CONFERENCE PROGRAMME

11TH CONGRESS ON ELECTRONIC STRUCTURE: PRINCIPLES AND APPLICATIONS

17-19 JULY 2018

TOLEDO
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Welcome words

Dear Colleagues,

On behalf of the organizing committee, it is my pleasure to welcome you to Toledo to the 11th Congress on Electronic Structure Principles and Applications (ESPA-2018). The ESPA meeting was an initiative that started 20 years ago in a first meeting in Miraflores de la Sierra (Madrid) and was conceived as an international conference promoted by the Spanish teams working in Theoretical Chemistry and Computational Modelling. The different editions of the ESPA conferences (2000-San Sebastian, 2002-Sevilla, 2004-Valladolid, 2006-Santiago de Compostela, 2008-Palma de Mallorca, 2010-Oviedo, 2012-Barcelona, 2014-Badajoz and 2016-Castellón) has served to establish ESPA as a reference conference in the field at international level.

This is also an initiative that aims to promote young scientist, especially those participating in the master and doctorate programmes in Theoretical Chemistry and Computational Modelling (TCCM). For this reason, the day after the conference there will be the annual workshop of the TCCM programme in which the TCCM PhD students will present their latest results.

This edition will also have a special celebration: a symposium in honour of Manuel Yáñez and Otilia Mó in occasion of their retirement and 70th Birthday. Otilia and Manuel were among the founders of the ESPA conference and TCCM postgraduate studies. They organized the first ESPA conference and have been the coordinators of the TCCM international master and doctorate programme. It will be a special pleasure to share with them this special day.

ESPA conferences have been always characterized by a relaxed atmosphere that, on top of exchanging ideas about scientific projects, offer the opportunity to meet old and new friends. I am sure that the historic city of Toledo, World Heritage Site, will provide the perfect environment.

Finally, I would like to thank our sponsors, specially the Universities of Castilla La Mancha and Autónoma de Madrid and the Spanish Royal Societies of Chemistry and Physics, for their support to organize the conference, and to The Journal of Physical Chemistry A, Springer and PCCP journal for providing prizes for the best posters.

I wish you a successful scientific and personal ESPA2018 conference and I hope that you will enjoy the city of Toledo.

Manuel Alcami
Chairman of the ESPA2018 conference
Committees

Local Organizing Committee
Manuel Alcamí, UAM (Chair)
Ibon Alkorta, CSIC
Inés Corral, UAM
Sergio Díaz-Tendero, UAM
Al Mokhtar Lamsabhi, UAM
Fernando Martín, UAM
Beatriz Martín, UAM
Camelia Muñoz, UCLM
Alfonso Niño, UCLM
Alicia Palacios, UAM

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Carmen Barrientos, Universidad de Valladolid, Spain
Leticia González, University of Vienna, Austria
Angel Martín-Pendás, Universidad de Oviedo, Spain
Vicent Moliner, Universitat Jaume I, Spain
Juan Novoa, Universidad de Barcelona, Spain
Francisco Olivares del Valle, Universidad de Extremadura, Spain
Enrique Sánchez-Marcos, Universidad de Sevilla
Mariona Sodupe, Universitat Autonoma de Barcelona, Spain
Miquel Solà, Universitat de Girona, Spain
Iñaki Tuñón - Universidad de Valencia
Jesús Ugalde, Universidad del Pais Vasco, Spain
Saúl Vázquez, Universidad de Santiago de Compostela
Manuel Yáñez, Universidad Autónoma de Madrid, Spain

Co-organizer
APQTC
(Associación para la Promoción de la Química Teórica y Computacional)
16th July - Monday

SYMPOSIUM IN HONOUR OF OTILIA MÓ AND MANUEL YÁNEZ

10:00 – 11:00  Registration
11:00 – 11:30  Opening session
11:30 – 13:30  First Session
Chairman: Enrique Sanchez Marcos - University of Seville, ES
11:30 – 12:00  Ria Broer - University of Groningen, NL
               “Magnetic and other interactions in Theoretical Chemistry and Computational Modelling”
12:10 – 12:40  Ibon Alkorta - Instituto de Química Médica (CSIC), ES
               “Halogen bonds: traditional, halogen-shared and ion-pair complexes”
               “Madrid, Evry, Paris: A wonderful interplay between theory and experiments for probing the structure and reactivity of gaseous ions”
13:30 – 15:00  Lunch
15:00 – 16:30  Second Session
Chairman: Juan Novoa - University of Barcelona, ES
15:00 – 15:30  Joan Bertrán - Universidad Jaume I. Castellón, ES
               “Self-cleaving pistol ribozyme”
15:30 – 16:00  Rosa Caballol - Universitat Rovira I Virgili, ES
               “Spin-crossover in a functionalized Ni-porphyrin complex”
16:00 – 16:30  Jesús Ugalde - Universidad del País Vasco, ES
               “Activating methane by ligated transition metal compounds”
16:30 – 17:00  Coffee Break
17:00 – 19:00  Third Session
Chairwoman: Mariona Sodupe – University Autonoma of Barcelona, ES
17:00 – 17:15  Alberto Luna - Universidad Autónoma de Madrid, ES
               “People chemically joined”
17:15 – 17:30  Inés Corral - Universidad Autónoma de Madrid, ES
               “The keys to DNA photostability: My last stopover in an exciting promenade from the ground to the excited state”
17:30 – 17:45  **Cristina Trujillo** - *Trinity College Dublin, IE*
“Improvement of anion transport systems by modulation of chalcogen Interactions: key role of the solvent”

17:45 – 18:00  **Jose Gámez** - *Covestro Deutschland AG, DE*
“Computational chemistry in an industrial environment”

18:00 – 18:15  **Al Mokhtar Lamsabhi** - *Universidad Autónoma de Madrid, ES*
“Uracil: continuous history of training”

18:15 – 18:30  **Pablo Sanz** - *Universidad Autónoma de Madrid, ES*
“Intramolecular Magnesium and Beryllium bonds. The importance of the resonance-assisted phenomena”

18:30 – 18:45  **Ana Martín** - *Universidad Autónoma de Madrid, ES*
“From electronic structure to molecular dynamics”

18:45 – 19:00  **Oriana Brea** - *Universidad Autónoma de Madrid, ES*
“Thermal decomposition of N-nitrosoamides in confined spaces”

19:00 – 19:30  **Closing ceremony**

19:30  **ESPA Reception**

20:45  **Bus departure for dinner**

21:00  **Dinner in Honour of Otilia Mó and Manuel Yáñez**
> 17th July - Tuesday

8:30 – 9:00  Registration

9:00 – 11:15  Session 1
Chairman: Enrique Ortí - University of Valencia, ES

9:00 – 9:30  Opening Ceremony

9:30 – 10:15  Plenary Lecture 1 (QuimComp Lecture): Donald Truhlar - University of Minnesota, US
“Advances in density functional theory and photochemistry”
Sponsored by the Chemistry & Computation division of the RSEQ

10:15 – 10:35  Invited Lecture 1: Shirin Faraji - University of Groningen, NL
“Excited-state dynamics of red fluorescent protein”

10:35 – 10:55  Invited Lecture 8: Oriol Vendrell - Aarhus University, DK
“Collective conical intersections in cavity femtochemistry”

10:55 – 11:15  Oral Contribution 1: David Casanova - Donostia International Physics Center, ES
“From electron correlation to photophysics”

11:15 – 11:45  Coffee Break

11:45 – 13:30  Session 2
Chairwoman: Carmen Jiménez Calzado - University of Sevilla, ES

11:45 – 12:30  Plenary Lecture 2: Karsten Reuter - TUM Munich, DE
“New avenues in first-principles computational energy research”

12:30 – 12:50  Invited Lecture 3: Eliseo Ruiz - Universitat de Barcelona, ES
“Magnetoresistance in single-molecule devices”

