzing the frequency distribution of publications and the time evolution of specific aspects of the topic considered.

In this work, we apply a previously developed bibliometric SMS approach [7] to perform a preliminary analysis of the current state and perspectives of QCC. Considering population and frequency of publication distributions over time, as well as co-citation relationships, we obtain a clear picture of the subjects in the field. Thus, we identify understudied topics which offer opportunities for new research programs.

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Solvent Effects on the Conformational equilibrium of Dipeptides

PO144

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The solvent effects on the conformational equilibrium of Glycine and Alanine dipeptides are studied using ASEP/MD[1-3] a QM/MM method based on the mean field approximation. Glycine and alanine are two of the structurally simplest amino acid found in nature and they are usually considered the amino acids that best conforms to the basic assumptions of the random coil model. It has been experimentally found, however, that in gas phase the conformational landscape of these dipeptides are dominated by only two structures (C5 and C7) characterized by the formation of an intramolecular hydrogen bond (HB). Here we show that a similar situation is found in water solution: the conformational equilibrium is also dominated by only two structures (PPII and α) that, furthermore, are not stable in gas phase and in which the intramolecular HB is replaced by an intermolecular HB. This behavior mimics that of other peptides which display less conformational freedom. We show that relative stability results from the interplay of two free energy components that operate in opposite directions: internal energy and dipeptide-water interaction energy[4,5]. The influence exerted by the solvent structure and the dipeptide charge distribution on the relative stability of the different conformers is also analyzed.

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A Hidden Bottleneck in the Accurate Computations of Vibrational Properties Using KS-DFT

PO145

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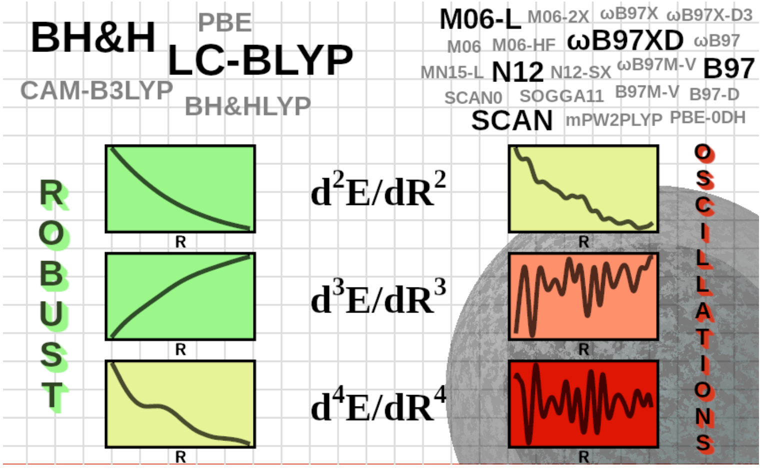
The increase of accuracy often comes hand-in-hand with the mathematical complexity of modern Density Functional Approximations (DFAs). Unlike most wavefunction methods, DFAs require the numerical integration of the exchange and correlation functionals, which is controlled by the size and type of the numerical integration grid. While an insufficient integration is popularly regarded as a technical problem introducing random uncertainties, Johnson and coworkers showed that it manifests through the regular oscillatory error patterns appearing in the potential energy surface (PES) [1, 2].

In this work, we reveal the true extent of this problem, much larger than is commonly anticipated. It is not limited to meta-GGAs or the dispersion-bonded compounds, and it leads to huge errors in the vibrational properties when unsolved. More strikingly, in many cases, these errors cannot be alleviated using grids even a few times larger than the largest predefined grids available in most computational packages. We propose an offline algorithm to efficiently detect and quantify such spurious errors. We determined which of the modern DFAs are grid-robust enough to provide the trustworthy property derivatives utilized in all vibrational spectroscopy. Hardly a handful of DFAs turned out to be safe to compute basic anharmonic corrections to the vibrational properties, whereas the most modern DFAs were valid enough only for the harmonic approximation. Our findings show that grid-dependency is a true bottleneck that limits all DFAs regardless of their physical truthfulness.



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The Intriguing Aromaticity of (Sub)Phthalocyanines

PO146

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The theoretical description of the aromaticity of (sub)porphyrins and (sub)phthalocyanines is challenging because of their size, topological flexibility and the existence of multiple π-electron circuits that can contribute to their aromatic character [1]. Most of the aromaticity studies found in the literature are limited to the use of nucleus independent chemical shift (NICS) [2,3]. However, taking into account the complexity of these molecules and the limitations of NICS it is necessary to go beyond NICS measurements and make use of more specialized methods. In this work, we will study the aromatic character of S_0 and T_1 states of eight systems employing a wide range of global [4,5] and local aromaticity descriptors. We also analyze similarities and differences between phthalocyanines and porphyrins. The study was performed at the CAM-B3LYP/cc-pVTZ level of theory, including a wide range of aromaticity indicators based on geometric (harmonic oscillator model of aromaticity, HOMA), magnetic (GIMIC) and electronic (fluctuation index (FLU), electron density of delocalized bonds (EDDB) [4], AV_{min} and AV1245 [5]) criteria. Our detailed analysis, provides new insights on the aromatic character of these molecules, which will be employed in the rational design of (sub)porphyrins and (sub)phthalocyanines derivatives with specific electronic structures.

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Theoretical study on lysine-targeting covalent inhibition mechanism in water and PI3Kδ enzyme

PO147

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Targeted covalent inhibitors have drawn attention over years because of its importance in drug design. Drug resistance is a crucial issue in oncology and targeted covalent inhibition is one of the promising strategies to overcome such problems. Covalent conjugation with conserved lysine residues is a new approach for selective inhibition of kinases. Recently, novel lysine-targeted ester inhibitors have been developed as selective irreversible inhibition of the heterodimeric lipid kinase phosphoinositide 3-kinase delta isoform (PI3Kδ) [1,2]. Even if their high potential in situ, the complex reaction mechanisms are not yet understood in a comprehensive manner. In this work, we have conducted computations at the MP2/aug-cc-pVTZ//B3LYP/6-311+G(d,p) level in aqueous environment on the aminolysis reaction of model ester compounds and enzyme cluster by method ONIOM (M062X/6-311+G(d,p):PM6) representing PI3Kδ inhibitors to provide insight into the reaction mechanism in the corresponding biological processes. We have shown that phenolic esters having electron-withdrawing groups are particularly reactive. The proposed mechanism involves tetrahedral zwitterionic intermediate formation, followed by dissociation to an alkoxide and a protonated amide. Our results reported[3] on structure-reactivity relationships and detailed reaction mechanism are shown to be useful guidance for developing future inhibitor candidates.

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Second-order NonLinear Optical Properties of A-Shaped Pyrazine Derivatives Enlarged with 2,5-Thiophene

PO148

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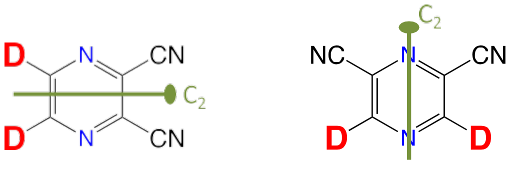
A-shaped chromophores have been proved as a good alternative to 1D chromophores to obtain large response properties adequate for electro-optic devices. Thanks to the existence of two low-lying excited states that contribute to first molecular hyperpolarizability β in an additive manner, these chromophores present a better trade-off between molecular nonlinearity and optical transparency, presenting low absorptive losses [1,2].

In this project linear and nonlinear properties of two new series of A-shaped pyrazine-derivative chromophores with (or almost) C_{2v} symmetry are investigated by means of density functional theory (DFT). The two series are differentiated by the orientation of the symmetry elements (C_2 axis and σ_v plane) of the point group, forming 2,3- and 2,6-isomers according Figure 1, and comprising cyano groups as acceptor units, methoxy groups as donor units, and 2,5-thiophene groups as π-conjugated linkers that systematically enlarge the Λ shape of the chromophore. Focusing on the different orientation of the C_{2v} symmetry elements and how these structural changes affect the electronic structure and the characterization of the electronic excited states of the chromophores, a rationalization of the second-order nonlinear responses (mainly Hyper-Rayleigh Scattering (HRS) hyperpolarizabilities and depolarization ratios (DR)) will be done from a fundamental point of view.

Moreover, the results obtained are compared with previously studied 2,3-"equivalents" where 1,4-phenyl linkers were used instead of 2,5-thiophene groups [3].



2,3-isomer 2,6-isomer

D = MeO, Thiophene $(Th)_n$ (where n=1-2), MeO-$(Th)_n$ (where n=1,2)

Figure 1. Pyrazine derivatives investigated in this work.

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Computational Studies on Endohedral Actinidofullerenes: Actinide-Cage Interaction and Asymmetrical Clusters

PO149

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Endohedral metallofullerenes (EMFs) are hybrid compounds that encapsulate metal atoms or clusters in their inner void space [1]. EMFs are stabilized by a charge transfer from the internal cluster to the carbon cage and in most cases, neither the cluster nor the cage would be stable independently. For example, the prototypical $Sc_3N@C_{80}$ can be explained simply by an ionic model, $(Sc_3N)^{6+}@C_{80}^{6-}$ [2].

During the last 20 years, many different metal atoms and clusters have been encapsulated inside fullerenes. Recently, the first metallofullerene containing an actinide, $Th@C_{82}$, was isolated and characterized[3]. Other mono-actinidofullerenes as $U@C_{80}$, $Th@C_{80}$, $U@C_{76}$, $U@C_{82}$ have been also characterized [4]. The actinide usually acts with formal oxidation state +4, which involves an important metal-cage interaction with significant covalent contributions what makes the ionic model less reliable than in lanthanofullerenes. Two actinides (U_2 and Th_2) and actinide clusters (U_2C, U_2N, …) have been also found inside different carbon cages, showing characteristic metal-metal and metal-cage interactions [5-6].

We here analyse at DFT (PBE0/TZP) level (i) The metal-cage interaction within a new family of mono-uranofullerenes $U@C_{2n}$ (2n=82, 86) showing that the most favourable position for a metal is determined upon the symmetry and the pattern of the cage[7]; and (ii) Asymmetrical U_2X (X=C, N and O) clusters inside different fullerenes focusing on $U_2N@I_h(7)\text{-}C_{80}$, with different oxidation states of +4 and +5, revealing a f^1/f^2 configuration of U atoms that would induce such distortion [6].

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ORAL COMMUNICATIONS
WORKSHOP ON TCCM

Second Principles Time Dependent Simulations of Electric Transport in Graphene

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The study of transport properties is a very important field of research due to its importance from the fundamental point of view and its many practical applications. The phenomena associated with these properties is immensely varied going from common conducting materials copper wires or lithium anodes of batteries, to novel and exotic structures as topological materials. Microscopically, the origin of resistivity resides in the collapse of translational symmetry occurring with the presence of impurities or the distortion of the lattice created by phonons. The global effect is strongly dependent on the temperature. A broad solution of transport problems from a computational perspective using *ab initio* techniques is still an open problem.

In the last decades, the advances of first principles methods such as Density Functional Theory (DFT) have allowed gaining a deeper knowledge of the electronic structure of materials. However, transport, like other properties that are strongly temperature-dependent or involve states beyond the ground state still represents a very important challenge for first-principles simulations. This fact motivates the development of a new family of methods, known as Second Principles (SP) [1], based on DFT. They allow large-scale materials simulations including both atomic and electronic degrees of freedom, at a very modest computational cost. The method is based on the construction of models written in localized Wannier functions [2] and includes the capacity to describe the changes in the electronic state induced by the application of electric fields, variations in the geometry (including electron-phonon coupling) and the electron density itself (electron-electron scattering).

In this work, we present both our novel technique to generate general SP models including the above characteristics (implemented in the code modelmaker and based on SIESTA [3] calculations) and the development of real-time time-dependent second-principles simulations to carry out transport simulations and their application to graphene.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/ 10.13039/501100011033 and “ERDF A way of making Europe”, by the European Union. T.F.R. Acknowledge financial support from Grant PRE2019-089054 funded by MCIN/AEI/10.13039/501100011033 and by ESF Investing in your future.

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Evidence for low-lying correlated gapped states in strained graphene and α-graphyne.

WOC2

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Graphene is a 2D gapless Dirac semimetal with ultrahigh charge/spin mobilities. The absence of a semiconducting gap means that currents in graphene cannot be easily modulated, as required in devices (e.g. on/off switching in transistors). Top-down strategies to induce a gap in graphene by introducing defects, distortions, doping, etc. in the 2D material have been largely unsuccessful. A new class of magnetic organic materials called Extended graphenic (XT-graphenic) or Covalent Organic Frameworks (CORFs), which keep the graphene hexagonal symmetry but introduce linkers between α-C [1], have been proposed, showing to be gapless too at their ground-state and bring some light to the opening of its gap by mechanical deformations [2] (compressing and stretching) or applying external electromagnetic fields. Here we focus on the nature of the ground-state of bi-axial strained graphene and α-graphyne. The standard methodology to analyse electronic structure of materials, Density Functional Theory (DFT), have shown to be a useful tool, specially if one uses hybrid density functionals. However, the description of the system depends on the amount of Hartree-Fock Exchange (HFE), which can be tuned [3]. Although nowadays is well known what is the proper way to apply DFT for a rich set of systems (e.g. metals and inorganic systems), due to its hexagonal symmetry and the different electronic solutions in competition (Semimetallic, Antiferromagnetic and Quinoid/Dimerized), CORFs have highlighted some of the deficiencies of DFT and the need of a consistent method in order to reach the physically meaningful description. In addition to DFT calculations, Hubbard type models will be used to rationalize the nature of low-energy electronic states and its dynamics [4]. Using accurate benchmark results for the latter, we show that the relative energetic stability of electronic states in this correlated 2D system can be accurately captured by DFT calculations using carefully tailored hybrid functionals to extract effective t and U Hubbard parameters. Our tuned DFT approach demonstrates that, while graphene maintains a SEM ground-state up to moderate strains, in α-graphyne a low energy correlated Mott-like antiferromagnetic insulating (AFI) statate emerges at low strains, which competes with the SEM state [5]. Accurate calculations show that strained graphene possesses correlated gapped states that are not recovered by GGA-based DFT. We show that an electronic analogy exists between this system and α-graphyne and that both are well-described by tuned hybrid (non-GGA) DFT.

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The role of pyridone assistance in the selective Rh catalyzed dimerization of terminal alkynes

WOC3

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Alkyne dimerization is a straightforward and atom-economical route for the synthesis of 1,3-enynes. This process allows for functionalization on a conjugated skeleton[1] making it highly sought-after in pharmaceutical and organic synthesis. However, the abundance of competing pathways such as the formation of head-to-head dimers, polymers and cyclic organic structures usually leads to poor regio- and chemoselectivity even with the use of a catalyst. Metal Ligand Cooperation (MLC), a form of reactivity in which bond-activation occurs across both a metal and a ligand, has been shown as a promising approach to further improve the efficiency and selectivity of a catalyst[2].

In this work, we present a theoretical study based on density functional theory (DFT) of the *gem*-selective dimerization of terminal alkynes. We focus on the pivotal role played by the pyridone present in the catalyst, see Figure 1, which enables the formation of the product via Ligand Assisted Proton Shuttle[3]. Comparing this mechanism to conventional pathways described for similar systems, like the insertion of the alkyne in the Rh—H bond, a lower activation energy and higher selectivity are achieved[4]. NBO charge analysis demonstrates the origin of the high selectivity and versatility of this novel mechanism.

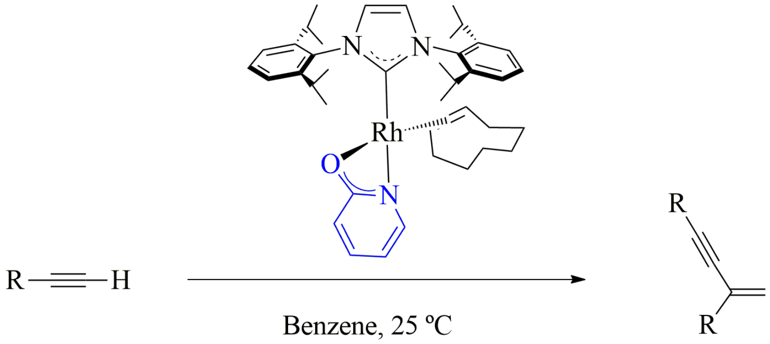

Figure 1. *Gem*-selective dimerization of alkynes

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The Intriguing Aromaticity of (Sub)Phthalocyanines

WOC4

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The theoretical description of the aromaticity of (sub)porphyrins and (sub)phthalocyanines is challenging because of their size, topological flexibility and the existence of multiple π-electron circuits that can contribute to their aromatic character [1]. Most of the aromaticity studies found in the literature are limited to the use of nucleus independent chemical shift (NICS) [2,3]. However, taking into account the complexity of these molecules and the limitations of NICS it is necessary to go beyond NICS measurements and make use of more specialized methods. In this work, we will study the aromatic character of S_0 and T_1 states of eight systems employing a wide range of global [4,5] and local aromaticity descriptors. We also analyze similarities and differences between phthalocyanines and porphyrins. The study was performed at the CAM-B3LYP/cc-pVTZ level of theory, including a wide range of aromaticity indicators based on geometric (harmonic oscillator model of aromaticity, HOMA), magnetic (GIMIC) and electronic (fluctuation index (FLU), electron density of delocalized bonds (EDDB) [4], AV_{min} and AV1245 [5]) criteria. Our detailed analysis, provides new insights on the aromatic character of these molecules, which will be employed in the rational design of (sub)porphyrins and (sub)phthalocyanines derivatives with specific electronic structures.