12:50 – 13:10  Oral Contribution 2: José Javier Plata Ramos - Universidad de Sevilla, ES
“An accurate and efficient framework for calculating lattice thermal conductivity of solids”

13:10 – 13:30  Oral Contribution 3: Mercè Deumal - Universitat de Barcelona, ES
“Magnetic fingerprint of dithiazolyl-based molecule magnets”

13:30 – 15:30  Lunch

15:30 – 17:15  Session 3
Chairman: Angel Martín Pendás - University of Oviedo. ES

15:30 – 16:15  Plenary Lecture 3: Gernot Frenking - Philipps-Universität, DE
“Travelling in Valence Space”

16:15 – 16:35  Invited Lecture 4: Celia Fonseca Guerra - Vrije Universiteit, NL
“Hydrogen bonding from a Kohn-Sham molecular orbital perspective”
16:35 – 16:55 Oral Contribution 4: Juan Aragó March - Universidad de Valencia, ES
“Exciton transport in organic crystals: The role of the dynamic disorder”

16:55 – 17:15 Oral Contribution 5: Mercedes Alonso - Vrije Universiteit Brussel, BE
“Topology/aromaticity switches: from chemical design to functional molecular electronic devices”

17:15 – 17:45 Coffee Break

17:45 – 19:00 Poster Session 1
P001 – P097

> 18th July - Wednesday

9:00 – 11:05 Session 4
Chairman: Ignacio Tuñon - University of Valencia, ES

9:00 – 9:45 Plenary Lecture 4: Ursula Rothlisberger - Ecole Polytechnique Fédérale Lausanne, CH
“Next generation first-principles molecular dynamics in ground and excited states”

9:45 – 10:05 Invited Lecture 5: Damien Laage - Ecole Normale Superieure, FR
“On enzyme-catalyzed hydride transfer reactions”

10:05 – 10:25 Invited Lecture 6: Josep Maria Lluch - Universitat de Barcelona, ES
“On the mechanism of oxygenation of polyunsaturated fatty acids catalyzed by cyclooxygenase-2 and its aspirin-acetylated form”

10:25 – 10:45 Oral Contribution 6: Ian Williams - University of Bath’s, GB
“Computational modelling of a caged methyl cation: structure, energetics and vibrational analysis”

10:45 – 11:05 Oral Contribution 7: Luis Miguel Azofra - KAUST, SA
“Manganese: a very welcome guest in hydrogenation transfer reactions”

11:05 – 11:30 Coffee Break

11:30 – 13:15 Session 5
Chairwoman: Leticia González - University of Vienna, AT

11:30 – 12:15 Plenary Lecture 5: Alexander Kuleff - Heidelberg University, DE
“Ultrafast electron dynamics as a route to explore chemical processes”

“How nuclear motion affects coherent electron dynamics in molecules”

12:35 – 12:55 Invited Lecture 2: Rosario González-Férez - Universidad de Granada, ES
“Ultralong-range Polyatomic Rydberg Molecules”

12:55 – 13:15 Oral Contribution 8: Jesús González-Vázquez - Universidad Autónoma de Madrid, ES
“Electron correlation in the Ionization continuum of molecules: Photoionization of N₂”
13:30 – 15:30  Lunch
15:30 – 16:30  Session 6
   Chairwoman: Carmen Barrientos - University of Valladolid, ES
15:30 – 16:15  Plenary Lecture 6: Mariona Sodupe - Universidad Autónoma de Barcelona, ES
   “Mineral induced chemical prebiotic processes. Insights from computational approaches”
16:15 – 16:35  Invited Lecture 9: Alejandro Toro-Labbe - Pontificia Universidad Católica de Chile, CL
   “Discussion on theoretical models for activation and reaction energies in chemical reactions”
16:35 – 16:55  Oral Contribution 9: Masataka Nagaoka - Nagoya University, JP
   “Red Moon Methodology: A computational molecular technology of complex chemical reaction systems - Its theoretical treatment and applications”
16:55 – 17:15  Oral Contribution 10: Aurora Costales - Universidad de Oviedo, ES
   “A computational study of the catalytic role of hydrogen bond interactions”
17:15 – 17:45  Coffee Break
17:45 – 19:00  Poster Session 2
   P098 – P193

> 19th July - Thursday

9:00 – 11:05  Session 7
   Chairwoman: Mar Reguero - University Rovira i Virgili, Tarragona. ES
9:00 – 9:45  Plenary Lecture 7 (ChemBio Lecture): Walter Thiel - Max-Planck-Institut für Kohlenforschung, DE
   “Recent advances in semiempirical quantum chemistry”
   Sponsored by the Biological Chemistry division of the RSEQ
9:45 – 10:05  Invited Lecture 10: Elfi Kraka - Southern Methodist University, US
   “A direct measure of metal ligand bonding - the Metal Ligand Electronic Parameter”
10:05 – 10:25  Invited Lecture 11: Marcel Swart - Universitat de Girona, ES
   “Characterization and prediction of short-lived transition-metal species”
10:25 – 10:45  Oral Contribution 11: Jose Gracia - Magnetocat S.L, ES
   “Spintro-catalysis”
10:45 – 11:05  Oral Contribution 12: Rita Prosmiti - IFF-CSIC, ES
   “Quantum computations of nanoconfined molecules”
11:05 – 11:30  Coffee Break
11:30 – 13:15  **Session 8**
Chairman: Remco Havenith - *University of Groningen, NL*

11:30 – 12:15  **Plenary Lecture 8: Ivano Tavernelli - IBM Research Zurich, CH**
“Mixed quantum-classical approaches for the description of electronic and nuclear quantum dynamics”

12:15 – 12:35  **Invited Lecture 12: Mario Piris - DIPC & EHU/UPV & IKERBASQUE, ES**
“Global method for electron correlation based on the NOF theory”

12:35 – 12:55  **Oral Contribution 13: Clàudia Climent - Universidad Autónoma de Madrid, ES**
“Theory of vibro-polaritonic chemistry”

12:55 – 13:15  **Oral Contribution 14: Ramón Sayós - Universidad de Barcelona, ES**
“DFT-based adsorption isotherms for pure and flue gases including SO\textsubscript{2} poisoning on Mg-MOF-74”

13:30 – 15:30  **Lunch**

15:30 – 16:30  **Session 9**
Chairman: Vicent Moliner. *University Jaume I, Castellón, ES*

15:30 – 16:15  **Plenary Lecture 9: Jeremy Harvey - KU Leuven, BE**
“Empirical valence bond methods for probing dynamics in the condensed phase”

16:15 – 16:35  **Oral Contribution 15: Katarzyna Swiderek - Universitat Jaume I, ES**
“Are electrostatic properties of proteins the origin of enzyme catalysis?”

16:35 – 16:55  **Oral Contribution 16: Riccardo Spezia - CNRS, FR**
“Theoretical mass spectrometry: from organic to biological molecules”

16:55 – 17:15  **Invited Lecture 13: Elena Formoso - UPV/EHU & DIPC, ES**
“A computational approach to the structural toxicity of aluminum with biomolecules”

17:15 – 17:30  **Closing ceremony**

20:30  **ESPA Dinner**
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<td>09:00 – 11:50</td>
<td>First session</td>
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<td>09:00 – 09:40</td>
<td>Plenary Lecture - <strong>Kirill Zinovjev</strong> - <em>University of Valencia, ES</em></td>
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<td>“Biochemistry in silico: enzymatic reaction pathways and transition states”</td>
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<td>09:40 – 10:00</td>
<td>Oral Communications</td>
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<td>09:40 – 10:00</td>
<td>Sara Gil Guerrero - <em>University of Vigo, ES</em></td>
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<td>“Rationalization of the electron transport in polymeric conjugated chains according to its electronic distribution”</td>
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<td>10:00 – 10:20</td>
<td>Carlos Ramos Guzmán - <em>University of Vigo, ES</em></td>
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<td>“A novel caspase-1 reaction mechanism. A theoretical study based in QM/MM potentials and the string method”</td>
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<td>10:20 – 10:40</td>
<td>Fernando Jiménez Grávalos - <em>University of Oviedo, ES</em></td>
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<td>“Assessing the Performance of the DFT Implementation of IQA in Water Clusters”</td>
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<td>10:40 – 11:00</td>
<td>Pedro Fernández Milán - <em>Autonomous University of Madrid, ES</em></td>
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<td>“XCHEM Approach to the Ionization of Pyrazine”</td>
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<td>11:00 – 11:20</td>
<td>Daniel Álvarez Lorenzo - <em>University of Oviedo, ES</em></td>
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<td>“Theoretical insights on the reactivity of rhenium carbonyl complexes towards activated alkynes”</td>
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<td>11:20 – 11:25</td>
<td>Jesús Cerdá - <em>University of Valencia, ES</em></td>
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<td>“Short-range effects on the excitonic coupling of N-heterotriangulenes”</td>
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<td>11:25 – 11:30</td>
<td>Xabier Telleria - <em>University of Basque Country, ES</em></td>
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<td>“An insight of the arbitrary order calculus for atomic and molecular sciences”</td>
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<td>11:30 – 11:35</td>
<td>Sergio Pérez - <em>University of Sevilla, ES</em></td>
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<td>“Molecular dynamics of aqueous [UO$<em>2$]$^2</em>+$ diffusion in clays”</td>
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<td>Iker Ortíz - <em>University of Basque Country, ES</em></td>
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<td>“Computational studies on the interaction of [Mo($\mu$-C$_5$H$_5$)Br (CO)$_2$(phen)] with G-quadruplexes”</td>
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<td>Natalia Serrano - <em>University Jaume I, ES</em></td>
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<td>“Theoretical Study of inhibition of 20S Proteasome core particle”</td>
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<td>11:45 – 11:50</td>
<td>María Izquierdo - <em>University of Valencia, ES</em></td>
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<td>“Non-radiative decay paths in organic $\pi$-conjugated compounds of interest in optoelectronics”</td>
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<td>Chairman: José Sánchez - <em>University of Valencia, ES</em></td>
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<td>12:30 – 12:50</td>
<td>Carlos Martín Fernández</td>
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<td>13:35 – 13:40</td>
<td>María Zubiria</td>
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<td>14:00 – 15:30</td>
<td>Lunch break</td>
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<td>15:30 – 15:50</td>
<td>Julen Munárriz Tabuenca</td>
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<td>15:50 – 16:10</td>
<td>Mauro A. Pererira Gonçalvez</td>
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<td>16:10 – 16:30</td>
<td>Paula Pla Terrada</td>
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<td>16:30 – 16:50</td>
<td>Raúl Rodríguez Segundo</td>
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<td>16:50 – 17:10</td>
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<td>Juan J. Villaverde Mella</td>
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Advances in density functional theory and photochemistry

Donald Truhlar

University of Minnesota, US
Excited-state dynamics of red fluorescent protein

Kiana Moghaddam and Shirin Faraji

Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
s.s.faraji@rug.nl

Far-red fluorescent proteins (FPs) enable deep-tissue in vivo imaging. Combination of FPs with large and small Stokes shifts can be used in single-excitation/dual-emission multicolor applications. The atomic-level understanding of excited-state relaxation causing Stokes shift is still incomplete, which hinders the design of new FPs with desired properties [1]. Our recent study [2] using the hybrid quantum mechanics/molecular mechanics (QM/MM) scheme revealed that the large Stokes shift observed in mPlum is due to the excited-state relaxation of the chromophore and the flexibility of its hydrogen-bond network. The following amino acids play the most important role: ILE65 and GLU11. The MD simulations reveal two ground-state populations with direct (Chro…ILE65…GLU11) and water-mediated (Chro…ILE65…Wat231…GLU11) hydrogen bond patterns. In the excited state, both populations relax to an emitting state with water-mediated hydrogen bond pattern.

The most recent time-resolved experimental findings reported two relaxation times for mPlum: 4 and 71 ps [3-4]. In this presentation the nature of the fluorescence response function of mPlum chromophore will be explored by means of excited-state ab initio molecular dynamics (AIMD) simulations. A quantitative description of the experimentally observed relaxation time-scales will be provided.

References
Collective conical intersections in cavity femtochemistry

O. Vendrell¹,*

¹Department of Physics and Astronomy, Aarhus University, Denmark
*oriol.vendrell@phys.au.dk

The photo-triggered dynamics and non-radiative relaxation pathways of a molecular ensemble coupled to a resonance cavity will be described quantum mechanically [1]. In the one-molecule and single excitation limits, the coupling of a vibrationally bound electronic ground state and a dissociative excited state result in a lower polariton state with dissociative character and an upper polariton supporting long-lived vibronic-polaritonic resonances. As the number of molecules increases, spectroscopically dark light-matter states appear between the two optically active polaritons. It will be discussed how these dark states feature a rich structure of true collective conical intersection crossings, whose location depends on the internal atomic coordinates of each molecule in the ensemble, and which lead to very fast non-radiative decay from the upper polariton [2]. At least three coupled molecules are necessary for cavity-induced collective conical intersections to exist and, for identical coupled molecules, they constitute a special case of Jahn-Teller-type state crossing. It will be argued that collective conical intersections mediate the ultrafast non-radiative decay in micro-cavities observed in recent experiments [3-4].

Figure 1. Upper polariton (red), lower polariton (blue) and dark polaritonic (dashed) states displaying state crossings along a one-dimensional cut in configurational space for five molecules coupled to a cavity mode. The energy scale is relative to the absolute ground state of the hybrid matter-light system.

References
From Electron Correlation to Photophysics

D. Casanova¹,

¹Donostia International Physics Center (DIPC), P. Manuel Lardizabal 4, 20018 Donostia, Euskadi, Spain
*Presenting author e-mail address: david.casanova@ehu.eus

In this work I will present the restricted active space configuration interaction (RASCI) wave function method with the use of an spin flip (SF) excitation operator for the electronic structure description of ground and excited states of molecular systems with the presence of strong electron correlations [1-3]. I will also discuss two strategies in order to recover instantaneous electron-electron interactions: (i) through second order perturbative corrections [4] and (ii) incorporating short-range density functional correlation energy [5].

The application of these methodologies will be exemplified in the study of di and polyradical systems [6,7] and in the mechanistic characterization of intricate photophysical processes such singlet fission [8-10].

References

New avenues in first-principles computational energy research

K. Reuter

Chair for Theoretical Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany
Presenting author e-mail address: karsten.reuter@ch.tum.de

For a long time, chemical accuracy was taken as a synonym for predictive quality in first-principles electronic structure theory calculations. Over recent years first-principles multiscale modeling approaches have increasingly taken this predictive power to larger length and longer time scales. In these approaches, sensitivity analyses assessing the effect of microscopic parameters on macroscopic observables provide a more differentiated view on required accuracy. Realizing that often only a few such parameters critically control targeted functionalities, computational screening approaches focus on these descriptors, compute them for a wide range of materials and thereby allow to search vast materials spaces for promising candidate systems. The large amounts of data created this way are now increasingly mined with machine learning techniques. This provides further insight into correlations between materials properties and function, and carries the predictive first-principles power over to the in silico design of improved systems. In my talk, I will discuss the status and unique prospects of this exciting new triangle of methods within the context of computational energy research. I will show that for bulk systems existing methodology already allows to realize the above described concepts. In contrast, significant methodological advances are required to also tackle the interfacial issues that often limit current sustainable energy solutions.
Magnetoresistance in Single-Molecule Devices

Eliseo Ruiz$^{1,*}$

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This presentation is devoted to a combined theoretical and experimental study of transport properties in single-molecule devices. Conductance through mononuclear complexes deposited on a gold substrate in contact with magnetic Ni STM tip have measured and non-equilibrium Green Functions method combined with DFT calculations have been employed to rationalize such results. Our first results provided a proof of concept strongly indicating that the STM conductance through Fe$^{II}$ or Co$^{II}$ complexes (that are also a spin-crossover system and a single-molecule magnet, respectively) changes one order of magnitude with the direction of the Ni tip magnetic field. Our study shows a theoretical analysis and the practical implementation through two-terminal devices using STM equipment to achieve the room temperature molecular-based spintronic nanodevices.[1,2] This study have been extended to similar complexes with other metal cations, Ni$^{II}$ and Mn$^{II}$ as well as to other family of complexes as those formed by metallloporphyrins (Co$^{II}$ and Cu$^{II}$, see Figure 1) with thiol-pyridine axial anchoring groups. In this case, the coordination of the anchoring group plays a fundamental role in the transport properties.