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Physicochemical, Structural and Conformational study of FMN-containing miniSOG

WOC5

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In recent experimental studies[1], it has been demonstrated that certain flavins (such as FMN) and flavoproteins (FMN containing proteins such as miniSOG) have the ability to activate Pt(IV) prodrug complexes under hypoxic conditions and in the presence of electron donor species as NADH, to form therapeutically active Pt(II) complexes. Furthermore, selected mutations at the position 103 at the binding pocket and position 50 at outside of miniSOG modulate this catalytic activity[2]. In this work, molecular dynamic simulations (MD) are used in order to analyze the structure of Wild Type (WT) and mutated miniSOG during the photoreduction process, and the role the flavin binding pocket might have in the latter. It is observed that these mutations alter the coordination of the flavin to the flavoprotein, also hindering the entrance channel to the FMN in some cases.

Furthermore, the influence of the flavin coordination to the different miniSOG mutations in the reactivity of the flavin is studied by means of Density Functional Theory (DFT). In particular it is observed that (i) the photoexcitation of the oxidized flavin and (ii) electrophilicity of the excited flavin change with the mutations, unveiling the physicochemical fundamentals of the experimental outcome.

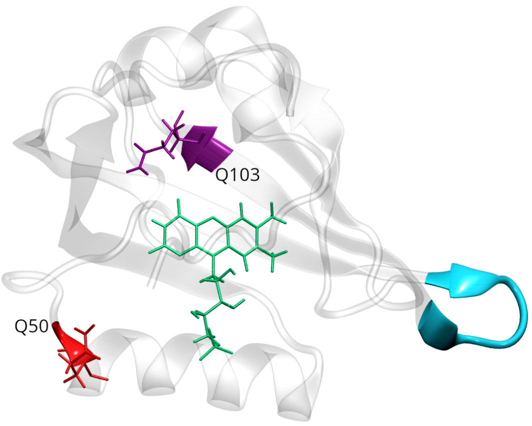

Figure 1. miniSOG's structural model. The backbone of miniSOG is shown in silver, FMN in green, and the amino acids in the mutation positions in red (Q50) and purple (Q103). Moreover, a mobile loop's residues are shown in cyan.

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Exploring guest-host (lattice) interactions in noble gas clathrate hydrates through first-principles computations

WOC6

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The scarcity of information on noble gas hydrates, makes their computational study an interesting and challenging task, since understanding their fundamental properties is crucial for their future exploitation and promising applications.

Focusing on the He@hydrates, motivated by the recent experimental synthesis of He@sII [1] and in relation with the emerging research on new low-density ice polymorphs [2,3], we have performed a computational study from the most basic finite-size clathrate-like structures [4,5] to the periodic 3D crystalline frameworks [6]. In this way, we have first found the most suitable DFT-D approaches available for computations in such large structures by means of benchmark studies on the fundamental units (e.g. He-H_2O) and building blocks (e.g. 5^{12} or $5^{12}6^4$) present in the most common sI, sII and sH clathrate hydrates. In turn, we have analysed the stability of the cages forming the He@sII clathrate, considering single and multi-occupancy, through thermochemical calculations at a range of T-P conditions comparable to the experiment [1]. Finally, we have explored the effects on the encapsulation of the He atom in the sI/sII crystals by computing structural and energetical properties in both empty and He-filled systems. For a more direct comparison with measurements on He@sII structural properties, we have considered multiple cage occupancy similar to those established by diffraction experiments [1]. All these insights serve to better understand the role of the entire guest-guest, guest-host and host-host interactions in the stabilization of clathrates and can benefit research into the development of new data-driven models.

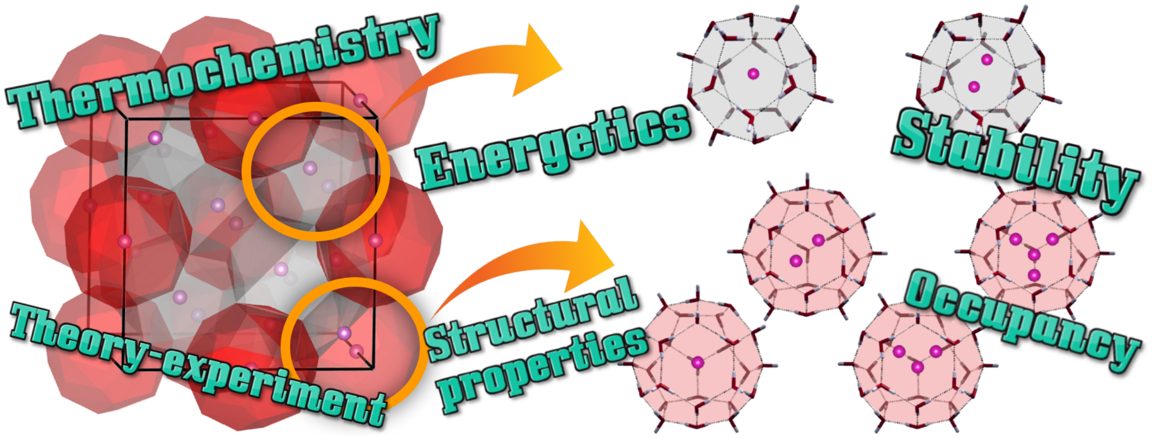

Figure 1. Computational DFT-D investigations on He@sI/sII clathrate hydrates from individual cages to bulk.

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Theoretical Study of Dicyanomethylene-Based π-Conjugated Compounds with Diradical Character

WOC7

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Organic diradicals present a wide range of potential for numerous advanced technological applications due to their unique electrical, optical and magnetic properties [1]. Owing to their stability remains the major obstacle, the object of many experimental and theoretical studies is the design and synthesis of stable ground-state open-shell molecules. A very efficient strategy to stabilize the diradical species is the insertion of terminal electron-withdrawing dicyanomethylene (DCM) groups in a π-conjugated skeleton. An interesting family of π-conjugated systems with diradical character is formed by quinoidal oligothiophenes (QTs) with terminal DCM groups[2]. These QTs behave as organic semiconductors and they have been successfully implemented as active components in organic field-effect transistors (OFETs).

From a theoretical standpoint, the description and characterization of the electronic structure of organic diradicals (or polyradicals) is a difficult task that generally requires the use of accurate but computationally-demanding multiconfigurational methods due to their unpaired electrons. Among the available multiconfigurational methods, the Difference Dedicated Configurational Interaction (DDCI) method[3] is able to treat diradical organic systems with an affordable computational cost. Herein, a series of conjugated systems that combine thiophene and benzene rings with end-capping dicyanomethylene groups (Figure 1) is evaluated by means of DDCI method to predict accurate singlet-triplet energy gaps, which is important for the design of new diradical compounds.

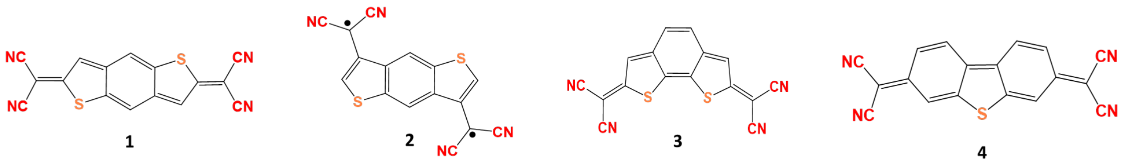

Figure 1. Chemical structures of the conjugated π-conjugated systems studied.

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Assignment of Oxidation States from Optimally Fragment-Localized Orbitals.

WOC8

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Oxidation states represent the ionic distribution of charge in a molecule and are significant in tracking redox reactions and understanding chemical bonding. While effective algorithms already exist based on formal Lewis structures, such as the IUPAC's ionic approximation [1-2], as well as using localized orbitals, e.g. Localized Orbitals Bonding Analysis [3], they exhibit differences in challenging cases where effects such as redox non-innocence are at play [4].

In this work we focus on developing a new approach to obtain fragment-localized orbitals, namely oxidation state localized orbitals (OSLO), together with an algorithm for assigning the oxidation state using the OSLOs and an associated fragment orbital localization index (FOLI) [5]. The FOLI evaluation requires fragment populations, and for this purpose we do not only made use of a robust real-space atomic definition, in particular the Topological Fuzzy Voronoi Cells (TFVC) [6], but also introduced a new version of the intrinsic atomic orbital (IAO) scheme in which the IAOs are evaluated using a reference minimal basis formed from on-the-fly superposition of atomic densities (IAO-AutoSAD) in the target basis set and level of theory [5].

The implementation of the OSLO algorithm has been performed in both the Q-Chem and APOST-3D packages and we applied it to a range of challenging cases including high valent metal oxide complexes, redox non-innocent nitrosyl and dithiolate transition metal (TM) systems, a variety of carbene-containing TMs and other examples including the potentially inverted ligand field in $[Cu(CF_3)_4]^-$. The results obtained are generally satisfactory and, in borderline cases, the OSLOs and associated FOLI values provide direct evidence of the emergence of covalent interactions between fragments that nicely complements existing approaches.

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MoBioTools: A Toolkit to Automatically Set up QM/MM Calculations from an Ensemble of Geometries.

WOC9

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Multiscale hybrid quantum/classical methodologies are nowadays used routinely to describe systems of considerable complexity, which nonetheless can be partitioned into two (or more) subsystems, the description of which depends on the level of accuracy requested by the problem at hand[1]. Quantum mechanics/molecular mechanics (QM/MM) is a popular approach in which one has a full-atomistic description of the system, but only the chemically relevant part is described quantum mechanically. The surroundings are treated classically and their main role is to polarize the QM subsystem, in the case of the electrostatic or polarizable formulations. Complex systems consisting of several thousands of atoms can only be properly described considering a statistical ensemble of configurations which, at the desired temperature, are all likely to be populated and, thus, contribute to the physical property of interest. These two paradigms (QM/MM and conformational sampling) are often put together to obtain an accurate description of the system at a reasonable computational cost. In this contribution we introduce MoBioTools[2], a toolkit that allows for setting up in an automatic manner a set of QM/MM calculations from a previously sampled ensemble of geometries of a system under study. The toolkit is not only easy to use but is also versatile in that it has been employed in a manifold of situations, from the study of interaction energies at the QM/MM level of theory in biological systems such as lipid membranes[3], to the study of electronic excited state properties of molecules in solution [4] and in the presence of DNA[5].

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Environment effects change FRET distributions in a fluorophore-tagged disordered protein

WOC10

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Förster resonance energy transfer (FRET) is a technique widely used as a spectroscopic ruler to measure distances in biosystems, and molecular simulations have emerged as an ideal complement to FRET due to its ability to explore the complex energy landscapes of biomolecules and provide structural models with atomic detail that can be compared with experi-ments[1,2]. These studies, however, typically rely on the approximations underlying Förster theory regarding donor-acceptor electronic coupling: a dipole-dipole term attenuated by a simple 1/n^2 factor, where n is the refractive index of the medium, that accounts for screening effects exerted by the dielectric environment. In this work, we aim at developing a more rig-orous theoretical framework to relate FRET experiments with conformational ensembles de-rived from classical molecular dynamics (MD) simulations. We apply a TrESP-MMPol meth-odology that goes beyond these approximations by describing the fluorophores through elec-trostatic potential-fitted transition charges (TrESP)[3] coupled to a polarizable molecular me-chanics (MM) description of the surrounding environment[4]. We apply this strategy to study the Ca^{2+}-dependent conformational preferences of calmodulin (CaM), a ubiquitous protein that plays a major role in the transmission of calcium signals to target proteins in eukaryotes. Our study shows that TrESP-MMPol provides coupling values in excellent agreement with QM/MMPol results based on transition densities[5], and shows than environment screening has a significant impact on the FRET distributions derived from MD simulations extended over a total of 15 μs, leading to corrections much larger than those due to breakdown of the dipole approximation.

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Rationalizing the photophysical properties of BODIPY derivatives

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WOC11

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During the past decades, the boost in biomedical research has called for the design of new tools for diagnosis and treatment of both animal and human medical conditions. Thus, the search for innocuous, efficient, and non-invasive tools for detection of diseases, being tumors one of the most desired targets, has become one of the hottest topics in multidisciplinary research. We have recently proposed a turn-on hypoxia sensor based on a BODIPY group coupled to an azo benzene moiety [1]. These non-emissive dyes are able to turn on their emission properties under chemical and biological reductive conditions and have opened the door to the rational design of new BODIPY derivatives with the desired photophysical properties.

Supported by state-of-the-art quantum chemical calculations, our aim is to understand the influence of the linker atom(s) connecting the BODIPY and aromatic chromophores in response to light upon irradiation. Our results reveal that both structural and electronic density rearrangement when reaching the excited state are key pieces to scrutinize the photophysical behavior of these systems following photon absorption.

Eventually, we aim at the rational design, and synthesis of highly efficient dual-fluorescent probes coupling two organic dyes through a specific linker that allows the electronic disconnection between the former, perpetuating their emissive properties.

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Photoinduced repair mechanism of various oxetane models of (6-4) photoproduct DNA lesions

WOC12

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DNA in living beings is continuously damaged by both exogenous and endogenous agents, such as UV radiation, giving rise to lesions in the DNA. The most common lesions are cyclobutene pyrimidine dimers and (6-4) photoproducts. The photoinduced (6-4) photoproducts DNA lesions can be initiated by Paternò–Büchi photocycloaddition between two adjacent pyrimidine bases, forming an oxetane ring. Then, the repair mechanism of these lesions can be characterized by the inverted mechanism of the Paternò-Büchi reaction.

In this contribution, two types of oxetanes have been studied as model compounds of the elusive oxetane intermediate present during the (6-4) photoproducts repair. The first type of oxetane arise from the reaction between two benzoquinone molecules (BQ-ox). The second type, is formed by two naphthoquinone monomers, called NQ-1. These models have been compared with previous results obtained for two stable head-to-head and head-to-tail isomers (HH-1 and HT-1, respectively) formed by reacting dimethylthymine and benzophenone[1].

CASPT2//CASSCF and DFT calculations have allowed to interpret the experimental observations. In addition, they also help us to determine the properties of relevant intermediates. It has been observed that both BQ-ox and NQ-1 will decay to the ground state, without the formation of the triplet exciplex, while HH-1 points to a favourable evolution to a triplet exciplex in a much higher extent than HT-1[1]. These findings agree with the results obtained by our experimental collaborators.

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Dual Allosteric Activation of the Prp2 ATPase/Helicase by RNA. A Computational Mechanistic Study on the ATP Hydrolysis.

WOC13

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A complex biomolecular machinery called spliceosome carries out the maturation of pre-mRNA to obtain mRNA[1]. During the splicing process this huge supramolecular complex is assembled, activated and disassembled after the splicing by a highly conserved group of ATPases/helicases[1]. Among them, Prp2 emerges as being essential for the activation of the catalytic complex. This activation chore is strictly dependent on ATP hydrolysis and, likewise, the hydrolysis reaction is possible exclusively in the presence of a RNA strand[2]. Beyond this, a deep understanding about the catalytic mechanism and regulation by RNA in the ATPase activity of Prp2 was still unknown. Herein, we present a comprehensive study at the atomic level using DFT/MM metadynamics simulations and microsecond-long molecular dynamics in the wild-type Prp2 with and without RNA. We elucidate the mechanism by which the hydrolysis reaction occurs. We found an exergonic reaction mechanism that agrees with previously reported experimental results, where the nucleophilic attack is the rate-determining step. Additionally, we disclose the paths by which the RNA allosterically activates the catalysis. We unravel that the hydrolytic power is modulated via two different allosteric pathways that communicate RNA binding regions with two key residues in the active site. Through these pathways, the presence of RNA correctly arranges the active site residues allowing the catalytic water molecule to explore in-line phosphate orientations that are crucial for the nucleophilic attack.

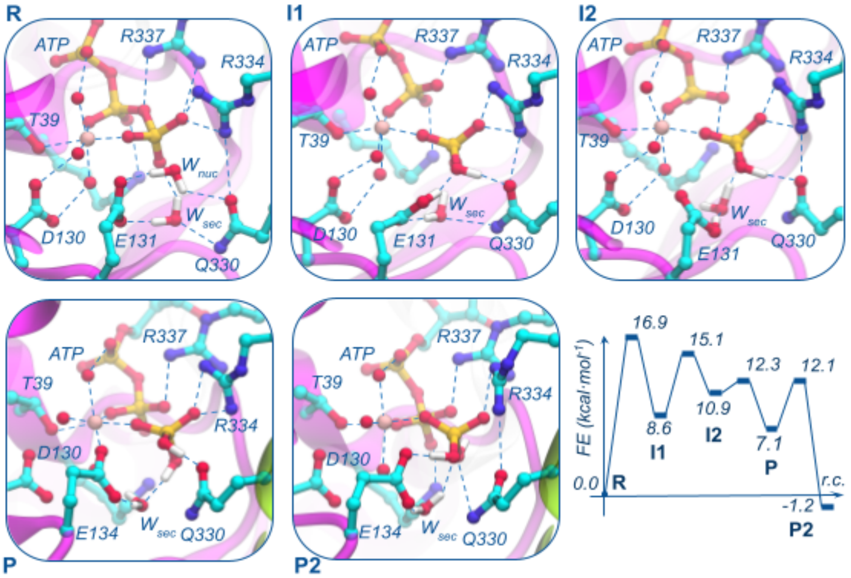

Figure 1. ATP hydrolysis mechanism catalyzed by the Prp2 ATPase/helicase and associated free energy profile.

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In search of the best polarizable embedding approach to calculate electronic excitations in aqueous solutions

WOC14

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Quantum mechanics/molecular mechanics (QM/MM) approaches have become very popular for the calculation of spectral properties of molecules in solution [1]. Within QM/MM methods, the solute is treated at the QM level, whereas the solvent is modelled by means of classical MM force fields, and solute-solvent interactions are usually treated at the electrostatic level, however they can be refined by exploiting polarizable QM/MM approaches, which take into account the mutual solute-solvent polarization.