Figure 1. Single-molecule conductance histograms for the Co$^{II}$ porphyrin complex with thiol-pyridine axial ligands bridging between Au and both $\alpha$-up spin polarized (gray) and $\beta$-down spin polarized (maroon) Ni electrodes.

References
An accurate and efficient framework for calculating lattice thermal conductivity of solids

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Quantitatively accurate predictions of the lattice thermal conductivity, $\kappa_l$, have important implications for key technologies ranging from thermal barrier coatings to thermoelectrics. To the best of our knowledge, solving the Boltzmann transport equation (BTE), starting from third-order anharmonic force constants, is the optimal method for systematically and accurately calculating thermal conductivity. Two main challenges are associated with this path: high computational costs and lack of automation in the frameworks using this methodology, which affect the discovery rate of novel materials with ad-hoc properties. Here, the Automatic Anharmonic Phonon Library (AAPL) is presented [1]. It efficiently computes interatomic force constants by making effective use of crystal symmetry analysis and it solves the Boltzmann transport equation. The software automatically predicts the lattice thermal conductivity of single-crystals and polycrystalline materials by using a single input file and with minimum user intervention. A new symmetry analysis has been optimized to further reduce the number of static calculations compared to other packages. AAPL is implemented into the high-throughput accelerated materials development framework, AFLOW. This technique can be combined with less expensive methodologies previously implemented in AFLOW [2-3] (Figure 1) to create an efficient and fast framework to accelerate the discovery of materials with interesting thermal properties.

![Figure 1](image.png)

**Figure 1.** Comparison with experiments of different techniques. Calculated lattice thermal conductivities vs. experimental at 300 K. Blue circles are used for AAPL results, empty orange triangles for the quick AGL screening method, and empty green squares for the QHA-APL method.

References

Magnetic Fingerprint of Dithiazolyl-Based Molecule Magnets

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Some magnetic properties of bistable purely organic molecule-based magnets cannot yet be explained with the current state-of-the-art theoretical models. Our attention is devoted to dithiazolyl (DTA, see Scheme 1) compounds, namely TTTA, PDTA, TDPDTA, and 4-NCBDTA, because they are promising candidates for potential technological applications [1]. These DTA-based compounds present a common trend in the solid state, since all planar DTA−radicals pack forming π-stacks. However, these π-stacks can pile up either quasi-uniformly or alternating eclipsed and slipped DTA−radical pairs, depending on the crystal phase being characterized at high or low temperature. The characterization of these four compounds within the DTA−based family is used here to evaluate the nature and the properties of bistable and spin switchable systems.

Scheme 1. DTA-compounds, namely TTTA, PDTA, TDPDTA and 4-NCBDTA.

The evaluation of the radical···radical $J_{AB}$ magnetic interactions is first pursued in order to identify the magnetic topology of these four molecular crystals, by means of the First-Principles Bottom-Up working strategy. The magnetic topology is found to be truly three-dimensional. Nevertheless, for simulation purposes it can be taken to be one-dimensional because the largest and dominant $J_{AB}$’s extend along the π-stacking direction of the planar DTA−radicals. Interestingly, the electronic factors (namely, DTA−chemical skeleton, interactions between substituent, etc.) are not decisive for the magnitude of the overall $J_{AB}$ magnetic coupling. Instead, it is the structural (geometrical) factors that govern the behavior of the $J_{AB}$ magnetic interaction. It is shown that the main antiferromagnetic contribution is coming from the π-overlap between directly aligned spin-carrying atoms. Remarkably, this study provides magneto-structural correlation maps in terms of two geometrical variables (namely, the interplanar distance ($d_{IP}$) and the degree of slippage ($d_{SL}$)) as a function of the substituents of the DTA−moiety to highlight the static ferromagnetic fingerprint region, which results to be very expensive in terms of interaction energy. Indeed, this is the reason why there are so few examples of DTA−based ferromagnets in nature. These magneto-structural maps could no doubt become a practical tool to help experimentalists to design more stable and efficient purely organic radicals with ferromagnetic properties in the solid state.

References

Travelling in Valence Space

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The lecture will focus on recent theoretical studies of compounds of main-group atoms, transition metals, lanthanides and actinides, which stretch the border of conventional understanding of valence space.
Hydrogen Bonding from a Kohn-Sham Molecular Orbital Perspective

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Theoretical and experimental studies have elucidated the bonding mechanism in hydrogen bonds as an electrostatic interaction, which also exhibits considerable stabilization by charge transfer, polarization by π electrons, and dispersion interactions. Therefore, these components have been used to rationalize the differences in strength of hydrogen-bonded systems. In this presentation I will show a completely new viewpoint obtained from bonding analyses based on quantitative Kohn–Sham molecular orbital theory and corresponding energy decomposition analyses (EDA). The quantum chemical computations on natural and mismatched DNA base pairs reveal that aromaticity can be irrelevant for the hydrogen bond strength and that steric repulsion can determine the hydrogen bond strength.[1-3]

Figure 1. Repulsive interactions in GG and CC

References

Exciton Transport in Organic Crystals: The Role of the Dynamic Disorder

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Exciton transport in molecular materials or aggregates is a fundamental physical process taking place in photosynthetic light-harvesting systems and organic semiconducting materials. A unique characteristic of organic crystals or aggregates is that they are held together by weak non-covalent intermolecular interactions. There is therefore a large number of low frequency intermolecular vibrations that cause a relatively large displacement of one molecule respect to their neighbors (dynamic disorder). We have recently shown that the large fluctuation of excitonic couplings cannot be treated as a perturbation and needs to be explicitly incorporated for a proper description of the exciton transport in molecular crystals or aggregates[1,2]. In this contribution, we present an appropriate theoretical framework to study exciton transport in molecular crystals or aggregates in different transport regimes where the effect of the dynamic disorder is incorporated. We have specially designed a diabatization scheme to compute the total excitonic couplings between the electronic excited states of interest in molecular pairs[3]. All parameters that enter in our theoretical models are computed from electronic structure calculations and molecular dynamics simulations. We present results for two molecular crystal models (anthracene and a heteroacene derivative), which have been widely studied in the context of organic electronics.

![Figure 1](image_url). Chemical structure and the neighbouring excitonic interactions for anthracene (a) and the heteroacene derivative (b).

References
Creating functional nanoscale devices using single molecules as active electronic components is the ultimate goal of the field of molecular electronics. Besides their potential to meet the growing demand for miniaturization of electronics, appealingly, molecular electronics opens up the possibility of devices with novel, unforeseen functionalities beyond silicon-based technologies, such as molecular switches. Our recent work on expanded porphyrins have shown that these macrocycles are flexible enough to switch between different π-conjugation topologies (Mobius, Hückel and twisted-Hückel) encoding distinct electronic properties and aromaticity [1]. Since the topological/aromaticity switch can be induced by different external stimuli [2], expanded porphyrins represent a promising platform to develop a novel type of molecular switches for molecular electronic devices.