In this work, we compute vertical transition energies of 11 molecules in aqueous solution by using different classes of QM/MM approaches [2]. In particular, we analyze the results which are obtained by exploiting QM/TIP3P[3], QM/Fluctuating Charges (FQ)[4], QM/Discrete Reaction Field (DRF)[5], and QM/Fluctuating Charges and Fluctuating Dipoles (FQFμ)[6]. Computed excitation energies and vacuo-to-solvent solvatochromic shifts are discussed and compared with available experimental data. Our results demonstrate that the choice of the best QM/MM model strongly depends on the nature of the molecular transition.

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Triplet Excimers of Small Aromatic Molecules

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WOC15

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Molecular interactions between ground and excited states are becoming quite appealing due to their crucial role in photophysics and photochemistry. One of the most paradigmatic example is the strong attractive interaction leading the formation of aromatic excimers [1]. Excimers are defined as two identical excited-state dimers which are more stable than those of the ground state [2]. This new specie results from the interaction between a molecule in the ground state (^{1}M) and an excited molecule ($^{1,3}M^{*}$), generating an electronic state of the dimer [3].

$$^{1,3}M^{*} + {}^{1}M \rightarrow {}^{1,3}E^{*}$$

In the case of singlet excimers, it has been seen that the excimer is stabilized through exciton and charge resonances. Although there are also a few works dedicated to the study of triplet states in molecular dimers [4], not much is known about the triplet excimer properties.

To this end, we have explored a series of small aromatic systems to characterize the electronic structure nature of low-energy triplets in molecular dimers. Based on optimized geometries, spin densities, and intermolecular electronic couplings obtained from the diabatization of low-lying triplet states, we can identify triplet states in molecular aromatic dimers as bonded triplet state dimers, localized triplets or triplet excimers. Moreover, our results rationalize the relative stability of the different low-energy triplets, describe the nature of intermolecular interactions and provide rules for the controlled design of the different kinds of triplet states.

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Computational approach to the hydride transfer in the human Apoptosis Inducing Factor enzyme (hAIF)

WOC16

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In human cells, the caspase-independent programmed cell death processes and the regulation of mitochondrial respiratory complex assembly are closely tight to the apoptosis-inducing factor (hAIF) enzyme [1]. It is believed that the redox balance of the cell environment modulates the hAIF conformational landscape through the reduction of its FAD cofactor with NADH. The formation of a stable charge transfer complex (CTC) leads to structural rearrangements and alterations in the monomer-dimer equilibrium of the protein.

Here we present a theoretical study of this hydride transfer event, considering the whole enzymatic environment, that offers valuable information on the regulatory mechanism of this enzyme and can give insights on the action of related known disease-associated mutations. The results from quantum mechanics/molecular mechanics (QM/MM) calculations allow us to describe the reaction in detail at an atomic scale and can reveal the interacting role of every residue during the catalysed pathway. Kinetic properties are also computed to be directly compared with experimental data.

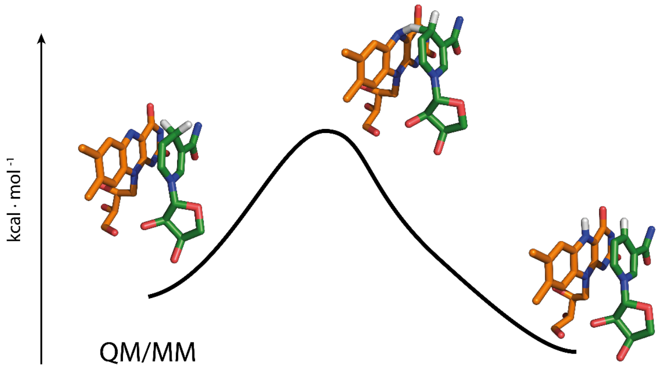

Figure 1. Computed free-energy reaction profile of a hydride transference between NADH (green) and FAD cofactor (orange) in hAIF.

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A quantum chemistry study on CO_2 clathrates: Exploring the formation, energetics and the stability

WOC17

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Understanding of formation, energetics and structural stability in inclusion compounds allows controlling properties involved in different industrial and technological applications like potential molecular materials in the fight against environmental problems related to greenhouse gases capture and storage. The objective of this work is to study the guest-host/host-host interactions in clathrate hydrates, dominated by hydrogen bonds and van der Waals forces [1]. We focus on the evaluation of first-principles methodologies and the description of structural and dynamic processes in gas and condensed phases by a DFT study of finite-size cages and periodic crystalline structures of sI, sII and sH type clathrates. We consider local dispersion corrections such as the exchange-hole dipole moment (XDM) and the semi-empirical model (DFT-D). We generate reference interaction energies from accurate quantum-mechanical calculations by testing different approaches on systems composed of CO_2 and sI, sII and sH structures of clathrates [2]. Such benchmark and systematic cross-check studies benefit new model research by providing high quality information, with new insights that indicate the underlying factors governing their structural stability and promoting more research for controlling the stabilization of these promising long term CO_2 storage materials [3].

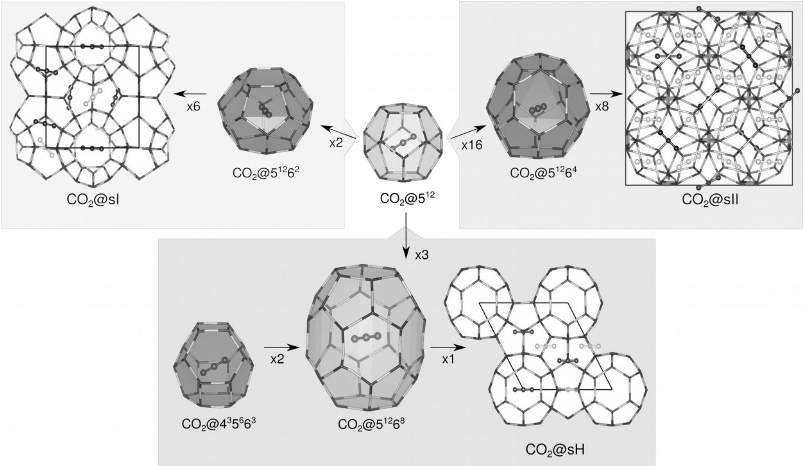

Figure 1. The $CO_2@5^{12}$, $CO_2@5^{12}6^2$, $CO_2@5^{12}6^4$, $CO_2@5^{12}6^8$ and $CO_2@4^35^66^3$ individual clathrate-like cages together with the periodic CO_2@sI, CO_2@sII and CO_2@sH unit cells.

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Ge as a promoter for the catalytic oxidation of CO by Pt clusters

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WOC18

Carbon monoxide (CO) is one of the major pollutants in the chemical and automotive industry. Thus the catalytic oxidation of CO plays an important role in the removal of CO from automobile exhausts, industrial emissions of incomplete combustions of hydrocarbons and hydrogen feedstock gas for fuel cells. CO oxidation is also used as a probe reaction to study more complex reaction such as the Fischer–Tropsch proccess[1-3]. Platinum group metals (PGM) are the most widely used catalyts[4]. Nonetheles, they present several drawbacks like high cost and low durability. The high afinity to CO is especially problematic as it can lead to the poisoning and degradation of the catalyst[5]. In this regard, bimetallic clusters have attracted widespread attention over the last decades as they offer several degrees of freedom to fine-tune the catalytic properties, such as size, composition and morphology[6]. In addition, more economical elements can be used and thus the PGM loading is reduced, making them more appealing for large-scale production. In this work, we have studied the effect of Ge doping small–size Pt clusters supported on MgO(100) on the oxidation of CO by means of a combination of density functional theory (DFT) and microkinetic modeling. To begin with, global minima search techniques were used to locate the most stable structures and adsorption sites for CO and O_2 molecules. Thereafter, a concise mechanistic study of the main reaction pathways was carried out, *viz.*: Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms.

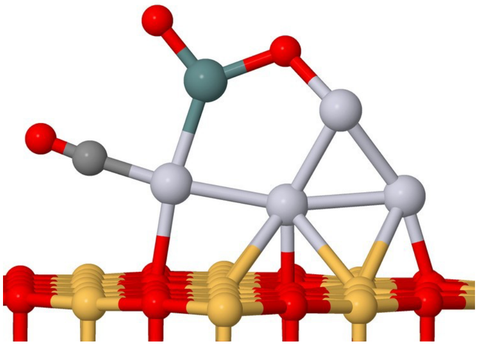

Figure 1. $Pt_4Ge/MgO(100)$ with co–adsorbed CO and O_2.

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Simulating Detection of Dioxine-like Pollutants with 2D Surface Enhanced Raman Spectroscopy using h-BNC substrates

WOC19

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Nowadays, the great pollution puzzle is undoubtedly the biggest challenge facing the world population. The reduction of pollutant emissions, as well as the reduction of pollution already generated, are two of the questions addressed in the lines of research related to the problem of pollution. In both cases, the importance of detecting the various existing pollutants is of utmost importance.

There are currently different carbon-based substrates that can be used in the treatment of persistent organic pollutants (POPs). Among these pollutants dioxins and dibenzofurans are some of the most abundant and harmful for living organisms, being 2,3,7,8-tetrachloro-p-dibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) their most toxics forms. Notably, in addition to the widely used active carbon, other carbon allotropes such as carbon nanotubes or graphene and graphite sheets have recently emerged as potential substrates, both for adsorption and detection of these organic pollutants.

In this work, we have explored, using computational chemistry, the potentiality of other family of 2D carbon based substrates, namely, the hybrid boron-nitrogen-carbon (h-BNC) surfaces, as adsorbents and detectors of dioxin-like molecules[1,2]. Using quantum chemical methods, we have first performed a comparison of the adsorption ability of graphene, white graphene and h-BNC sheets by TCDD and TCDF molecules and analysed the nature of the different molecule-surface interactions by means of an energy decomposition analysis (EDA)[3,4]. Afterwards, simulations of the optical response and surface enhanced Raman spectra of the complexes formed by TCDD/TCDF and a h-BNC model substrate was carried out under static conditions and introducing electromagnetic radiations of common laser sources. These simulations showed that h-BNCs amplify significantly the Raman activity of these compounds, pointing out to their potentiality to be integrated in chemical sensors of these and other related environmental pollutants.

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Analytical Interaction Potentials for Carbon Dioxide

WOC20

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Because of its incontrovertible importance, specially in relation with global heating and climate change, additional improvements in the interaction force fields for CO_2 are still required [1]. Under these circumstances, first principles quantum mechanical calculations, followed by an appropriate fitting, are frequently used to establish precise representations of molecular interactions. Nevertheless, the to-date most accurate reported calculation on the intermolecular interaction between two carbon dioxide molecules cannot be represented in analytical form inside a sufficiently large region of the potential energy hypersurface [2]. Furthermore, a mathematical function depending on the four independent geometrical variables (the distance between the centres of mass of the two molecules, the angles subtended by them to the line joining those centres and the corresponding dihedral angle) are not well-suited for most of the available Molecular Dynamics codes.

In this context, we have applied previously developed protocols [3-5] to construct different analytical force fields representing the intermolecular interactions in CO_2. Specifically, here around one thousand randomly generated conformations of the dimers are calculated at the CCSD(T)/QZVPP level of theory and the corresponding counterpoise corrected interaction energies are fitted to several combinations of electrostatic and non-electrostatic potentials. We stress that using extended basis sets is mandatory to properly account for the large quadrupole moment of CO_2 (–3.186 a.u. according to our calculations). Furthermore, the complexity of the hypersurface prevents the use of simple DFT-based methods. The influence of using different charges schemes (from elementary 3-centers schemes to explicit consideration of the quadrupole) is also examined.

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How to safely assess the oxidation state?
Pros and cons from the EDA-NOCV scheme

WOC21

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The oxidation state (OS) is a key concept in chemistry. This has been widely used to rationalize properties such as reactivity, electrochemistry, and photoactivity for many decades. However, the OS assignation is not exempt from debate since these global properties are commonly assigned to a specific atom within the molecule. IUPAC defines the oxidation state of an atom as “the atom’s charge after ionic approximation of its heteronuclear bonds”. However, this criterion does not always lead to an acceptable representation of the OS. In the recent years, the use of oxidation state computational methods has become popular, but still without full consensus. The density based methods extract the OS from the electronic distribution (Effective Oxidation State (EOS)[1], Localized Orbital Bonding Analysis (LOBA)[2] or Oxidation State Localized Orbitals (OSLO))[3]. The molecular orbital based methods assess OS accordingly to an energetic component of their fragmentation schemes. The Energy Decomposition Analysis (EDA) has been extremely used to assign OS based on the maxim “lower orbital relaxation energy (ΔE_{orb}) better representation”[4].

This work present arguments to question such a statement. As an eye opener, I will present the comparison between fragmentation schemes and split the inter and intrafragment charge transfer for Lewis base stabilized systems. This alternative builds a bridge between the OS criteria.

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Natural-orbital based multireference diagnostic for wavefunction methods

WOC22

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The treatment of electron correlation is always a challenge in theoretical chemistry computations and simulations. The popular Single Reference (SR) correlated wavefunction methods (MP2, CCSD, etc.,) and Kohn-Sham DFT are good at capturing dynamic correlation, but poorly describe nondynamic correlation. When running a calculation, a diagnostic tool can help users decide whether to choose SR methods or Multi-Reference (MR) methods (CASSCF, DMRG,etc.,), the latter is usually more complicated and expensive.

Although a series of diagnostics exist currently, a recent work of Kulik and coworkers[1] have reported the disagreement between different diagnostic criteria, so it is still hard to use these diagnostics to evaluate dynamic or nondynamic correlation. In recent years, our group proposed the dynamic and nondynamic indices I_{D} and I_{ND} in terms of natural spin-orbital occupancies[2,3]. Later, Martin and coworkers[4] have pointed out that our I_{ND} is not size-intensive as it scales with system size. Hence, in this work, we firstly propose the following normalization factor to ensure our indices are size-intensive, we also suggest a new index $I_{\mathrm{ND}}^{\max}$ for measuring non-dynamic correlation,

$$I_{\mathrm{D,norm}} = \sqrt{\frac{8}{M\,N}}\left(\frac{1}{4}\sum\nolimits_{\sigma,i}[n_i^\sigma(1-n_i^\sigma)]^{1/2} - \frac{1}{2}\sum\nolimits_{\sigma,i} n_i^\sigma(1-n_i^\sigma)\right) \tag{1}$$

$$I_{\mathrm{ND,norm}} = \frac{1}{N}\sum\nolimits_{\sigma,i} n_i^\sigma(1-n_i^\sigma) \tag{2}$$

$$I_{\mathrm{ND}}^{\max} = \max\{n_i^\sigma(1-n_i^\sigma)\} \tag{3}$$

M being number of molecular orbitals, N the total electron number and n_i^σ the natural spin-orbital occupancies. We analyze the performance of over 20 diagnostics in an extensive dataset using CCSD and MP2 wavefunctions. We determine the agreement between each pair diagnostics, and classify according to their ability to identify the non-dynamic correlation. We find that our new index $I_{\mathrm{ND}}^{\max}$ can indicate the same information of MR character compared with D_2 diagnostic of CCSD and MP2, and the $I_{\mathrm{ND}}^{\max}$ can be obtained in a much easier and cheaper way.

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Nitroaromatic pollutants on graphene: from physisorption to redox properties

WOC23

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Graphene and its derivatives are not only sustainable and abundant, but also extremely efficient in a variety of practical applications compared to their conventional transition metal and silicon counterparts. One such application is the electrochemical sensing and remediation of nitroaro-matic contaminants in water and soil. However, structural complexity and diversity of gra-phene-based materials (GBMs) necessitates efficient and resource-conscious pre-screening of future materials to improve their sensitivity, selectivity and conversion yield whilst guiding the experimental efforts [1].

In a typical electrochemical sensing device, nitroaromatic compounds[2] are reduced on the surface of GBMs, generating a signal and turning into less toxic and more synthetically valuable adducts. Our goal is two-fold: 1) to identify to what extent the initial physisorption on the GBM and the subsequent step-wise reduction affect the performance of a given sensor, and 2) to establish the structure-activity relationships between the GBMs' structures and their redox properties.

In this presentation, we will highlight our methodological tips for modelling the graphene-based sensors for nitroaromatics,[3] e.g., the choice of reliable *in silico* models, the sampling of adsorption sites, and the simulation of redox reactions on extended materials, using a combination of metadynamics, semiempirical tight binding, density functional theory, and symmetry-adapted perturbation theory [2]. We will also discuss how the studied chemistry of graphene and its derivatives affects their sensing and redox properties, and how this chemistry can be manipulated through targeted functionalisation.

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Novel computational techniques within the multiconfigurational approach applied to metal cyanin complexes

WOC24

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(Transition) metal-anthocyanin complexes have been envisioned to explain the bluing of some flowers containing anthocyanins[1]. Characterisation of different metal-anthocyanin complexes requires a multiconfigurational treatment, even more so when first row transition metals are considered. Herein, we present the study of cyanin complexed with such metal cations as Al^{3+}, Mg^{2+}, Ga^{3+}, Cr^{3+} and iron in both its most stable oxidation states: Fe^{2+} and Fe^{3+}. Experimental evidence of the UV-vis absorption spectra has been already obtained for what are supposed to be analogous species of the complexes mentioned before[2]. In order to rationalise the features shown experimentally by these kind of compounds, an in-depth ground and excited states analysis has to be carried out. Firstly, CASSCF and CASPT2 methods are applied, however, the so-called double-shell effect caused by some transition-metals and the quite large cyanin anion dramatically increase the size of the active space for the iron complexes. Therefore, a set of more advanced multiconfigurational techniques allowing for the treatmemnt of such species at an affordable computational cost and no loss of accuracy is required. The work here developed focuses on the application of the density matrix renormalisation group followed by second-order perturbation theory methods, implemented in the OpenMolcas software, and the employment of the novel AutoCAS program developed within the Reiher group, which allows for the automatic selection of the active space. The relevance of this study lies not only on the employed methodology, but also on the obtained results as they seem to bring up cyanin's ligand-radical character (Figure 1), entailing an antioxidant behaviour that has never been described before.

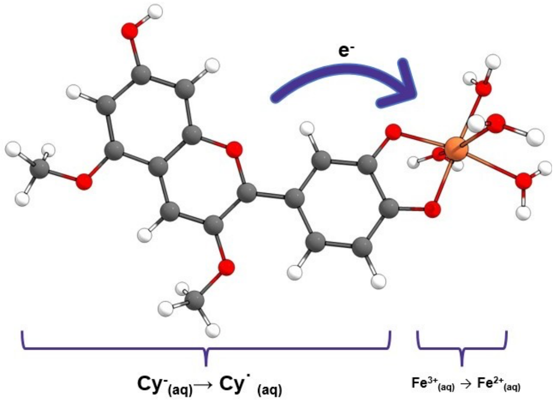

Figure 1. Cyanin complexed with ferric cation.

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The effect of Feschbach resonances on the different vibrational states of N_2 in a RABBIT experiment.

WOC25

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Due to the high photon energy of attosecond light sources, the theoretical description of attosecond experiments requires a proper representation of the ionization continuum. For polyelectronic molecules, the description of the ionization process requires the use of electronically correlated wave functions for the molecular bound states as well as the system's ionization continuum. Despite the huge success of state-of-the-art Quantum Chemistry Packages (QCP) for describing molecular bound states, the combination with their ionization continuum at the same level of theory is still challenging.

The XCHEM code, recently developed in our group, overcomes these difficulties by using a hybrid Gaussian-B-Spline (GABS) basis interfaced with existing QCPs via close-coupling scattering methods [1, 2]. The XCHEM approach has produced excellent results in different atomic and molecular systems [2, 3, 4, 5, 6, 7, 8].

By solving the time-dependent Schrödinger equation one can simulate attosecond experiments in which combinations of several pulses lead to complex interferometric patterns in the ionization continuum. We have extendeded the TD-XCHEM code to include both electronic and nuclear degrees of freedom.

We have employed this new method to simulate a Reconstruction of Attosecond Beating By Interference of Two photon Transitions (RABBIT) experiment of N_2 in an energy region that contains Feshbach resonances converging to $A^2\Pi_u$ and $B^2\Sigma_u^+$ states. Due to the inclusion of nuclear movement and to the capability of the XCHEM code to describe the electronic correlation, this simulation is able to consider the population of Feshbach resonances by different vibrational states.

In this work, we present the results obtained, which have an excellent agreement with experimental data [9] and allow to understand different unexplored features.

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WOC26

Multiphoton double ionization of H_2 induced by attosecond pulses

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Pump-probe experiments are nowadays able to unravel the role of nuclear motion and electron correlation in excitation and ionization processes in molecules on the ultrashort time scale. The interaction of intense short light pulses with molecular systems necessarily implies the solution of the time-dependent Schrodinger equation (TDSE) in a configuration space that comprises all break-up channels. The resolution of the TDSE in full dimensionality for two electrons targets, such as He or H_2, already represents a non-trivial task, but it is the only sensible approach to extract reliable information on the role of electron-electron and electron-nuclear correlation terms. For the hydrogen molecule, the main difficulty lies on the fact that, for solving the problem of molecular double ionization, it is mandatory to solve the four-body coulomb break-up to include all the possible paths and be able to extract the observables of the double ionization from the out-going wave packets. On this work, we have implemented a new computational tool allowing us to describe the four-body coulomb break-up accounting for both electronic and nuclear motions at equal footing, thus beyond the Born-Oppenheimer approximation. We employ a description of the wave function written in a basis set of FEM-DVR (finite element method combined with a discrete variable representation) [1,2]. We use an exterior complex scaling procedure to impose the appropriate many-body Coulomb boundary conditions in a defined volume [1,3,4]. We have first checked our implementation by comparing with existing theoretical data on one- and two-photon double ionization within the fixed nuclei approximation [5,6], and examine what is the role of nuclear motion, in particular, when the two-photon sequential double ionization path is energetically allowed.

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Computational design of conjugated molecules with lower (or isoenergetic) S_1 than T_1 excited-state energies

WOC27

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Thermally Activated Delayed Fluorescence (**TADF**) process has been recently identified as one of the most promising strategies to achieve 100% internal quantum efficiency in Organic Light-Emitting Diodes (**OLEDs**)[1, 2]. The TADF process enhances the upconversion of triplet-excited states to singlet emitting states via a Reverse Inter-System Crossing (**RISC**) mechanism[2]. As molecular template, we selected the (open-shell) Clar's Goblet **(CG)** nanographene, to tune the molecular properties upon substitution; which is been exceedingly used in organic electronics and spinelectronics[3]. In this contribution, we will mainly discuss the influence of both the type and site of heteroatoms substitution on CG molecules in order to decrease the energy difference between the first singlet excited state **S1** and the first triplet excited state **T1** (**ΔE^{ST}**) and allow RISC mechanism to occur, by using various quantum chemical methods such as **TD-DFT (e.g. PBE0, M06-2X or double- hybrid functionals)**, **CIS(D)** and **SCS-CC2**. Overall, the topology of substitutions is found to be the key to alter the excited-state energies, while concomitantly disclosing the accuracy of the various methods assessed as well as the importance of double excitations[4].

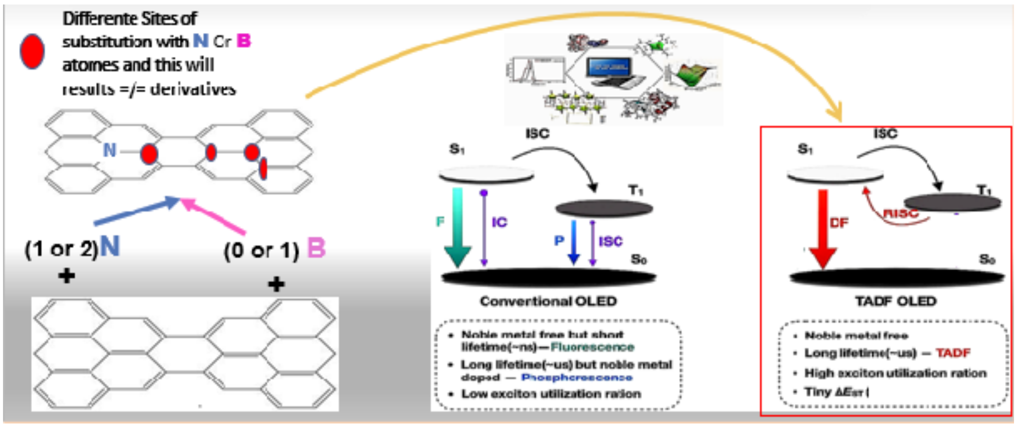

Figure 1. Schematic illustration of the study

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A simple model to engineer single-molecule conductance of acenes by chemical disubstitution

WOC28

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Molecular electronic devices have been studied during the last years as alternatives for those based on silicon technologies, their development is based on understanding and controlling their electrical conductivity[1]. The different options offered by the molecular structure, the nature of the electrodes, and all possible molecule-electrode anchoring configurations, give the possibility of engineer new electronic devices which are experimentally tedious and theoretically very expensive to study[2]. In this work we present a systematic theoretical study of the conductance of di-amino, di-methylthio and di-(4-methylthio)phenyl acenes, from benzene to pentacene, and for all possible distributions of two identical linkers symmetrically placed on opposite sides of the same ring. We show a very good agreement in the tendency of HOMO energies predicted by an extended-Hückel approach and the DFT+Σ conductances for all the compounds. Our approach predicts nicely that diamino acenes are better conductors than their corresponding di-methylthio analogues, and both much better than the di-(4-methylthio)phenyl counterparts, irrespective of the linkers' relative positions. It also predicts, for a given pair of linkers, the conductance tendency resulting from changing the acene size and/or the relative position of the linkers. Finally, we show that a our approach should be useful to predict trends in a variety of disubstituted acene isomers with same conductance length, including various linkers[3].

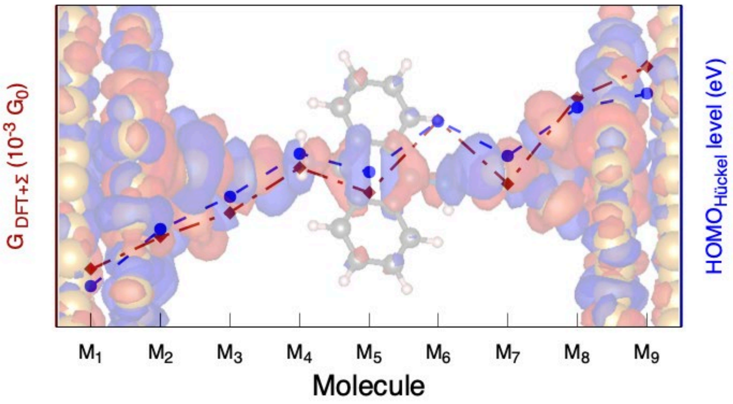

Figure 1. Comparison of the conductance trends for several acene molecules predicted by the extended Hückel model (blue circles) and those obtained by DFT+Σ (red rhombus).

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POSTERS

WORKSHOP ON TCCM

Theoretical investigation of a DNA non-covalent photosensitizer able to form inter-strand cross links

WPO1

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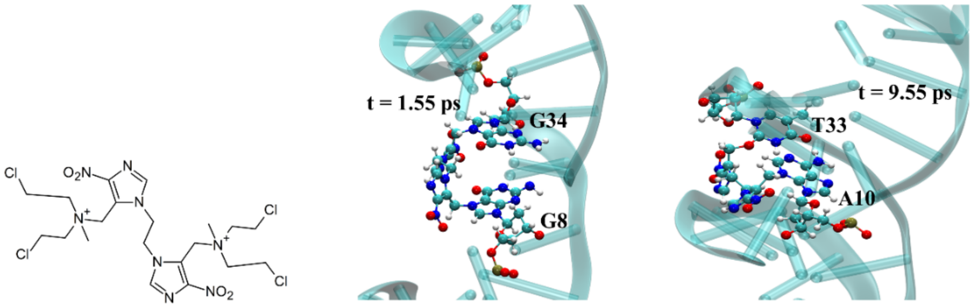
A tumor is a group of abnormal cells that can threaten the biological integrity of the organism. It is formed when cell growth gets out of control due to damages in the DNA codes of the numerous types of genes that control cellular replication. From a therapeutic point of view, tumors can be suppressed by interfering DNA transcription, replication, and translation by damaging DNA, thereby inducing cell death. One approach to prevent the separation of the two antiparallel DNA strands is by forming DNA inter-strand cross links (ICLs). In the last years, a remarkable number of studies devoted effort to investigate agents that can form ICL and can therefore be used as anti-tumor drugs [1]. This work aims to study a nitroimidazole derivative with known non-covalent photosensitization activity (see Figure 1) activated by irradiation, inducing DNA ICLs [2]. A combination of density functional theory (DFT), classical molecular dynamics (MD), and hybrid quantum mechanics/molecular mechanics (QM/MM) simulations have been carried out to investigate the DNA reactivity with this non-covalent photosensitizer. Results describe the possibility to form ICL between either opposite nucleobases or adjacent Watson-Crick base pairs (see Figure 1).



(A) (B) (C)

Figure 1. A) Structure of Binitroimidazole derivative. B) Major groove ICL between Guanine 8 and 34. C) Minor groove ICL between Adenine 10 and thymine 33.

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Rational design of cathepsin inhibitors for biomedical applications combining theoretical and experimental techniques

WPO2

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By observing the current paradigm of molecular biology one can notice the crucial role proteins perform and, consequently, catalytic processes have become of great interest. Among them, proteolytic enzymes such as cysteine proteases (CPs) proven to be promising drug targets since their overexpression is related to human diseases including rheumatoid arthritis, osteoporosis, atherosclerosis and cancer. These enzymes have been widely studied experimentally providing great in vitro results, mainly against parasitic CPs.[1],[2]

A step further towards the complete understanding of how synthesized molecules inhibit CPs is through computational techniques. Some hidden for experimentalists aspects of CP inhibitors such as the origin of selectivity of the inhibitor towards different CPs[3] or the positioning of the inhibitor in the binding cavity crucial for the catalytic activity[4] have been already elucidated by computational biochemistry tools. At this stage, our main goal is to use computational chemistry tools for improving the quality of CP inhibitors as well as using the knowledge accumulated at the molecular level to rationally design new molecules.

This scenario is what over the years both theoreticians and experimentalists have been pursuing and nowadays it appears to be closer than ever before. In this communication the results of a computational study on the covalent inhibition of human cathepsins by two different dipeptidyl Michael acceptor inhibitors (a keto vinyl sulphone and a keto vinyl ester) are presented (see **Figure 1**). In order to reveal the crucial features determining both the affinity and the activity of these two inhibitors, the molecular dynamics (MD) and QM/MM MD methods were employed. Comparative analysis of recognition and kinetic steps was done. Revealed differences and similarities observed in the inhibition process may help in designing a novel structure that surpasses originally proposed molecules, correcting their flaws by removing or changing the parts that do not favour the inhibition.

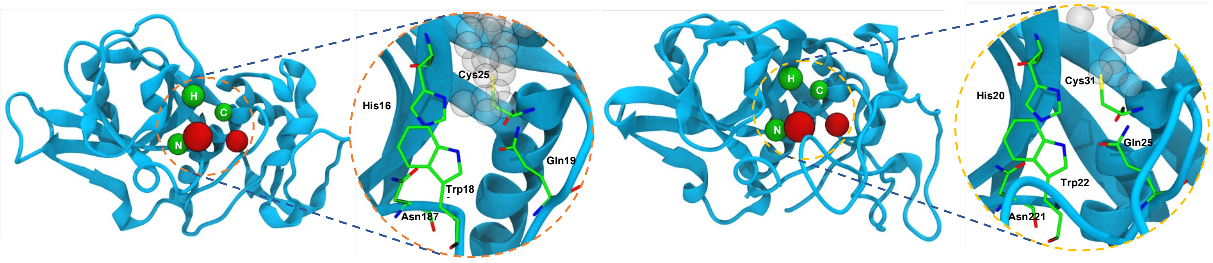

Figure 1. Structure of two human CPs, cathepsin L (a) and B (b) and their active sites

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Characterization of halogen bonding between fluorescent pyridine-functionalized fluoroborate dyes and perfluorohalobenzenes

WPO3

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In the last two decades halogen bonding has gained importance in the scientific community due to its role in material science, organic synthesis, organocatalysis and medicinal chemistry [1], to name a few areas. Theoretical methods can be invaluable in understanding of various aspects of interactions and bonding, thus contributing to the design of new structures with tailored properties. In the present work we study a set of complexes composed of fluorescent dyes presenting BF_2 group (halogen bond acceptors) and halogenated fluorobenzenes (halogen bond donors). This set of dyes has been studied recently on experimental basis. The experimental results demonstrated a link between formation of halogen bond and Stokes shifts thus making a stimulus for development of theoretical model.

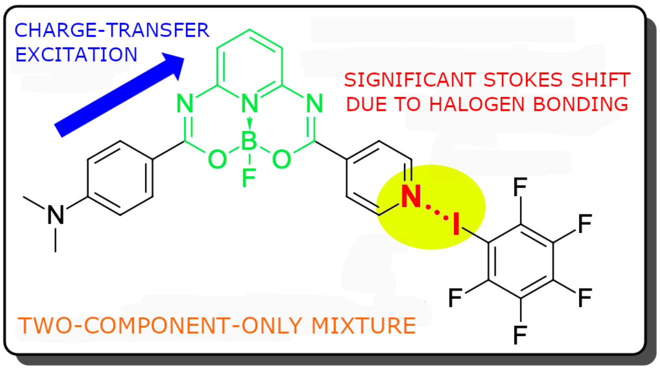

Figure 1. Structure of the system and its properties

In order to understand this interesting phenomenon, we applied quantum chemistry methods to study intermolecular interactions for these complexes and their photophysical properties. In order to gain insight into the nature of intermolecular interactions several schemes have been developed, where the interaction energy is partitioned into different physical terms. One of the most commonly used approaches is the Symmetry Adapted Perturbation Theory (SAPT) [2]. We used a SAPT-based Variational-Perturbational Energy Decomposition Scheme (VP-EDS) which allows to decompose MP2 interaction energy into terms of clear physical interpretation. The Time-Dependent Density Functional Theory was used to study photophysical properties. The results of computations rationalize the origin of experimental significant band shift in the emission spectra on passing from one complex to another and we demonstrate a link with strength on halogen bond.

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Multicentre electron delocalization analysis: untangling pericyclic and pseudopericyclic mechanisms

WPO4

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The unequivocal differentiation between the pericyclic or pseudopericyclic character of a chemical reaction has been, for long, a topic of great controversy in synthetic organic chemistry. Its study has seen extensive application of topology-based quantum chemical tools like the electron localization function (ELF) or the topological analysis of the electron density. Among these tools, one finds the multicentre electron delocalization indices (MCIs) [1-3], the remarkable sensitivity of which is exploited in this work for the characterization of a series of [1,3] sigmatropic rearrangements. These reactions are an example of the fuzzy frontier drawn between pericyclic and pseudopericyclic character when some atomic modifications on the migrating group, the donor and acceptor atoms or alkene unit functionalizations are introduced. Hence, by exploring the above-mentioned chemical modifications, a progressive transition from one type of mechanism to the other is achieved. When following the multicentre bonding along the reaction paths, a clear correlation between reaction barriers, an often-used experimental criterion for the characterization of either type of reaction, and the 4-centre ring delocalization is established.

The obtained results showcase the many advantages of MCIs over other commonly used quantum-chemical tools, as well as their ability to correlate with experimental observables, eventually providing a pericyclic/pseudopericyclic scale in the most controversial cases.