In this work, we assess computationally the feasibility of conductance switches based on expanded porphyrins for the first time. Thus, the electron transport properties of single thiol-terminated expanded porphyrins bound to gold electrodes with different π-conjugation topologies and aromaticity were investigated using DFT methods and Green’s function formalism. This study is particularly relevant since the link between transmission and key concepts in chemistry, such as aromaticity and polarizability, is established allowing a chemical understanding of conductance [3]. To gain further insight about the factors that control the conductance switching across Hückel and Möbius macrocycles, we recently provide a set of qualitative rules to predict the presence of a quantum interference around the Fermi level at the Hückel level of theory [4].

Figure 1. Conductance switching through aromaticity and topology changes in expanded porphyrins.

References
Next generation first-principles molecular dynamics in ground and excited states

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Simulations can provide a decisive contribution to the molecular understanding of enzyme catalysis and they have successfully been used to determine the contributions to catalytic activity of e.g. electrostatic rearrangements, entropic effects and conformational fluctuations [1,2]. However, although kinetic isotope effects (KIEs) are a powerful experimental tool to study enzyme mechanisms, their interpretation and modeling in enzymatic reactions remains sometimes ambiguous. While KIEs values are usually taken as an indication of the extent of tunneling for proton- and hydride-transfer reactions, the origin of their temperature dependence is less consensual. Several explanations have for example been suggested for the pronounced difference between wild type enzymes that exhibit an almost temperature-independent KIE and their mutants which display a pronounced change with temperature, including the presence of multiple conformational sub-states and a change in the catalytic rate-limiting step [3-5]. Reproducing this temperature dependence has remained a challenge for simulations and is a critical test of computational approaches in enzyme catalysis.

Here, we consider the hydride-transfer reaction catalyzed by two dihydrofolate reductase (DHFR) enzymes, respectively the wild type and M42W-G121V double mutant, whose experimental KIEs display very different temperature dependences[4]. We show that the combination of extensive conformational sampling by REST2 replica exchange simulations with reaction free energy profile calculations using an empirical valence bond (EVB) description and an adequate collective reaction coordinate are able to unambiguously reproduce the experimental KIE temperature dependences of both enzymes for the first time. Our simulations provide a molecular picture that elucidates the different behaviors of the two homologs and we determine the key molecular features that govern the changes in the measured KIE.

References

Cyclooxygenase-2 (COX–2) is a homodimeric bifunctional hemoprotein that catalyzes the oxygenation of polyunsaturated fatty acids to generate prostaglandins, whose production is associated with many disease pathologies, including inflammation, cardiovascular diseases, and cancer. As a part of a more general project, we focus here on arachidonic acid (AA) as a substrate.

COX-2 catalyzes the biosynthesis of hydroperoxy endoperoxide prostaglandin G₂ (PGG₂) by the addition of two molecules of oxygen to AA, and then reduces PGG₂ to PGH₂, a precursor of different prostaglandins and thromboxanes. Very surprisingly the molecular details of this catalytic mechanism remain quite unknown so far and none theoretical work has still been devoted to figure it out in depth.

In this work, we have explored the conformational landscape of COX-2:AA Michaelis complex by means of classical Molecular Dynamics (MD) simulations. Subsequently, some MD snapshots were selected to calculate the potential energy surface by a QM(DFT)/MM approach, in order to study the steps of the all-radical catalytic mechanism derived from the initial proposals by Hamberg and Samuelson.

We have also considered the alternative carbocation (C₁₀) mechanism, and we have discussed the rearrangement of AA inside the active site of COX-2 in order to understand the regioselectivity along the catalytic mechanism and, specially, why COX-2 produces the natural trans ring isomers in contraposition to solution, where the formation of cis ring isomers is highly favoured.

On the other hand, it is indeed well known that Aspirin inhibits the formation of PGG₂ by the acetylation of Ser530. However, the molecular way this fact turns out in a substantial alteration of COX-2 activity is again quite unknown. We have here found out why PGG₂ generation is blocked in aspirine-acetylated COX-2.

The results we have obtained can be useful for the design of new molecules, or even molecular photoswitches, that inhibit selectively COX-2 without side effects.
Computational Modelling of a Caged Methyl Cation: Structure, Energetics and Vibrational Analysis

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DFT calculations for CH\textsubscript{3}\textsuperscript{+} within a constrained cage of water molecules permit the controlled manipulation of distances $r_{ax}$ and $r_{eq}$ to “axial” and “equatorial” waters [1]. Equatorial CH···O interactions catalyze methyl transfer (MT) between axial waters. Variation in $r_{ax}$ has a greater effect on CH bond lengths and stretching force constants in the symmetric S\textsubscript{N}2-like transition structures than variation in $r_{eq}$. In-plane bending frequencies are insensitive to these variations in cage dimensions, but axial interactions loosen the out-of-plane bending mode (OP) whereas equatorial interactions stiffen it. Frequencies for rotational and translational motions of CH\textsubscript{3}\textsuperscript{+} within the cage are influenced by $r_{ax}$ and $r_{eq}$. In particular, translation of CH\textsubscript{3}\textsuperscript{+} in the axial direction is always coupled to cage motion. With longer $r_{ax}$, CH\textsubscript{3}\textsuperscript{+} translation is coupled with asymmetric CO bond stretching, but with shorter $r_{ax}$ it is also coupled with OP (equivalent to the umbrella mode of trigonal bipyramidal O···CH\textsubscript{3}\textsuperscript{+}···O); the magnitude of the imaginary MT frequency increases steeply as $r_{ax}$ diminishes. This coupling between CH\textsubscript{3}\textsuperscript{+} and its cage is removed by eliminating the rows and columns associated with cage atoms from the full Hessian to obtain a reduced Hessian for CH\textsubscript{3}\textsuperscript{+} alone. Within a certain range of cage dimensions the reduced Hessian yields a real frequency for MT. The importance of using a Hessian large enough to describe the reaction-coordinate mode correctly is emphasised for modelling chemical reactions, and particularly for kinetic isotope effects in enzymic MT [2].

References
Manganese: a very welcome guest in hydrogenation transfer reactions

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Hydrogenation transfer reactions are key technology processes in the modern industrial chemistry. So far most of these catalytic systems rely on the use of precious metal catalysts. However, the limited availability, toxicity and high prices call for the substitution of the precious metal catalysts with earth-abundant bio-common metal catalysts.[1]

In general rules, hydrogenation transfer reactions catalysed by organometallic catalysts follow a two-stages mechanism (see Figure 1). First, $\text{H}_2$ being provided as dihydrogen gas or any other $\text{H}_2$ source, is inserted on the structure of a metal-containing polar bond (catalyst hydrogenation). Subsequently, this is transferred onto the structure of a given substrate (substrate hydrogenation),[2] in a cyclic process in which the organometallic compound acts as $\text{H}_2$-borrowing assistant.

![Figure 1. Schematic representation of hydrogenation transfer process catalysed by Mn organocatalyst.](image)

In this communication, we present our state-of-the-art advances in the field, with special emphasis on the discovery of novel organocomplexes containing manganese as active transition metal, which are stabilised by the presence of cheap and stable non-innocent ligands (PNP, NNP, and NNN). Amongst the recent advances carried out by us, can be highlighted the stereoselective semihydrogenation of alkynes,[3] the free-of-waste hydrogenation of CO$_2$-derived carbonates, or the synthesis of pyrroles by merging both acceptorless dehydrogenation and hydrogen autotransfer concepts (ADHA). Both experimental evidences and in-depth DFT studies support our results.