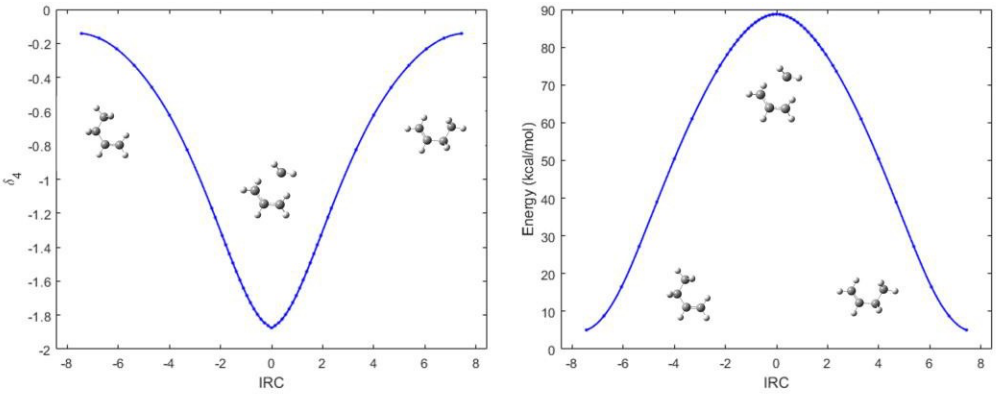

Figure 1. 4-centre (ring) delocalization index (left) and reaction energy barrier (right) along the intrinsic reaction coordinate for [1,3] sigmatropic rearrangement 1-butene.

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An Alternative Approach to the g-Matrix: Theory and Applications

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The g-factor (often called g-value or g-Matrix) is a magnitude that parameterizes the Zeeman effect, involving the interaction of the spin magnetic moment with a magnetic field. One of its most known applications is its use in electron paramagnetic resonance (EPR) spectroscopy [1], in which anisotropic shifts of the g-values relative to the free electron g-value provide significant information about the environment of unpaired electrons.

In the last years, g-factors have been mostly calculated by ab initio methods based on density functional theory (DFT) or wavefunction theory approaches [2]. In this work, Hélène Bolvin's procedure for the calculation of the electronic g-matrix is applied [3]. Herein, molecular wave-functions whose ground state is a non-degenerate spin doublet (and thus can be expressed as Kramer doublets) are determined in a two-step method: firstly the spin-free states are determined and then spin-orbit coupling between these states is introduced. This method allows the analysis of the contributions of each excited state to the anisotropy of the g-matrix.

For the first time, this procedure is applied using restricted active space spin-flip (RAS-SF) method [4]. Different molecules g-values are compared with experimental results and with previous highly correlated results.

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Theoretical Study of the Sulfonylurea Family of Herbicides

WPO6

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This poster presents a study of the structures and chemical properties of sulfonylureas, which are a group of herbicides derived from sulphonamide and ureas with a triazine substituent. They act as inhibitors of acetolactate synthase. Some of the molecules that form this family are amidosulfuron, cinosulfuron, tritosulfuron, prosulfuron, sulfometuron methyl or chlo-rimuron ethyl [1].

We have determined the most stable tautomers and most stable conformations for each tautomer using the CREST and CENSO programmes [1,2]. The molecules were studied in gas-phase, in octanol and water. Finally, the final properties are obtained at the B3LYP-D3/6-311+G(d,p) level of theory.

As a result, the NH-CO-NH structure is obtained as the most stable tautomer. The use of different properties as gibbs free energies, HOMO/LUMO gap, cavity size, polarizability... to predict properties of environmental interest as the octanol/water partition coefficient for a large family of compounds are also discussed.

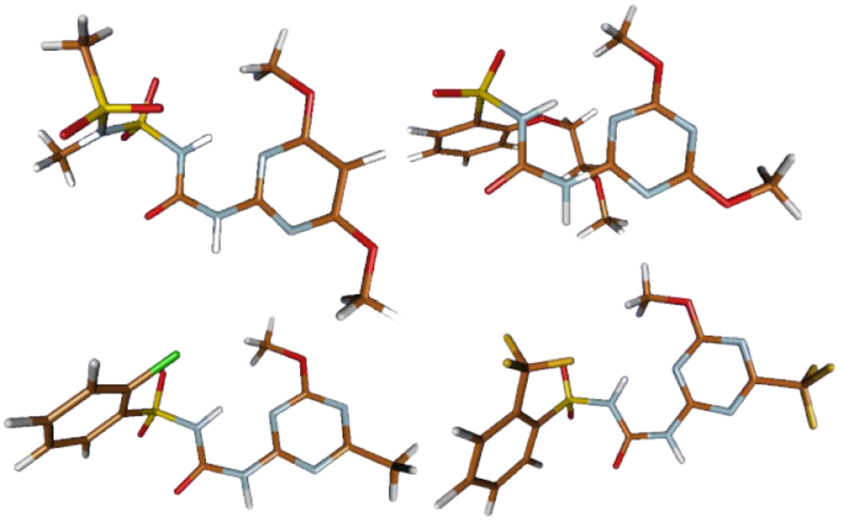

Figure 1. 3D structure of the amidosulfuron, chlorosulfuron, cinosulfuron and tritosulfuron molecules.

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Computational modelling of N-annulated perylene bisimides supramolecular aggregates: relationship between structural, electronic and optical properties

WPO7

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Perylene bisimide (PBI) and its derivatives have aroused considerable attention due to their applications in diverse fields ranging from optical switches to organic light-emitting diodes (OLEDs)[1]. PBIs are organic π-conjugated compounds and show excellent optical, photophysical, and optoelectronic properties. PBIs are prone to self-assembly due to the π-π interaction of the π-conjugated cores, and the structure of the aggregate can be controlled by peripheral substitution. The structure and the nature of the interactions present in these supramolecular aggregates play a crucial role in the absorbance and fluorescence properties of the corresponding material [2].

In this work, we present a quantum-chemical characterization of the structural, electronic, and optical properties of N-annulated PBI derivatives and their possible supramolecular aggregates by using the density functional theory (DFT) and the tight-binding semiempirical GFN2-xTB quantum-chemical method. Moreover, to get a better understanding of the optical properties of PBI derivates supramolecular polymers, an Frenkel/CT-type excitonic Hamiltonian was constructed to simulate the absorption electronic spectra. The study has been performed on two PBI derivatives (Figure 1), which share the same π-conjugated core, but different peripheral substituents attached to the imide positions (ethyl benzoate groups for 1 and phenyl groups for 2). The change of the peripheral substituents has a strong effect on the aggregation and optical properties [3].

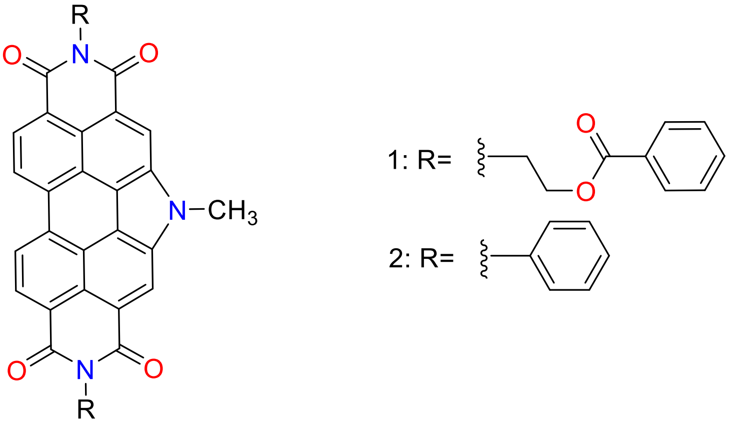

Figure 1. Chemical structure of the PBI derivatives.

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Drawing curly arrows on Ruthenium-prompted amine fixation

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WPO8

The activation of the N–H bond of ammonia by transition metal-based complexes is a very difficult task due the fact that it tends to coordinate via the nitrogen lone-pair, yielding very stable Werner-type complexes. However, the straightforward preparation of such metal complexes would pave the way to the direct catalytic functionalization of ammonia and its derivatives. In this sense, Milstein and co-workers reported a series of Ru-based complexes bearing non-innocent ligands able to mediate the direct fixation of ammonia under soft reaction conditions, which was a milestone in the field, and enormously stimulated the research in this field [1]. In general, the active systems involve non-innocent pincer ligands that operate via an aromatization−dearomatization mechanism (sse Figure 1). Nonetheless, despite several advances, the electronic features that govern these processes are far from being completely understood.

In this context, we selected the original system reported by Milstein (Figure 1) as a representative model system to attain a further understanding on the factors that affect the performance of such systems at a molecular level. Namely, we studied the reaction pathway by means of Bond Evolution Theory (BET) [2]. We also studied the interaction between the metal center and the N atom by means of the Interaction Quantum Atoms (IQA) energy decomposition scheme. This allowed us to elucidate the bond formation and breaking events, as well as the electronic rearrangements derived from them. On the basis of the results, we proposoed rational ligand modifications to improve the kinetics and thermodynamics of the process.

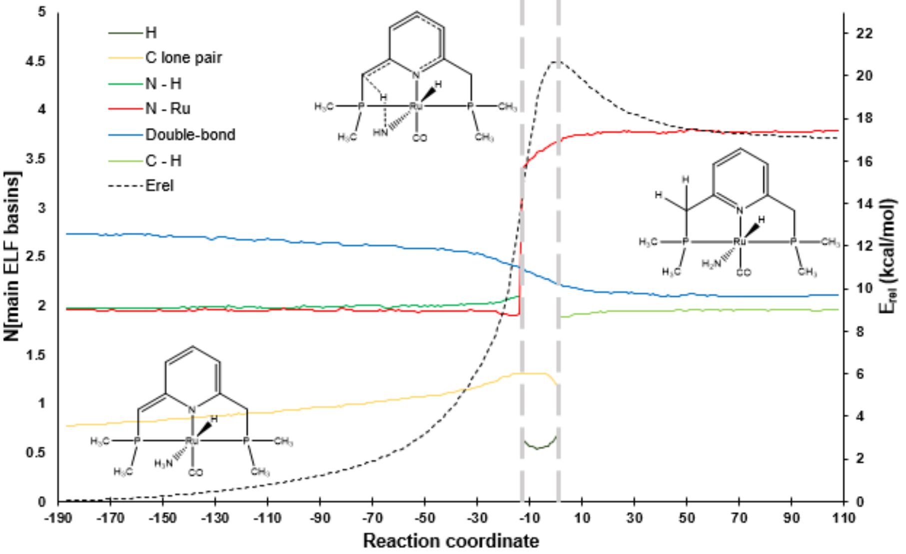

Figure 1. Evolution of the population of selected ELF basins along the reaction pathway (Intrinsic Reaction Coordinate) for one of the systems under study.

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WPO9

Enthalpy-Entropy compensation in metal-bound neurofilament peptides

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In the last decades aggregation of Intrinsically Disordered Proteins has been found to be close-related with some neurodegenerative disease such as Alzheimer's and Parkinson's[1]. However, despite of the considerable amount of work that has been done, aggregation mechanisms remain yet unknown. Here, we have utilized a multi-scale approach (QM + MD) to unravel the possible implications of the $Al^{(3+)}$ cation in the conformational changes of a neuropeptide involved in the Alzheimer's disease, following the metal-ion hypothesis. Results show that binding type leads to different spatial arrangements which entails variable aggregation probabilitiy[2]. Furthermore, these spatial arrangements modify inevitably the accesible conformational space[3]. Thus, we aim to quantify the contributions of both enthalpy and entropy magnitudes and characterize the balanced interplay that determine the population of the most favorable species.

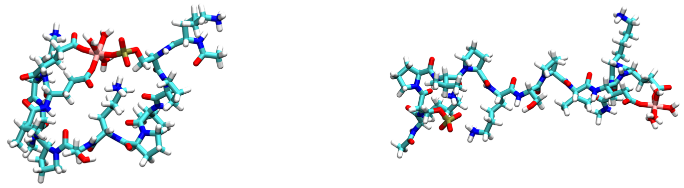

Figure 1. Examples of two structures: $NF13Al^{S2}_{E10E11}$ (left) and $NF13Al^{S2}_{S2E10E11}$ (right), showing the two main spatial arrangements characterized, extended arrangement and contorted arrangement respectively.

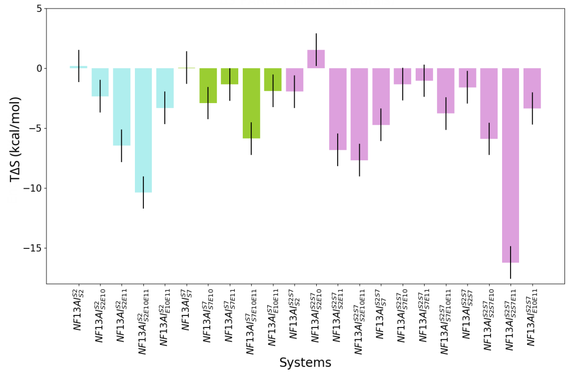

Figure 2. TΔS values for the studied systems. Larger negative bars correspond to entropically unfavored systems. Color code correspond to phosphorylation type: single phosphorylation at serine 2 (blue), single phosphorylation at serine 7 (green), double phosphorylation in both serine 2 and serine 7 (pink.)

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Cage-size Effects on the Encapsulation of P_2 by Fullerenes

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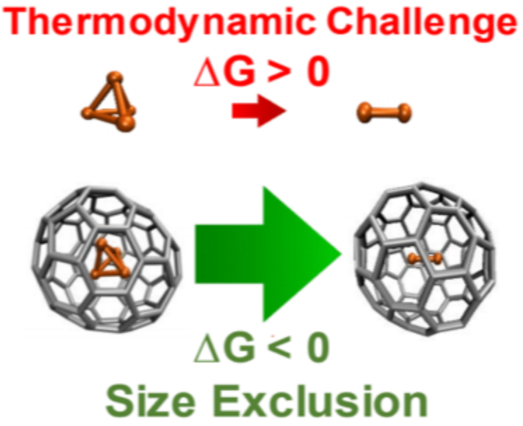
WPO10

The classic pnictogen dichotomy stands for the great contrast between triply bonding very stable N_2 molecules and its heavier congeners, which appear as dimers or oligomers [1]. A banner example involves phosphorus as it occurs in nature as P_4 [2] instead of P_2 [3]. The synthetic value of the P_2 moiety has brought a number of Lewis base and metal coordination stabilization strategies [4].

Herein, we discuss the unrealized encapsulation alternative using the well-known fullerenes' capability to form endohedral and stabilize otherwise unstable molecules [5]. We chose the most stable fullerene structures from C_n (n = 50, 60, 70, 80, 90, and 100) to computationally study the thermodynamics and the geometrical consequences of encapsulating P_2 inside the fullerene cages. Given the size differences between P_2 and P_4, we show that the fullerenes C_{70} to C_{100} are suitable cages to side exclude P_4 and host only one molecule of P_2 with an intact triple bond. The thermodynamic analysis indicates that the process is favourable, overcoming the dimerization energy. Additionally, we have evaluated the host-guest interaction to explain the origins of their stability using Energy Decomposition Analysis [6].



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Theoretical investigation of the electronic and structural factors that govern the photostability of nucleobases

WPO11

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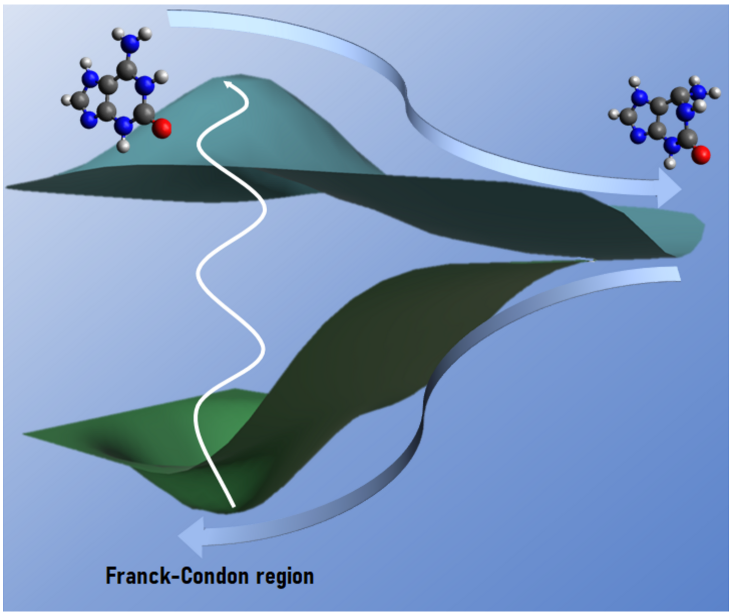
Only five different monomers integrate the canonical nucleic acids' alphabet. This is believed to be, at least in part, due to their notable photostability, which allows the efficient and ultrafast return of the electronically excited population to the ground state, minimizing the photoreaction yields. Efficient ultrafast ground state recovery occurs via internal conversion funnels that need to be accessible along the relaxation of the system from the Franck Condon region[1].

Recent investigations have revealed that the topography of the ground and excited state potential energy surface is related to the substitution pattern of the purine or pyrimidine cores which can strongly modify the photophysics of the formers[2,3]. Studying the effect of the nature and position of the substituents in the shape of the potential energy surfaces can help understanding the mechanisms that govern photostability in nucleobases.

In this communication, we will analyze the potential energy surface landscape of several purines, isoguanine, guanine and xanthine, using state of the art quantum mechanical methods. We will also examine which is the impact of the structural modification of the heterocyclic core in the photophysics of these systems by scrutinizing the potential energy surfaces of 7-deazaguanosine and 5-aza-7-deazaguanine[4].



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Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules

WPO12

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Ever since the first models of organic solar cells were proposed more than 40 years ago, the search for new materials with the ability to produce a charge separation, necessary for photovoltaic applications, has kept drawing the scientific community's attention. Organic photovoltaic devices usually achieve charge photogeneration by using charge transfer complexes, which act as an intermediate step between exciton dissociation and charge extraction.

In order to capture the real time evolution of such electronic process, which takes place in the time range between tens of attoseconds to a few femtoseconds, a sub-femtosecond time resolution is required. Therefore, in this work we propose the use of a pump-probe scheme employing ultrafast laser sources to track the charge transfer process using as target a typical donnor-acceptor molecule in the gas phase. In particular, we investigate the ultrafast dynamics following the excitation of para-nitroaniline (PNA), which has been extensively studied in a solvent, both theoretically [1, 2, 3] and experimentally [1, 4, 5, 6], while scarcer works have been performed in gas phase to date.

We thus propose the use of a pump-probe scheme, using a few-fs UV pulse to excite the target. The ensuying electron-nuclear dynamics will be later probed by a time-delayed attosecond XUV pulse which will ionize the molecule. The time-varying ionization yields are expected to capture the complex dynamics triggered in the excited molecule.

In a first approach, using the fixed nuclei approximation, we retrieve the time evolution of the excited wave packet by analyzing the electron density variation, computed through a transition density matrix formalism. The imprint of these dynamics is later retrieved into the cation with the time-delayed absorption of the probe pulse.

We later explored how these electron dynamics evolved when coupled with the nuclear degrees of freedom, when non-adiabatic couplings come into play. The coupled electron-nuclear motion is described by means of a surface-hopping method, i.e. within a semi-classical picture. In short, the time-dependent wave function is retrieved at each time step, computing the electronic structure on-the-fly by means of a quantum mechanical description, while the nuclear dynamics follows the classical equations of motion.

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Sampling Effects on the Photophysics of Oxyluciferin within the Luciferase Environment

WPO13

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Nature presents a wide variety of bioluminescent systems, which are able to promote chromophores to electronically excited states by means of chemically stored energy, as in adenosine triphosphate (ATP), which upon relaxation emit light in the visible region[1]. This process is the result of the enzymatic reaction of a luciferin/luciferase system, which has potential medical applications[2,3], especially when the chromophore is tuned to improve its photophysical properties. Thus, the first step to design efficient luciferin/luciferase complexes is to characterize and understand their photophysics. This can be done from a computational perspective, but different issues have to be considered in the theoretical protocol.

In this work, the effect of different computational factors on the emission spectrum of the D-luciferin/luciferase system present in fireflies is analysed. First, we investigate the impact of the potential energy model used during the sampling process by evolving classical and QM/MM MD simulations to explore the potential energy surface of the first electronically excited state. Then, in a second step, the emission spectrum is computed based on the selection of several geometries, which are chosen in three different ways: random selection, equidistant selection, and according to the Metropolis criterium. The impact of all these approaches on the emission spectrum will be discussed.

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Spin-crossover complexes in interaction with the substrate

WPO14

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Iron (II) spin crossover (SCO) complexes belong to the family of bistable molecules, in which the ligand field around the Fe ion influences the electron configuration in such a way that the molecule has two different spin states, low spin (LS) and high spin (HS). The spin state can be manipulated by external stimuli such as a variation in light, temperature, pressure, electronic field, or magnetic field [1]. The use of spin crossover (SCO) complexes in spintronic devices would need connecting a single molecule with surfaces.

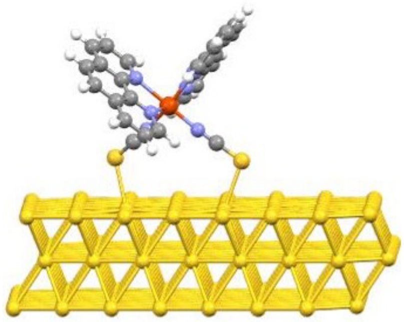

Figure 1. The complex on the surface of Au (1 1 1).

In this work, we show an overview on the spin crossover behavior of $Fe(phen)_2(NCS)_2$ complex adsorbed on Au (111) and Cu (111) surfaces from periodic density functional theory (DFT) calculations [2]. The complex has been deposited on Au (111) and Cu (111) with the −NCS ligands pointing to the surface, and several adsorption sites have been explored (Figure 1).

In the LS state, the sulfur atoms are on top positions on both surfaces. On the other hand, in the HS state, iron atoms are at fcc position on Au, and on hcp position~~s~~ on Cu surface. Adsorption energies are larger for the complex adsorbed on Cu (111), what means a larger interaction with this metal surface. Finally, we have analyzed the spin-polarized density of states (DOS) projected on Fe, NCS groups, and phen groups of the Fe phen free complex and we have simulated STM images to visualize the molecules on the surfaces.

Our results show that the HS-LS energy difference of isolated complex is 32.3 kJ/mol. This value increases to 45.6 and 51.6 kJ/mol when the complex is adsorbed on Au (111) and Cu (111) respectively. This result is in line with previous experimental works, which show a suppression of SCO properties once $Fe(phen)_2(NCS)_2$ is adsorbed on metallic surfaces [3].

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New Ideas for Understanding the Structure and Magnetism in AgF_2: Prediction of Ferroelasticity

WPO15

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Since the discovery of high-temperature (high-T_C) superconductivity in 1911, many efforts have been made to observe superconducting states at increasing temperatures. In the 1970s, superconductivity was found in some Nb-based metallic systems at temperatures above 20 K. However, the breakthrough came in 1986 with the discovery of superconductivity in copper oxides at about 92 K. In these compounds, high-T_C superconductivity seems to be driven by three main ingredients: (1) layered crystal structure, (2) the presence of elongated CuO_6 complexes and (3) strong antiferromagnetic (AFM) coupling in the Cu layer [1].

Superconductivity in cuprates arises from the strong interaction among d^9 electrons, localized on the metal planes. Along this line, in the last two decades superconductivity has been sought in materials containing Ag^{2+} ions, whose electronic configuration is $4d^9$ [2]. In particular, it has been proposed that the fluoroargentate AgF_2 can reach a superconducting state, due to the apparent similarities with the high-T_C superconductor La_2CuO_4, namely, layered structure and a charge-transfer insulating state with intraplanar AFM order [3]. In this work, we have focused on this fluoroargentate, performing a first principles analysis of its crystalline and magnetic structure in order to understand the underlying relationship between them.

To determine the origin of the AgF_2 structure, its *parent high-symmetry phase* has been optimized. Our results show that this parent phase is cubic and thus lacks a layered structure. Furthermore, in the parent phase Ag^{2+} ions are placed in trigonal lattice sites (local D_{3d} symmetry) and therefore the AFM order is geometrically frustrated. Under these conditions, the ground state of the sixfold coordinated AgF_6 complexes is orbitally twofold degenerate, allowing the existence of a Jahn-Teller (JT) effect, which lifts the degeneracy and lowers the energy. Cooperative JT effect leads to the observed orthorhombic crystal structure and the AFM coupling in the layers, as magnetic frustration is broken with deformation. By contrast to La_2CuO_4, where the origin of layers is chemical, in AgF_2 JT distortion causes the softening of two Ag-F bonds, but this effect is far from destroying the interlayer interaction [4]. On the other hand, one of the main consequences of cooperative JT effect is ferroelasticity, since the magnetic order of AgF_2 is controlled by the distortion. This fact is tightly related with the existence of multiple equivalent minima in the potential energy surface of a cubic system.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/ 10.13039/501100011033 and by “ERDF A way of making Europe”, by the European Union.

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Elucidating the photolytic properties of atmospheric sulfur compounds by means of multiconfigurational quantum chemistry

WPO16

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Sulfur dioxide (SO_2), a gaseous pollutant of global concern, is a precursor of sulfuric acid (H_2SO_4), one of the main components of acid rain. The latter, due to its high hygroscopicity, can form light-reflecting aerosol particles in the atmosphere. Thanks to this property, a promising solar geoengineering technique called stratospheric aerosol injection aims to counteract global warming by introducing large quantities of SO_2 in the stratosphere to induce the subsequent formation of sulfur-based aerosols. Then, these aerosol particles would act as a mirror for incident solar radiation, decreasing in this way the global temperatures of our planet. However, the atmospheric chemical implications and the potential environmental effects of this large-scale sulfur injection need to be evaluated. In order to do that, the impact of light-induced reactivity on the production of H_2SO_4 in the stratosphere must be analyzed.

Recently, a series of quantum chemical studies have been carried out to shed light into the absorption properties and photodissociation pathways of key sulfur species in the generation of stratospheric sulfate aerosols: the hydroxysulfinyl radical (*cis*-HOSO) [1], the hydroxysulfonyl radical ($HOSO_2$) and sulfur trioxide (SO_3) [2]. The former species arises from the reaction of SO_2 in its lowest excited triplet state with water, while the remaining systems act as intermediates in the traditional acid rain generation scheme from SO_2, the central chemical mechanism of this proposal. Firstly, absorption properties were analyzed by computing theoretical ultraviolet and visible absorption spectra making use of a nuclear-ensemble approach in combination with multiconfigurational methods (SA-CASSCF and MS-CASPT2). Then, *ab initio* non-adiabatic molecular dynamics simulations were carried out, making use of the surface hopping including arbitrary couplings algorithm and MS-CASPT2 for the electronic structure computations, to identify the main photodissociation channels and the corresponding yields upon light absorption in the stratosphere. With this information, the lifetime against photolysis of each system was determined and compared with other competitive atmospheric reactions. The results obtained suggest that the photochemistry of *cis*-HOSO and $HOSO_2$ may only have a significant impact in atmospheric regions with low O_2 concentration, the primary sink species for these sulfur radicals. In contrast, SO_3 appears to be photostable with a long photolysis lifetime in Earth's stratosphere, indicating that the efficiency of H_2SO_4 generation may be affected by largely unknown SO_3 removal processes. Future modelling studies will be necessary to further estimate the viability of the proposed solar geoengineering technique.

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Computation of the One-Electron Oxidation Potentials for Nucleobases in Aqueous Phase and Absorbed into a Gold Surface: Setting up a Protocol

WPO17

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DNA-based biosensors are nowadays powerful tools for detecting specific analytes. In order to understand the functioning of these devices, the knowledge of the redox properties of nucleobases is fundamental since the charge-transfer processes play an important role in the detection task [1,2]. Although a wide variety of theoretical and experimental studies has been performed, the value of the one-electron oxidation potentials of the nucleobases is not well defined and there is not a proper established theoretical protocol to model this redox property. In this work, different static and dynamic approaches to compute the one-electron oxidation po-tentials of solvated nucleobases have been implemented and evaluated, using a combination of density functional theory, within QM/continuum and QM/MM frameworks, combined with classical molecular dynamics. Within the static approach, two versions of a thermodynamic cycle have been tested to assess their accuracy against the direct determination of the oxida-tion potentials from the adiabatic ionization energies. Then, the introduction of vibrational sampling, the effect of implicit and explicit solvation models, and the application of the Marcus theory have been analyzed through the dynamic methods. After setting up the most appropriate protocol, it was possible to compute the oxidation potentials for more complex systems, namely, the nucleobases anchored to a gold surface by a small organic linker.

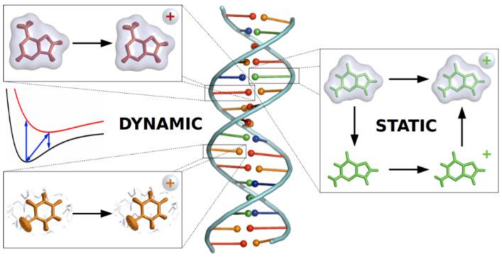

Figure 1. Schematic representation of the different theoretical protocols employed.

Acknowledgements

We thank the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM) for generous computational time. J.J.N. and G.C. acknowledge the Comunidad de Madrid for funding through the Attraction of Talent Program (Grant ref 2018-T1/BMD-10261). N.A.O. acknowledges the Comunidad de Madrid and European Social Fund for funding through the Programa Operativo de Empleo Juvenil y la Iniciativa de Empleo Juvenil. J.L.T. acknowledges the FPU19/02292 grant from the Spanish Ministry of Education and Vocational Training.

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Dinitrogen Activation Mediated by the (P_2P^{Ph})Fe Complex: Electronic Structure, Isomerization Mechanism, and Magnetic Coupling

WPO18

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We have studied the extent of dinitrogen activation by different charged and structural forms of the (P_2P^{Ph})Fe biomimetic catalysts, which in the presence of light exhibit significant yield in the N_2-to-NH3 conversion[1]. CASSCF calculations have been used to evaluate the electronic structure of the mononuclear complex (P_2P^{Ph})Fe(N_2)$_2$. These calculations revealed the formation of Fe^{2+}-$(N_2)_2^{2-}$ species, where the dinitrogen is activated because of the back-bonding from the Fe^0 centre. Using DFT calculations, the mechanism and energy profile of the isomerization between models of the mononuclear (P_2P^{Ph})Fe(N_2)$_2$ adduct and the dinuclear mono-N_2-bridged [(P_2P^{Ph})Fe]$_2$(μ−N_2) one has also been figured out (Figure 1). The isomerization process was found to involve a spontaneous three step mechanism thermodynamically favoured (ΔG_{isomer} = -30.49 kcal·mol^{-1}).

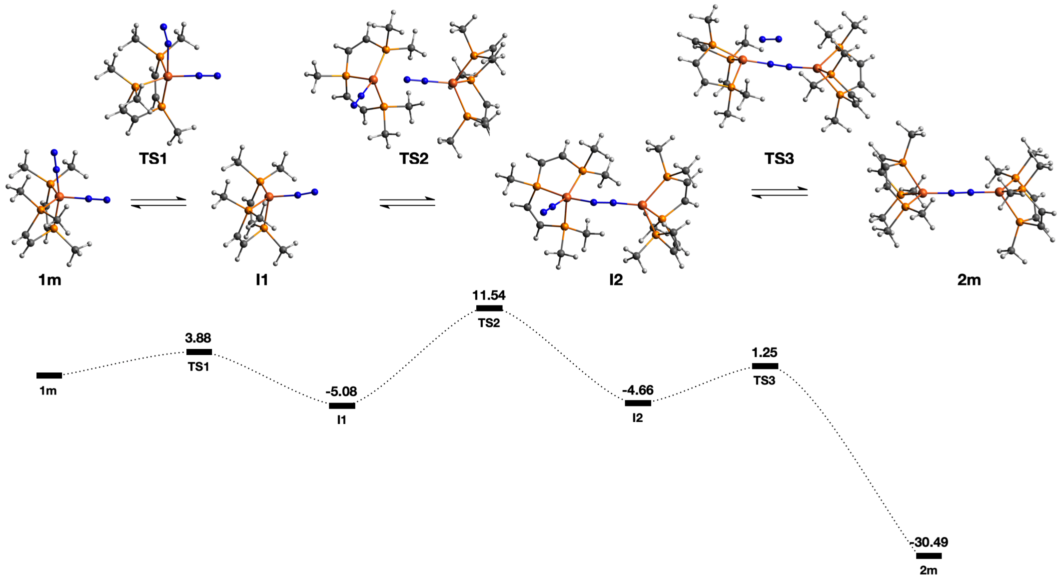

Figure 1. Gibbs free energy profile (kcal·mol^{-1}) for the isomerization mechanism between the mononuclear complex 1m and the dinuclear mono-N2-bridged adduct 2m.

We have also estimated a strong antiferromagnetic coupling in the model diiron (μ−N_2) complex (J = -1528 cm^{-1}) by means of NEVPT2 calculations. The electronic structure of this dinuclear system is in line with a dominant Fe^+-N_2^{2-}-Fe^+ species, i.e., a highly activated dinitrogen, with two electrons on the π* orbitals of N_2 moiety and a low spin d^7 configuration on each Fe atom. These local spins on the irons and dinitrogen account for the antiferromagnetic behaviour[2].

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Dynamic Correlation for MCSCF Wave Functions by Means of an Effective Potential

WPO19

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The treatment of electron correlation is a central problem in electronic structure methods, due to its crucial role for a proper quantitative description of the properties inherent to molecular systems. The problem is partially solved within MCSCF theory, which accounts for the near-degeneracy effect in the wave function, and thus it allows to describe to the so-called static correlation. A further improvement needs to deal with the dynamic correlation contribution, which cannot be properly treated on a low level of theory (SCF or MCSCF). A desired method needs to treat both types of correlation in a balanced way, which is desirable for the description of ground and excited states [1].

In this work, we explore a previous proposal stated by Roos and co-workers [2], which consist in the addition of an effective potential to the Hamiltonian. This potential is constructed in order to reflect the nature of the Coulomb hole by reducing the repulsion term in the Hamiltonian. As shown by Roos, the latter strategy treats dynamic correlation in a balanced way, giving accurate results (see Table 1). In order to establish the validity of this method, we developed a computational strategy, which involves a local implementation of the integrals involved in the effective potential term and use the modified Hamiltonian in conjunction with the CASSCF method [3] by using the PySCF package. We provide results computed from different basis sets and explore the features of the method through its parameters.

Atom		IP	EA
C	CASSCF	10.14	-0.002
	Eff. Pot.	11.36	1.01
	Exp.	11.25	1.12
F	CASSCF	15.71	1.24
	Eff. Pot.	17.26	2.75
	Exp.	17.42	3.45

Table 1. Example of the performance of the method. Atomic ground state ionization potentials (IP) and electron affinities in eV, results taken from Ref. 2.