References
Ultrafast electron dynamics as a route to explore chemical processes

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Exposing molecules to ultrashort laser pulses can trigger pure electron dynamics in the excited or ionized system. In the case of ionization, these dynamics may manifest as an ultrafast migration of the initially created hole-charge throughout the ionized molecule and were termed charge migration [1]. Charge migration can be solely driven by electron correlation and appeared to be a rich phenomenon with many facets that are rather characteristic of the molecule studied [2]. Importantly, due to the coupling between the electronic and the nuclear motion, the control over the pure electron dynamics offers the extremely interesting possibility to steer the succeeding chemical reactivity by predetermining the reaction outcome at a very early stage. This is the paradigm of the emerging field of “attochemistry”. It will be shown how by appropriately tailored ultrashort laser pulses one can control the ultrafast charge migration in experimentally interesting molecules [3,4]. Full quantum electron-nuclear dynamics calculations of the charge dynamics initiated by ionization will be presented and the possibilities to realize the dream of attochemistry – control of a chemical reaction by manipulation of electron coherences – will be discussed.

References

How nuclear motion affects coherent electron dynamics in molecules

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Because of their light mass, electrons are expected to move on the attosecond (1 as = $10^{-18}$ s) timescale. The first synthesis of attosecond pulses in 2001 has opened up the possibility of probing electronic motion on its intrinsic timescale. Excitation or ionisation of a molecule with such a short pulse leads to the coherent population of several electronic states, called an electronic wavepacket. The interference between electronic states in such a superposition, alternating between constructive and destructive, leads to oscillating motion of the electron cloud. This purely quantum process relies on the coherence of the electronic wavepacket. A fundamental challenge is to understand to what extent the electronic wavepacket retains its coherence, i.e., how long the oscillations in the electron cloud survive, in the presence of interactions with the nuclei of the molecule. To address this question, we have used semi-classical and quantum mechanical methods to simulate the dynamics upon ionisation of poly-atomic molecules \cite{1,2}. The presentation contains a review of some applications \cite{3,4,5} illustrating new important physical insights about the predicted decoherence process.

References

An exotic type of ultralong-range Rydberg molecules are theoretically predicted to exist if a heteronuclear diatomic molecule, a Λ-doublet or a rotating polar molecule, is immersed into the wave function of a Rydberg atom [1,2,3,4]. The anisotropic scattering of the Rydberg electron from the permanent electric dipole moment of the polar molecule is responsible for the binding mechanism in these Rydberg molecules.

In this talk, we explore the electronic structure of ultralong-range triatomic Rydberg molecules formed from a potassium Rydberg atom and the heteronuclear diatomic molecule KRb. We investigate the metamorphosis of the Born-Oppenheimer potential curves, essential for the binding of the Rydberg molecule, with varying distance of the KRb molecule from the Rydberg core. These electronic states show many consecutive minima with depths of a few GHz or a few MHz depending if they evolve from the Rydberg degenerate manifold or from the Rydberg states with low orbital angular momentum [1,4]. In both cases, we find vibrational bound states where these Rydberg molecule could exist.

These molecules could be created by exciting Rydberg atoms, using standard two-photon excitation schemes, in a mixture of ultracold atoms and ultracold molecules, i.e., molecules as K(nS)-KRb or K(nD)-KRb would be created experimentally. Due to the coupling mechanism between the Rydberg atom and the polar molecule, we have found adiabatic electronic states evolving from the Rydberg degenerate manifold with a significant contribution from a low angular momentum Rydberg state. These mixed electronic states are a few GHz deep and have several vibrational bound states, being good candidates to be created experimentally [5]. The large charge separation between the Rydberg core and the diatomic molecule gives rise to huge permanent dipole moments scaling as n² of a few kilo-Debye. We also analyse the orientation and alignment of the KRb molecule within this triatomic Rydberg molecule.

References

Electron Correlation in the Ionization Continuum of Molecules: Photoionization of \( \text{N}_2 \)

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The theoretical description of observables in attosecond pump-probe experiments requires a good representation of the system’s ionization continuum. For polyelectronic molecules, however, this is still a challenge due to the complicated short range structure of correlated electronic wave functions. Whereas calculations aimed to describe bound electronic states using Quantum Chemistry Packages (QCPs) are routine calculations nowadays; comparable tools for the continuum are not widely available yet. To tackle this problem we present a new approach developed in our group, the XCHEM method [1].

In order to simulate ionization, the parent ions are obtained using a modified version of the MOLPRO package [2] with a Complete Active Space Consistent Field calculation (CASSCF) in the state average formalism. In this way, a common set of orbitals is obtained to describe the \( \text{N}_2 \) bound electronic wavefunctions for all parent ions and the required neutral electronic states. These orbitals are exported to the MOLCAS code [3] and complemented with a Gaussian and B-splines basis set [4] (GABs). The molecular system is thus divided in two parts. On the one hand, the bounded part is treated by using standard polycentric Gaussian functions. On the other hand, the continuum is constructed with GABs functions [4], where the asymptotic part is represented by B-splines and the close range is described using monocentric Gaussians. Matrices elements of the Hamiltonian and dipole operators are also computed in two steps: calculation between Gaussian functions (handle by the MOLCAS code) and between monocentric Gaussian and B-splines (handle directly by the XCHEM code).

To illustrate the validity of this approach, we report results for the multichannel ionization of molecular Nitrogen, the ionization of which cannot be easily treated by existing methods, thereby showcasing our method’s usefulness in the study of ionization in polyelectronic, molecular system [5].

**References**

Chemical evolution from simple inorganic molecules to macromolecules of life is one of the most enigmatic questions in chemistry. More than a half-century of theory and experiments have pointed out to the critical roles of mineral surfaces in many prebiotic chemical reactions. However, very little is known about the mechanistic steps at the surface of these materials. In this context computational studies can provide useful insights and complement with atomic scale information spectroscopic measurements, chemical reactivity experiments and numerical astrochemical models. Two major topics will be addressed along this talk: i) the H$_2$ formation, the most abundant molecule in the astrophysical media, on olivine-based interstellar grains,[1,2] and ii) the peptide bond formation on different oxide surfaces.[3,4,5] The most favorable reaction mechanism and the importance of surface morphology and of Lewis and Bronsted sites for the catalysis of these processes will be discussed.

![Figure 1. H$_2$ formation on olivines.](image)

**References**

Discussion on Theoretical Models for Activation and Reaction Energies in Chemical Reactions

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Activation processes have been studied in many different contexts, mainly with the aim of getting insights on the physical nature of the forces that trigger these processes. Among many theoretical models intended to rationalize chemical processes and the energies involved, the Marcus equation [1] is one of the most successful analytic forms that provides nice ways to rationalize the activation energy and to characterize the transition state through the Hammond postulate [2] and the Brönsted coefficient [3]. The Marcus’ equation involves the reaction energy and the so-called Marcus’ intrinsic activation energy that describes the structural distortion of reactants and products at the transition state. An analytic potential function consistent with the Marcus equation for activation energy, is formulated and used to reveal new insights on activation processes in chemical reactions. Moreover, since the parameters necessary to define this new potential energy function can be obtained experimentally, the present model may produce experimental analytic potentials allowing for new and interesting applications and emerging as a powerful tool to characterize activation processes in chemical reactions.

On the other hand, activation and relaxation processes analyzed from the perspective of the reaction force [4,5] lead to rational partitions of activation and reaction energies that are characterized in terms of reaction works defined at the different regions along the reaction coordinate. This produces new insights on activation and reaction energies as well as on rate and equilibrium constants. In this presentation, different approaches to activation and relaxation processes are discussed in the light of results obtained for different kind of chemical reactions.