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Theoretical modelling of mechanoluminescent properties of an organic dye

WPO20

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Mechanoluminescent (ML), “smart” materials which show color changes resulting from environmental stimuli such as shearing, grinding or external pressure, are of particular interest to the materials science community due to their vast potential in optical, electronic and medical applications. Luminescence properties of organic crystals and aggregates are governed by the molecular structure and supramolecular arrangement. Application of pressure might trigger changes in the molecular conformation and packing that translate into changes in emission wavelength and intensity. Understanding of already reported experimental ML properties and rational design of ML organic materials requires a detailed mechanistic study of such complex phenomenon. So far, very few theoretical studies have comprehensively assessed ML in organic materials, from the individual molecular structure and photophysical properties to their solid-state ML response.

This work is based on the experimental study by Dong et al. who reported that the exertion of external pressure on crystals of 9,10-bis((E)-2-(pyrid-2-yl)vinyl)anthracene (BP2VA) led to a drastic change in its photoluminescence color[1]. Concretely, I aim to characterize the excited electronic states of an isolated monomer and packed dimers of BP2VA and calculate their absorption and fluorescence emission properties using time-dependent density functional theory (TD-DFT). With Quantum Espresso, pressure will be simulated on three polymorphs and changes in molecular arrangement and consequent intermolecular interactions will be analyzed. Differences in electronic and optical properties induced by intermolecular interactions will be accounted for with TD-DFT and decomposition of the computed excitations will be used to analyze the nature of the electronic transitions.

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Dynamics of fragmentation and isomerization of small cations in gas phase

WPO21

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Pump-probe experiments involving strong laser fields are at the center of many studies in molecular science. Due to the high intensity of pump and probe pulses, available theories necessarily make use of approximations that, although crude, have been shown to be very useful to model the molecular dynamics occurring between the two pulses, providing much needed insight to the experiments. Ab initio molecular dynamics in the Atom Centered Density Matrix Propagation (ADMP) formulation, which belongs to the extended Lagrangian approach, is able to provide results that compare fairly well with the experiments.

In this work we have performed ADMP calculations for three small molecular cations generated by a strong IR pulse: propanol, isopropanol and acetonitrile; and also compared those three systems with a fourth one from previous works, ethanol. In parallel with experiments, we have described the dynamics of the systems after ionization and relaxation of the energy into vibrational modes, providing theoretical explanation of the fragmentation channels and describe the processes of isomerization and hydrogen migration that accompany the observed fragmentation of the molecular cations.

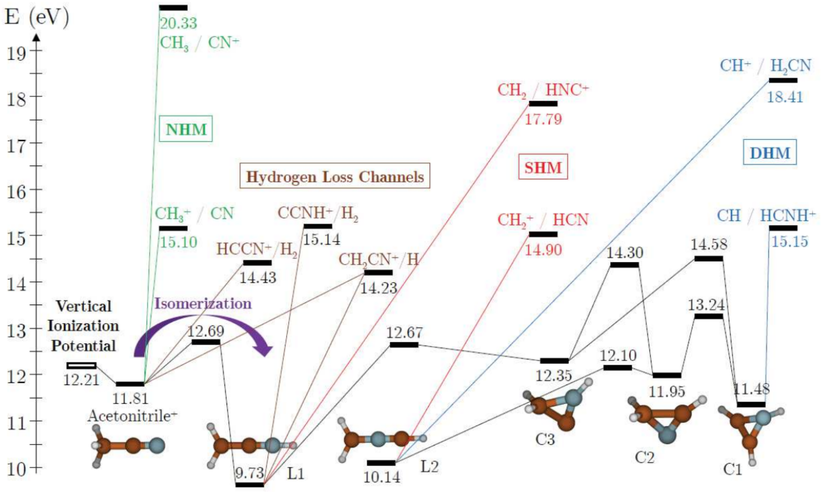

Figure 1. Isomerization processes leading to each fragmentation channel for acetonitrile

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Influence of Zn(II) cations in the conformational dynamics of amyloid-β from multiscale molecular modelling and quantum mechanics calculations

WPO22

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Amyloid fibrils are stable forms of misfolded proteins associated with numerous neurodegenerative diseases[1]. Among these, Alzheimer's disease may be the most prevalent, with over 55 million dementia cases reported by the World Health Organization in 2021[2]. The molecular origin of Alzheimer's is linked to amyloid fibril formation by misfolded Aβ-peptide (Aβ). These fibrils form aggregates that are stabilized by the presence of Zn(II) cations[3]. Nevertheless, the specific interactions governing Aβ-Zn(II) coordination are still largely unknown. Many possible Aβ-Zn(II) structures have been proposed experimentally (see figure 1) where Zn(II) adopts different coordinations [4]. In order to understand the intricate Aβ-Zn(II) interactions and conformational dynamics of Aβ, it is essential to obtain a good representation of the metal centres Aβ-Zn(II) system display. Standard Zn(II) models employed by classical force fields, i.e., nonbonded models, tend to fail[5]. These models heavily favour octahedral coordination although it has been reported that tetrahedral coordination is favoured in protein environment[6]. In this work, we will employ bonded models to accurately capture Aβ-Zn(II) coordination and extract precise conformational dynamics of the systems.

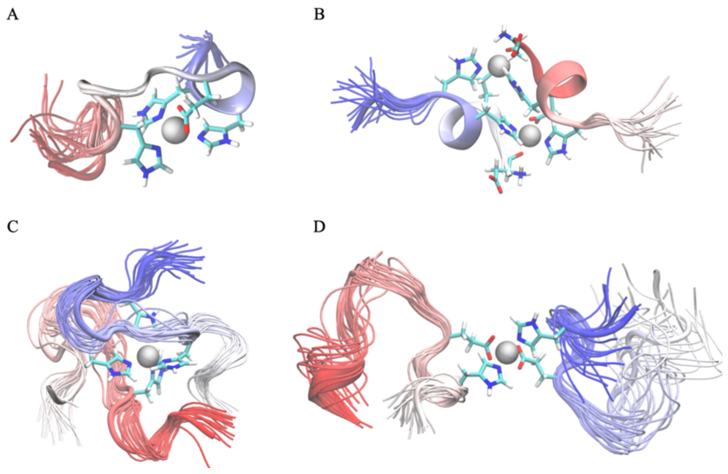

Figure 1. Various Aβ-Zn(II) experimental structures. PDB ID: 1ZE9 (A), 5LFY (B), 2LI9 (C) and 2MGT (D).

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Time-optimal quantum driving in a time-dependent drift Hamiltonian

WPO23

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Time-efficient control schemes for manipulating quantum systems are of great importance in quantum technologies, where external forces from the environment rapidly degrade the quality of states over time[1]. We derive an approach to time-optimal control that circumvents the boundary-value problem that plagues the quantum brachistochrone equation[2] at the expense of unlocking the form of the control Hamiltonian. In this setting, a coupled system of equations, one for the control Hamiltonian and another one for the duration of the protocol, realize a `no prior-guess' approach to quantum control theory. As an example, we show how external time-dependent forces, in the form of a Landau-Zener type Hamiltonian, can be maneuvered to speed-up a given state transformation[3,4] (see Fig. 1) without implying significant deviations from the adiabatic path (see Fig. 2). These results have implications in the field of quantum information processing by providing a scheme to manage background interactions.

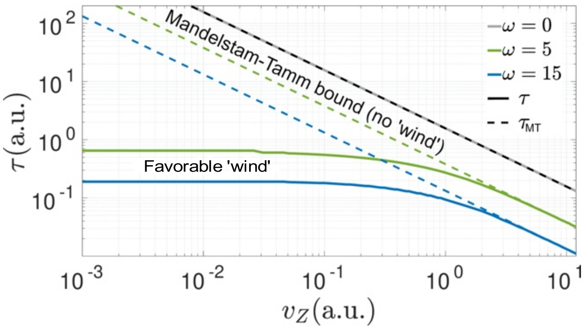

Figure 1. Time of the evolution as a function of the energy disposal of the control.

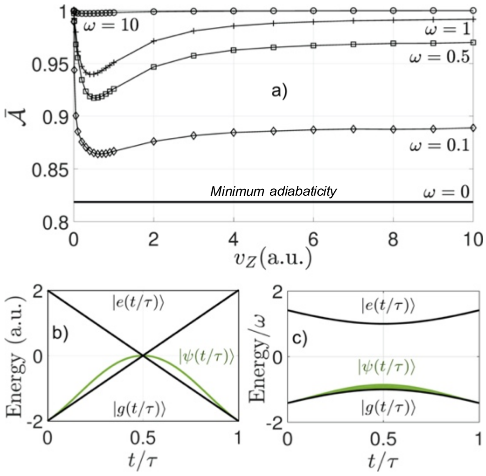

Figure 2. Mean adiabaticity of the evolution.

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Energy Decomposition Analysis of Drug/Protein Interactions

WPO24

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The study of drug-protein interactions is very important to understand the mode of action of those drugs once they are in our organism, and to develop novel therapeutic agents with enhanced efficacy. However, the experimental characterization of a huge number of drug-protein pairs is very costly and time-consuming. Therefore, computational methods have gained popularity since they can be applied in a systematic and efficient way and can provide molecular information, which is not attainable with experimental measurements [1].

In this study, the interaction energy between several hundreds of drug-aminoacid pairs has been quantitatively characterized. Specifically, an electron density-based energy decomposition analysis method [2,3] has been used for the calculation of the different contributions of the intermolecular interaction energy, namely, electrostatic, repulsion, dispersion and induction. In a second step, the drugs are classified in different families considering their interaction energy components and structural features, which are obtained by applying different similarity methods. The goal is to unveil possible structure/energetics relations which could contribute to design novel drugs able to bind the proteins in a more controlled and efficient way.

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CO_2 conversion on single metal atom catalysts supported on silicalite

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WPO25

In the last few years, single-atom catalysts have emerged in popularity as a novel class of catalysts that present high activity and selectivity for various catalytic reactions thanks to their easy tuneability. Zeolites can be used as supports since they supress the aggregation of metal particles and provide encapsulated metal atoms with high stability on their porous structure. They are composed by Si, O and Al atoms. In this context, first of all, using Density Functional Theory computation, we have exhaustibly studied the adsorption of 29 different transition metals (TM) supported on silicalite (no Al atoms), abbreviated as TM@S-1, looking for their most stable sites for each TM [1].

Our main goal is to study the hydrogenation of CO_2 on TM@S-1, because it is the main gas responsible of the global warming effect and can be converted it into light fuels such as CH_4, CH_3OH or CH_2O. For this reason, all TM@S-1 adsorption energies and energy barriers were evaluated for the CO_2 and H_2 species [2], looking for potentially active and stable TM@S-1 catalysts that exhibit low energy barriers and high resistance to aggregation. In addition, a study of CH_4 and H_2O adsorptions was also performed for all catalysts since they are the Sabatier reaction products ($CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$). Later on, once evaluated two different CO_2 conversion mechanisms [2]: the redox – direct CO_2 dissociation - and the associative - hydrogen-assisted CO_2 dissociation –, we embark on analysing the complete reaction network of CO_2 conversion into possible light fuels, beginning with Ru@S-1 catalyst, as this presents the lowest energy barrier for the CO_2 dissociation.

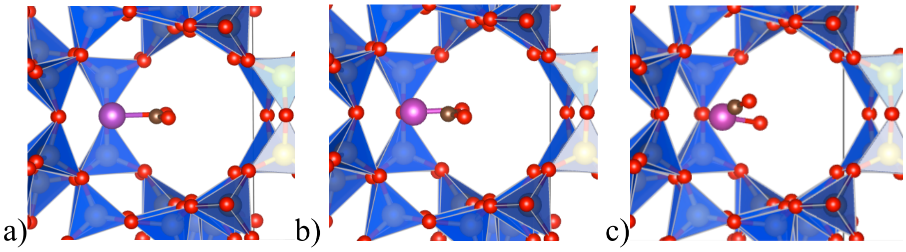

Figure 1: Figures showing the redox CO_2 mechanism ($CO_2 \rightarrow CO+O$) on Ru@S-1 with 3 different states. a) corresponds to CO_2 adsorption, b) transition state and c) CO and O coadsorption in Ru. Atoms are shown in spheres of red, yellow, brown and purple colours for O, Si, C and Ru, respectively.

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Theoretical study of semiconducting Hydrogen-Bonded Organic Frameworks based on a Tetrathiafulvalene derivative.

WPO26

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Hydrogen-bonded organic frameworks (HOFs), a class of porous materials that rely on the assembly of organic building blocks by means of hydrogen-bonding interactions, have attracted attention during the past decade due to their unique characteristics [1]. Since H-bonds are weaker than the covalent bonds used for the construction of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), HOFs have some unique features such as mild synthesis conditions, solution processability, easy healing and regeneration. These features make HOFs a tunable platform to construct functional materials with several applications such as gas separation and storage [2]. However, exploitation of HOFs in next-generation applications involving charge storage and conversion, is hampered by the absence of electrical conductivity due to the poor electronic communication between the constituting moieties[2, 3].

Herein, we present a theoretical study on the structural, electronic, and conducting properties of three TTF-based HOFs, named MUV-20a, MUV-20b and MUV-21, formed by the assembly of TTFTB ligand through a H-bonding network (Figure 1). Based on experimental evidence, our calculations confirm the possibility of MUV-20a/b to form a zwitterionic HOF upon spontaneous oxidation of TTF, which leads to an unpaired electron localized on the electron-donor TTF core. The generation of these charge carriers in the HOF promotes semiconductivity due to the presence of efficient hole-transporting 1D TTF channels along the structure.

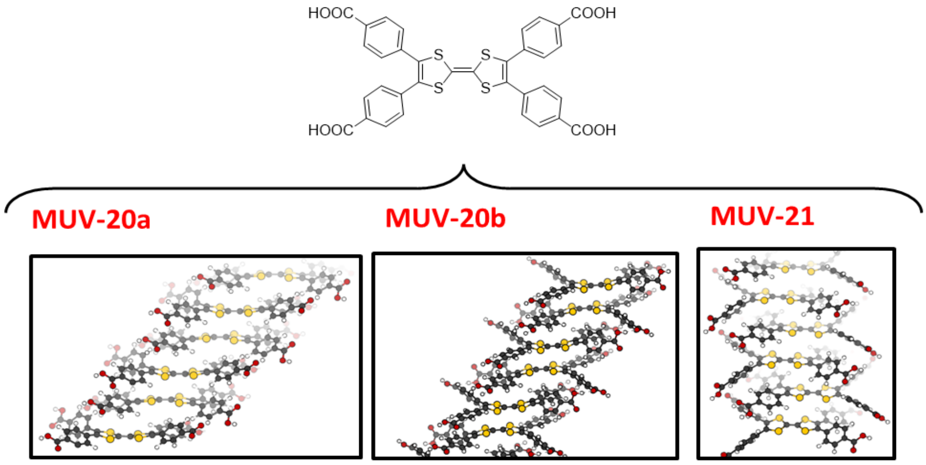

Figure 1. Motifs and crystal structures for the TTF-based HOFs.

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Chemiexcitation mechanism of the dioxetane derivate of the melanin monomer 5,6-dihydroxyindole-2-carboxylic acid: A quantum-chemistry study

WPO27

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It is well known that our skin is protected against UV radiation by the pigment melanin. However, in recent years an obscure role of this pigment has been discovered. It has been suggested that chemiexcitation (chemical electronic excitation) is responsible for the production of melanomas when there is no UV radiation. The source for this type of excitation process is a dioxetane derivate of the melanin monomer 5,6-dihydroxyindole-2-carboxylic acid (DHICA-DO, Figure 1), whose decomposition induces the formation of dimerizations in the DNA pyrimidine bases[1]. In this work, we have carried out a theoretical study to determine the molecular basis of the mentioned process.

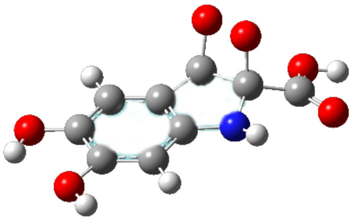

Figure 1. Optimized geometry of the ground state of the chemiexcitator DHICA-DO.

Firstly, we have studied the mechanism of the decomposition of dioxetane, using two different conformers of the chemiexcitator proposed by Premi and co-workers[1]. In both cases, the mechanism goes through a diradical intermediate that allows to populate the triplet excited state[2] making plausible the chemiexcitation process. Secondly, we have constructed many aggregates formed by a nucleobase and the most stable conformer of the DHICA-DO, to study how the mechanism is affected by the presence of the DNA base. We have analysed in this context different factors which can be relevant such as the ionization potential of the nucleobases, the formation of hydrogen bonds, the spin density delocalization and the presence or absence of π-stacking interactions.

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The Steric Energy : an Interacting Quantum Atoms descriptor of steric hindrance

WPO28

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Steric Hindrance (SH) has been classically considered to arise as a repulsive force emerging from the interaction between two nearby chemical entities. This, apparently, simple concept has shaped most of the rules and models that have been, and still are, used in the so-called "chemical thinking". However, just as it happens with many others concepts, its lack of rigor has raised much debate among the scientific community, questioning the true nature and driving force behind SH. In this work [1] we make use of the Interacting Quantum Atoms (IQA) formalism to derive a real space descriptor, the steric enery E_{ST}, of steric effects. The E_{ST} energy is obtained after removing the charge transfer (CT) bias inherent to the atomic or molecular deformation (E_{def}), as measured by the changes in the intra-atomic energy. Such a new descriptor is put to the test in a variety of scenarios, going from chemical reactions [2,3] to the classical clashing between closed shell molecules. Moreover, special attention is paid to the SH experineced by H atoms, whose ability to undergo or induce steric repulsion has been severly questioned for several decades. Altogether, the results obtained in this work prove that the E_{ST} energy is a more sutibale descriptor of SH than previous propossals (i.e plain E_{def}) being even capable of providing an appealing, yet rigorous, meassure of the steric clash undergone by H atoms.

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Human L-Asparaginase: A Theoretical Study of the Active Form and Reaction Mechanism

WPO29

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L-asparaginases (ASNases) are enzymes catalysing asparagine (Asn) hydrolysis reaction to aspartate and ammonia. Bacterial asparaginases have been widely used for years in the treatment of leukemia due to their ability of depriving cancer cells of Asn [1,2] . However, this approach is limited by the severe side effects arising from the immune responses due to the bacterial origins of the enzyme. A potential strategy to overcome such limitations involves replacement of enzymes of bacterial origin with mammalian enzymes such as human asparaginase type III (hASNase3) [3]. Despite substantial experimental work on the catalytic reaction, there are still controversies regarding the mechanism and no theoretical study has yet been done on hASNase3.

In this work, the binding process of the substrate and the reaction mechanism in hASNase3 have been studied, using a combination of molecular dynamics simulations (MD), hybrid quantum mechanics/molecular mechanics (QM/MM), the adaptive string method (ASM) [4] and free energy methods. Human ASNase3 is a homodimer with the active site residues originating from a single protomer. Therefore, in order to elucidate whether the dimer or the monomer are the physiologically relevant forms, both simulations of monomer and dimer structures were run.

First, due to the lack of a complete model of the enzyme, a flexible loop was added using AlphaFold2 [5]. Then, alchemical free energy calculations were employed to determine the protonation state of the N-terminal group of Thr168, showing that the protonated state is predominant at experimental conditions but the deprotonated form is easily accessible. Analysis of classical MD simulations revealed that dimeric structure of hASNase3 is crucial for maintaining the substrate in the active site and its stability. Using a DFTB3/MM description, our results indicate that the reaction of acyl-enzyme formation starts with the activation of the nucleophile, the hydroxyl oxygen atom of Thr168, by its own N-terminal amino group acting as a base, followed by the nucleophilic attack and final proton transfer. The free energy barrier obtained for the formation of the acyl-enzyme intermediate is in good agreement with the experimentally-derived free energy barrier (16.9 kcal·mol^{-1}) [6].

Results found in this work do not only provide a theoretical basis for understanding the catalytic cycle of hASNase3, but can be also important to guide further studies directed to improve the treatment of leukemia.

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Automatic procedure to obtain tight-binding parameters for second-principles simulations. The case of $SrTiO_3$

WPO30

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First-principles calculations allow to compute the energy and properties of a compound from essential information about its structure and composition. In principle, even the finite temperature behavior of materials is accessible from first-principles simulations since the early stage of density functional theory (DFT). Nowadays, however, such simulations remain practically limited by computational resources to very small length scales (a few hundreds of atoms per cell) and timescales (a few picoseconds). Nevertheless, many important fundamental and applied problems require to explore these large time and length scales at operating conditions (finite temperature, electric fields, etc). A practical way to overcome these limitations is to work with effective atomistic models, integrating out the electronic degrees of freedom and providing a simple parametric description of the Born–Oppenheimer energy surface in terms of structural degrees of freedom. This might be a constriction in some cases, specially, in those problems where the relevant physics is dominated by the electronic degrees of freedom. Recently, a method has also been proposed to reintroduce explicitly the treatment of the meaningful electronic degrees of freedom in the form of a tight-binding model, while avoiding double-counting with the effective atomic potentials [1].

This tight binding approach is based on the Taylor expansion of the DFT energy around a reference electronic density. The deformation density with respect this reference, as well as the hamiltonian matrix elements, is expressed in a basis of Wannier functions which are obtained from the band manifolds of interest in the problem. Only the relevant electrons to the problem can be retained in the description, reducing by orders of magnitude the computational cost. This gain in efficiency would come at the cost of finding the right parameters in the tight binding hamiltonian matrix elements, that would reproduce as close as possible the first-principle hamiltonian matrix elements.

Here we propose a method implemented in python, the MODELMAKER code, for the automatic parametrization of such tight binding hamiltonian. The starting point is made of first-principles calculations (from the SIESTA code [2]) in training sets with a small number of atoms in the unit cell. Since there is not input coming from the experiment, our method retains full predictive power, and that is why it is coined as second-principles simulations. Both electron-lattice coupling, studied by calculations characterized by geometry distortions, and electron-electron interactions, caught by simulations exploring electronic states beyond the Born-Oppenheimer surface, are included in the parametrization of the electronic model. The obtained parameters are validated comparing the band structures computed from first and second-principles in configurations that are not included in the training set. This methodology has been applied to a paradigmatic functional oxide such as $SrTiO_3$.

The authors acknowledge financial support from Grant PGC2018-096955-B-C41 funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” by the European Union.

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Modelling Ion Selectivity and Permeation through Voltage-Gated Ion Channels

WPO31

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Voltage-gated ion channels are transmembrane proteins that produce electrical signals in excitable cells to regulate various biological processes, such as muscle contraction or signal transduction [1, 2, 3]. In response to a change in the transmembrane electrical potential, the channels open their pores through which ions move passively, crossing the membrane [4]. Hence, it is fundamental to study the mechanism of ion permeation and selectivity in ion channels for understanding many cellular functions and for the discovery of new drugs targeted to these membrane proteins.

In this project the conduction mechanism for eukaryotic voltage-gated sodium channels, which is still under discussion, is being investigated by means of conventional and electric-field biased classical molecular dynamics simulations, the last one being employed to enhanced the number of permeation events. The key factors involved in the ion conduction events, such as the ion desolvation upon the pore entry, the presence of an electric field, and the interactions between the ions and the selectivity filter, among others, is discussed [2]. In addition, the ability of classical force fields to describe ion selectivity is addressed.

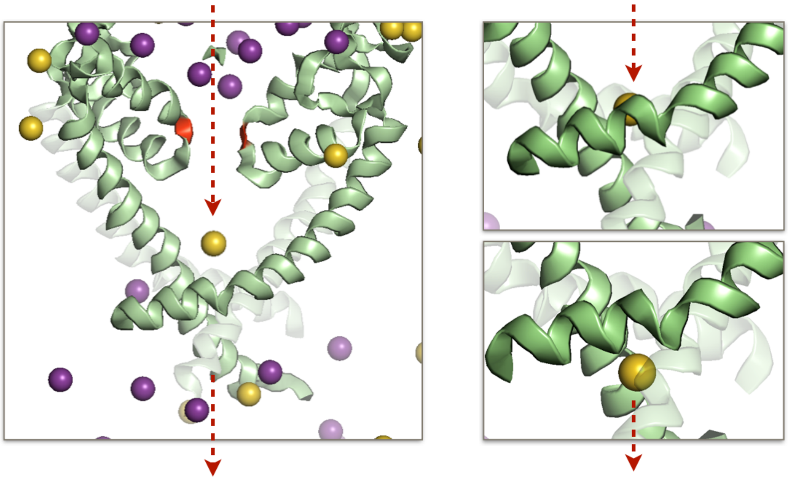

Figure 1. Schematic representation of ion conduction through a eukaryotic sodium-selective channel.

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Combined QM-ML Approach to Accelerate Photodynamics Simulation with High Robustness

WPO32

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Trajectory surface hopping (TSH) has been applied to study various systems that include excited-state dynamics. Nevertheless, the cost of high-level QM calculation limits the number and lengths of the trajectories. Some previous works have shown the possibility to accelerate photodynamics simulation with neural networks by ~10000 times[1, 2]. Despite having supreme speed, the robustness and transferability of the grey-box machine learning model remain concerns.

In this work, localized orbital locator (LOL)[3] is applied to transform the molecular coordinates into voxelized features in the 3D grid. The LOL descriptor is based on low-level DFT calculation, which is more than 100 times faster than MS-CASPT2. In addition, using the ground state energy calculated by DFT with Δ-learning provides a standard for coordinates outside the training set domain.

The dataset contains 73 QM trajectories that simulate the photolysis of the hydroxysulfinyl radical (HOSO), with 5 doublet states concerned[4]. Combining the LOL descriptor with SchNet[5], energies and forces can be predicted accurately and show great transferability. In Figure 1, it is illustrated that the state populations of ML-predicted trajectories and QM trajectories are similar. On the other hand, the ratios of photoproducts from both methods agree well, as listed in Table 1. Moreover, the ensembled LOL and SchNet model can query under-explored geometries more efficiently in the active learning scheme.

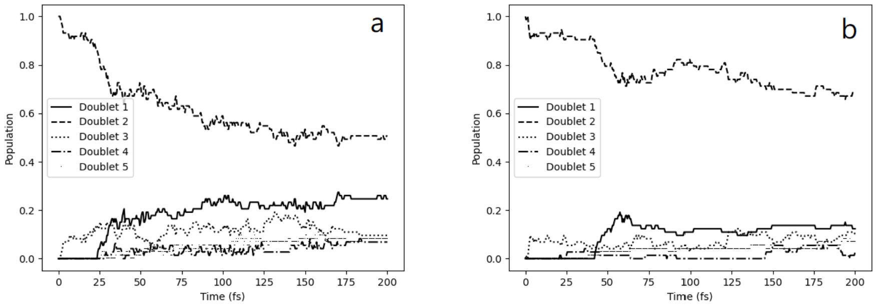

Figure 1. State population of 73 trajectories with (a) ML+ZNSH, (b) QM

Photoproduct	HO+SO	HOS+O	No photolysis
ML+ZNSH	41	0	32
QM	38	2	33

Table 1. Number of trajectories leading to different photoproducts

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In_2O_3 as multifunctional material: Fundamentals and progress of a versatile semiconductor

WPO33

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Indium oxide (In_2O_3) based materials have attracted a remarkable interest for their unique features and multifunctional properties, which can be finely tuned by controlling the interplay between their structure, morphology and composition. To enable their widespread practical usage, significant efforts have been devoted to finding relationships among the nature of chemical bonds, geometrical arrangements and their unique properties.

A detailed insight into chemical/physical properties by using advanced experimental techniques and first principle calculations provide significant advantages from both a fundamental and an applicative point of view [1,2].

The modulation of morphology, surface modification, doping process, formation of solid solutions, constructions of heterojunctions have been discussed in detail. They were employed to promote the optical properties, gas sensor capacity and to enhance the (electro-, photo-, and catalytic-) activity [3,4].

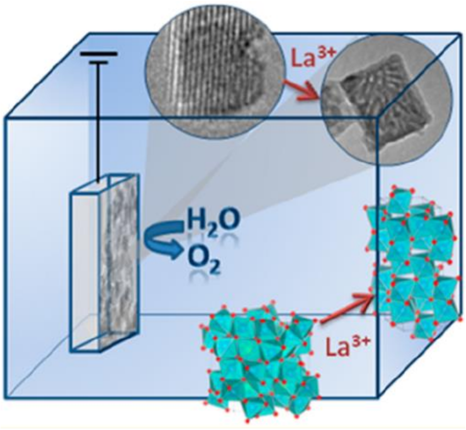

Figure 1. A schematic representation of the structure and morphology changes along the doping process of La^{3+} in In_2O_3 to enhance the oxygen evoluction reaction (OER).

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Theoretical study of triazole-containing pesticides and their protonated forms

WPO34

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We present a systematic study of the structure and chemical properties of a family of pesticides, in particular several DeMethylation Inhibitors, containing a triazole ring in their struc- ture. The compounds selected are: Azaconazole, difenoconazole, diniconazole, fenbucona- zole, metconazole, penconazole, tebuconazole, triadimefon, triadimenole and triticonazole and their protonated forms.

We have use CREST and CENSO programmes [1] to determine in a systematic way the most stable conformations for both the neutral and protonated forms, and we have considered the molecules in gas phase and water and octanol environments. Final properties are obtained at the B3LYP-D3/6-311+G(d,p) level.

Our results allow us to better understand chemical properties that can be related with the envi- ronmental impact of these pesticides[2]. We have also identified the most stable protonation sites inside each molecule and discuss the different effects observed: proton transfer mecha- nism, formation of internal bonds or lose of aromaticity.

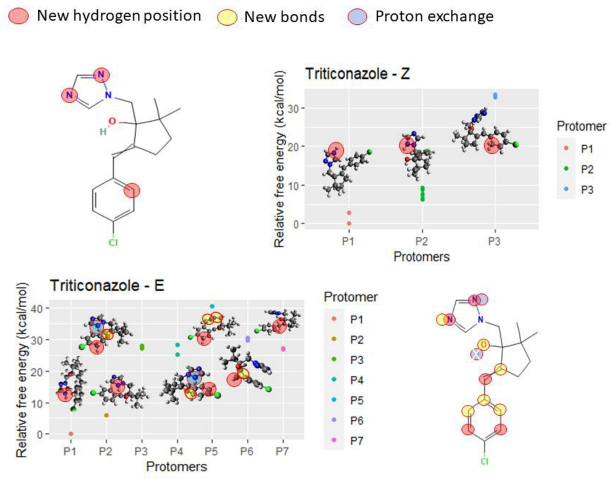

Figure 1. Relative free energies of the most stable protomers of two different isomers of Triticonazole pesticide.

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Photoswitchable Agonist of the 5-HT$_{2A}$ Receptor

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WPO35

The majority of drugs used in psychiatry were developed during an era where we understood very little about neuropsychiatric disorders [1]. After six decades, the use of psychedelics became one of the most exciting developments in neuropsychiatry since these drugs appear to produce rapid and substantial therapeutic effects in curing depression, post-traumatic stress disorders and drug addiction [2]. Despite their complex polypharmacology, the 5-HT$_{2A}$ receptor has emerged as the main molecular target for hallucinogenic actions of psychedelics, such as LSD or N,N-DMT, in humans [3]. However, the interaction mechanism between the drugs and the receptor in not clear, and even the binding mode of its endogenous ligand serotonin (5-HT) in unknown.

In the present research, the binding modes of 5-HT and one of the strongest psychedelics, N,N dimethyltryptamine (DMT), are compared to gain molecular insights on the different residues involved in the binding of those two extremely similar molecules, which have very different physiological effects. A combination of molecular docking, molecular dynamics, 1A-MMGBSA and pairwise residue ligand energy decomposition analysis are employed to characterize the different binding modes of those two drugs. In addition, the binding modes of two photoswitchable analogues, azo-5HT and azo-DMT, are also explored since the use of photoswitches and light can allow a high spatio-temporal control of the action mechanism.

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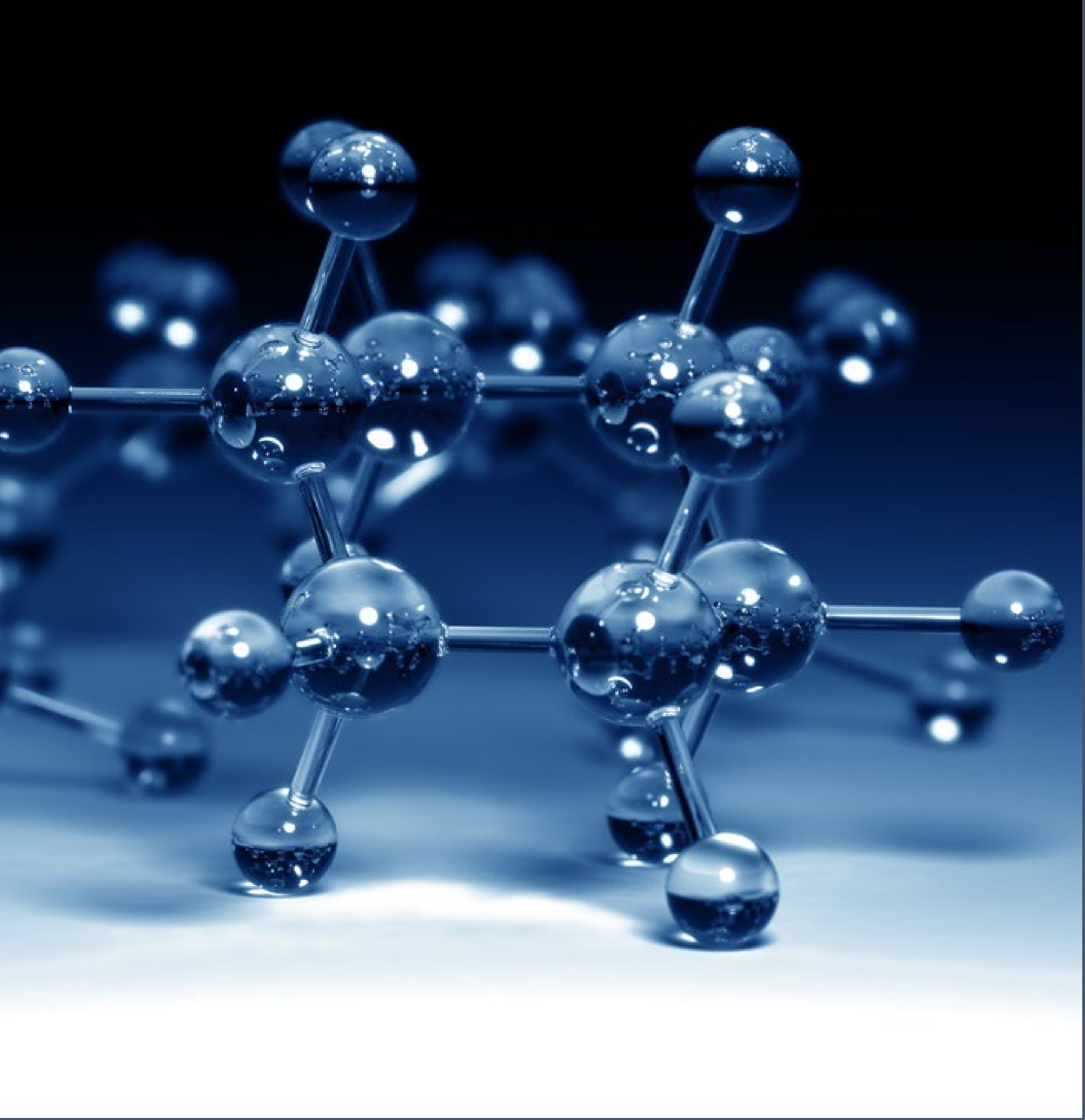

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