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References
Red Moon Methodology: A Computational Molecular Technology of Complex Chemical Reaction Systems
- Its Theoretical Treatment and Applications -

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Recent development of experimental measurement techniques have made us notice how significant we consider chemistry by the number of molecules, not the amount of substance in mole, leading to the increasing important role of computational chemistry as a molecular science. On the other hand, when we try to treat computational chemically diffusion and chemical reactions in “molecular aggregation states” where a large number of atoms and molecules are gathered in condensation, such fact that these phenomena occur only very rarely has made it restrictive or sometime impossible to deal with them by the first principles methods of computational chemistry. Even with traditional classical molecular simulations, it is really difficult to determine long-term properties and stereochemical characteristics. Under the circumstances, we have recently developed Red Moon Method, a new efficient and practical ‘atomistic’ simulation method combining Monte Carlo (MC) and molecular dynamics (MD) method with a Rare Event-Driving Mechanism, for large-scale chemical reaction systems [1] and applied successfully to analyze several materials important and valuable in next-generation industrial development [2, 3].

In this talk, several applications of Red Moon Method will be shown from the practical viewpoint of molecular controlling of complex chemical reactions, stereochemistry and aggregate structures [2, 3]. In particular, we would like to take a novel olefin polymerization catalyst (pyridylamide)Hf(IV) complex (I), which is activated by a cocatalyst B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} to form a cationic active species [4, 5] and explain the role of the counteranion in the reaction mechanism of propylene polymerization [5] (Figure 1). Finally, I would like to discuss the microscopic mechanism of chain transfer polymerization of I and ZnEt\textsubscript{2} in solvent toluene, which is clarified by applying Red Moon simulation to the present system [6].

References

A computational study of the catalytic role of hydrogen bond interactions

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Classically, hydrogen bonding has been described to play a critical role on the interactions in both organic and inorganic frameworks involving electron withdrawing and/or electron attracting groups. Similarly, it is well known that this type of bonding dominates the net binding interaction within different fields including molecular self-assembly, host-guest chemistry, supramolecular chemistry and molecular docking[1]. Additionally, the existence of hydrogen bond mediated catalysis in different chemical process such as acid rain formation or tautomerization reactions has been recently reported[2].

The amino-imino tautomerization reaction of simple aromatic organic molecules such as functionalized pyridines is well-known to easily proceed by photochemical means. On the other and, the large activation energy of these reactions in the fundamental state unables the spontaneous tautomerization of these molecules at room temperature[3]. In order to understand the effect of the catalytic activity of hydrogen bonding in the amino-imino -carboxylic acid assisted- tautomerization reaction, a family of 2-aminopyridines has been studied by means of DFT and TD-DFT calculations. All these calculations were supported by spectroscopic experimental findings, by analyzing the main absorption and fluorescence emission bands which allow us to identify the processes involved in the reaction.

In accordance to these calculations, hydrogen bonding assistance of simple carboxylic acids, such as formic or acetic acids, reduces dramatically the activation energy of the studied reaction. Thus, this catalytic effect allows the spontaneous tautomerization reaction of these amino derivatives to take place in the fundamental state.

These results validate and prove the catalytic activity of these weak intermolecular forces in such simple reactions, which furthermore might be extended to more complex ones.

References
Recent Advances in Semiempirical Quantum Chemistry

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Semiempirical quantum-chemical methods are well-established tools for computational studies of large molecules [1]. Methods with explicit orthogonalization corrections (OM1, OM2, OM3) offer better overall accuracy in standard statistical evaluations of ground-state properties as well as qualitative improvements for hydrogen bonding and conformational properties [2,3]. OMx-based studies of electronically excited states employ a general implementation of the GUGACI approach in a semiempirical framework which provides analytic gradients and nonadiabatic couplings. Comparisons with high-level ab initio benchmark data show that OMx/MRCI methods describe electronically excited states reasonably well [4]. They can thus be used in mixed quantum-classical dynamics to investigate fast nonradiative relaxation processes after photoexcitation [1,5].

The lecture will address the theoretical background of the OMx methods and report on recent comprehensive benchmarks. Thereafter it will cover unpublished work that has led to the development of the ODM2 method with integrated orthogonalization and dispersion corrections. In addition, it will present selected OM2/MRCI studies of surface-hopping excited-state dynamics; recent examples include simulations on light-driven rotary molecular motors [6], GFP chromophores [7], arylazopyrazole photoswitches [8], and tetraphenylethene derivatives [9].

References

A Direct Measure of Metal Ligand Bonding - the Metal Ligand Electronic Parameter (MLEP)

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The prediction of the catalytic activity of transition metal complexes is a prerequisite for homogeneous catalysis design. The Tolman Electronic Parameter (TEP) was derived to provide this information. It is based on the symmetric CO stretching frequency of metal-tricarbonyl complexes L-M(CO)₃ with varying ligands L. It has been used in hundreds of cases as is documented by as many publications.

We show that the TEP is misleading as i) it is not based on mode-decoupled CO stretching frequencies and ii) a quantitatively correct or at least qualitatively reasonable relationship between the TEP and the metal-ligand bond strength does not exist. This is demonstrated for a set of 181 nickel-tricarbonyl complexes using both experimental and calculated TEP values. Even the use of mode-decoupled local CO stretching frequencies or corresponding local force constants kₗ [1] does not lead to a useful relationship between the CO and the metal-ligand vibrations (see Figure 1), which could justify the use the CO stretching vibration as a measure for the ligand metal bond strength.

A reliable descriptor replacing the TEP is obtained with the help of the metal-ligand local stretching force constant. For the test set of 181 Ni-complexes, a direct metal-ligand electronic parameter (MLEP) in the form of a bond strength order is derived, which reveals that phosphines and related ligands (amines, arsines, stibines, bismuthines) are bonded to Ni both by σ-donation and π-back donation [2-4]. The strongest Ni-L bonds are identified for carbenes and cationic ligands. The new MLEP quantitatively assesses electronic and steric factors and it can be determined for any metal or transition metal complex, whether it contains CO ligands or not.

References
Characterization and prediction of short-lived transition-metal species

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Oxidation processes of hydrocarbons in a selective, efficient and environment-friendly manner remains one of the major challenges at present today \cite{1}. The majority of these studies is based on experiment, and computational chemistry plays sometimes an important role \cite{2,3}, in giving a description of e.g. spectroscopy or transition states to lead to a deeper understanding of what is going on. This is in particular true for the influence of the spin state on reactivity \cite{3}. Here I will give an overview of the spin-state consistent tools needed \cite{2} and how these can be used for finding the pathways for the oxidation reactions of high-valent metal-oxo (Fe\textsuperscript{IV}=O, Ni\textsuperscript{IV}=O) species \cite{4,5}, based on a consistent and accurate computational description of IR, Raman, UV-Vis, and Mössbauer spectroscopy. Furthermore, I will show how the barriers can be decomposed in terms of ligand structure, orbital patterns and steric vs. electronic interactions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Modified Fe\textsuperscript{IV}=oxo ligand (right) and effect on barrier (left) \cite{5}.}
\end{figure}

References
Spintro-catalysis

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Water oxidation by magnetic metal oxides resulted in the rise of all higher living beings on the earth today, and is the future of a sustainable society with clean fuels. Optimum catalysts for the transference of electrons during the oxygen evolution reaction show a relationship between increasing ferromagnetism, enhanced at oxidation conditions, and activity; described by wavefunctions antisymmetric in space: spintro-catalysis. Spin-dependent quantum exchange potentials appear as important terms in the orbital interactions of magnetic catalysts, they adjust the activation energies and bond distances, according to the composition and orbital filling.

![Figure 1. The Sabatier’s principle considering spin-dependent interactions in electro-catalysis.](image-url)

Spin dependent interactions add to the Sabatier’s principle in catalysis, Fig. 1, fluctuations with the overall magnetic ordering.

References

Quantum computations of nanoconfined molecules

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Encapsulated molecules or clusters aroused great interest in both fundamental and technological research, due to environmental, medical and industrial applications, such as capture/sequestration of gases (e.g. CO₂) and drug delivery. Such confinement inside nanocavities, like those of clathrate hydrates or carbon (like fullerenes) compounds, offers the opportunity to study intrinsic properties of single chemical species, and leads to interesting quantum phenomena, that are still not fully understood. The results from experiments by X-ray/powder X-ray, neutron diffraction and inelastic neutron scattering methods, as well as via Raman, nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy have spurred interest and subsequently motivated theoretical studies.

Thus, we report here a rigorous quantum treatment within the MCTDH framework to characterize structural and spectroscopic properties of trapped triatomic molecules (such as CO₂ and H₂O) into different type of cages (e.g. the 5₁² and 5₁²6₂ cages of the sl clathrate structure or fullerenes, see Figure 1). In particular, exact kinetic energy operators were derived, and semiempirical potentials were initially employed to investigate the quantum translational-rotational-vibrational dynamics of the encapsulated molecules. Currently, more sophisticated ab initio-based interaction potentials are in progress[1]. This allows the investigation of the dynamics of the guest molecule, and the effect of the size, shape, and composition of the host cavity, as well as the occupancy and identity of the trapped molecule. The results will be discussed in comparison with recent X-ray and FTIR measurements on fundamental and combination stretching CO₂ modes in the sl clathrate hydrate[2], as well as with the INS spectra splittings of the ortho-H₂O spin isomer, and far-IR transitions for the H₂O@C₆₀ endofullerene[3].

Figure 1. CO₂ and H₂O molecules trapped in the sl clathrate hydrate and in C₆₀/C₇₀ fullerenes, respectively.

References
Mixed quantum-classical approaches for the description of electronic and nuclear quantum dynamics

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Initially restricted to a single adiabatic state, DFT-based molecular dynamics (MD) was recently extended to the non-adiabatic regime becoming an important tool for the study of photophysical and photochemical processes. Among the most commonly used trajectory-based mixed quantum-classical schemes are Ehrenfest dynamics and Tully’s fewest switching surface hopping (FSSH). Despite their enormous impact in the quantum chemistry community, these methods suffer from many limitations e.g., the impossibility to describe wavepacket branching in Ehrenfest dynamics and the presence of over-coherence in FSSH. These failures are mainly associated to the approximate character of these approaches, which can hardly be improved due to the lack of a solid theoretical derivation.

To overcome these limitations, several alternative trajectory-based methods have been developed, which all share the common feature of being derived from a well defined mixed quantum-classical limit of the underlying exact time-dependent Schrödinger equation. Among others, there are multiple spawning [1], Bohmian dynamics [2], exact factorization [3] and the conditional wavefunction approaches.

In this talk, I present some novel and promising trajectory-based non-adiabatic MD schemes derived from different rigorous mixed quantum-classical limits of the exact electron-nuclear quantum dynamics. In particular, I describe the derivation and the implementation of the mixed quantum-classical limit of the exact factorization theorem, which leads to a new trajectory-based non-adiabatic scheme [4,5] (named coupled-trajectory mixed quantum-classical dynamics, CT-MQCD) that can capture important nuclear quantum coherence/decoherence effects neglected in FSSH.

The CT-MQCD approach and its single-trajectory limit (i.e., Ehrenfest dynamics) are then applied to the study of the ultrafast electron and nuclear dynamics of photoexcited oxirane [4] and of ionized amino acids [6] in the gas phase, for which ultrafast experimental results are also available [7,8].

References
Global method for electron correlation based on the NOF theory

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In electronic structure theory, accurate solutions require a balanced treatment of both static (non-dynamic) and dynamic correlation. Nowadays, it is necessary to resort to multi-reference methods for correctly handling both types of correlation, however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. In this talk, I present a new single-reference method [1], capable of achieving both dynamic and static correlation even for those difficult cases in which both types of correlation are equally present.

In our approach, a natural orbital functional (NOF) [2] is firstly used for capturing all static correlation effects. Then, the total energy is approximated as $\tilde{E}_{\text{HF}} + E_{\text{dyn}} + E_{\text{sta}}$, where $\tilde{E}_{\text{HF}}$ is the Hartree-Fock energy obtained with the natural orbitals (NOs). The dynamic energy correction $E_{\text{dyn}}$ is derived from a properly modified second-order Møller-Plesset perturbation theory (MP2) [3], while the non-dynamic correction ($E_{\text{sta}}$) is obtained from the NOF.

The success of the method, called NOF-MP2, is determined by the NOs used to generate the reference. Recently [4], we have analyzed several systems with strong static correlation, specifically, the one-dimensional Hubbard model with up to 14 sites and rings with up to 16 hydrogens. Comparing with accurate diagonalization calculations, our results indicate that inter-pair phase factors must be negative. Taking into account the static electron correlation in the NOF from the outset, we arrive at the formulation of a new functional called PNOF7s [5]. In general, the NOs obtained from PNOF7 are localized in certain regions of space, depending on the degree of interaction between the electron pairs. In this presentation, we also analyze the reformulation [5] of the dynamic energy correction based on the orbital-invariant MP2 [6].

The new procedure is extraordinarily simple, has fifth order formal scaling of computational cost, and the property of size-consistency, essential for applying the method to extended systems. It is applied successfully to the homolytic dissociation of a selected set of diatomic molecules that encompass very dissimilar interactions ranging from weak to strong bonds, thus sweeping a wide range of interelectronic interactions and correlation regimes. The method can also properly dissociate noble gas dimers. The test calculations in a selected set of 30 polyatomic molecules demonstrate an improvement not only in the relative energies but also in the total energies calculated with the NOF-MP2 method. The values obtained are in excellent agreement with the experimental data.

References
Theory of vibro-polaritonic chemistry

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When matter strongly couples to confined light modes, new hybrid light-matter states so-called polaritons can form. Within this context, polaritonic chemistry aims to manipulate molecular structure under such strong coupling regime. While the general theory of polaritonic chemistry due to electronic strong coupling is well established [1], theoretical studies describing the modification of ground-state chemistry through strong coupling between molecular vibrations and microcavity modes [2,3] are still missing. In this communication we will show our recent efforts in this direction. We use the cavity Born-Oppenheimer [4] description of the coupled light-matter system as a starting point and show that the effective light-matter potential energy surface governing ground-state reactions depends sensitively on the uncertainty of the molecular dipole moment. Based on full electronic-structure calculations for complex molecules, we identify several reactions that could be promising candidates for control through vibrational strong coupling.

References
DFT-based adsorption isotherms for pure and flue gases including SO$_2$ poisoning on Mg-MOF-74

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CO$_2$ capture and separation from flue gas mixtures using solvents or solid materials as Metal–Organic Frameworks (MOFs) are receiving significant attention in the last years due to their industrial interest. Moreover, the presence of gas impurities (e.g., SO$_2$, NO$_x$..) in the flue gas mixture affects the efficiency of carbon dioxide capture processes.

The use of computational chemistry techniques as Molecular Dynamics (MD) or Grand Canonical Monte Carlo (GCMC) simulations with suitable force fields based on Density Functional Theory (DFT) or experimental data can be very useful to select the most suitable solid absorbents and their optimal working conditions [1-2]. However, the application of accurate but more simpler models in a first stage before MD or GCMC studies, can be even a more powerful tool following this goal.

In the present work [3] we will present a simplified model for the prediction of gas/solid adsorption isotherms of pure gases (i.e., CO$_2$, N$_2$, SO$_2$) and some flue gas mixtures with small amounts of SO$_2$ on Mg-MOF-74. The model is based on periodic DFT calculations and a dual-site Langmuir approach using a mean-field approximation for the inclusion of the lateral interactions. This model not only provides reliable adsorption isotherms (P ≤ 1 atm, 293 ≤ T ≤ 373 K) but also isosteric heats of adsorption in good agreement with both available experimental data and more refined previous models [4]. Moreover, the effect of SO$_2$ in the efficiency of adsorption of the other components of the mixture has been evaluated showing that a very low presence of SO$_2$ is enough to poison the Mg-MOF-74 structure. Finally, three different swing adsorption processes (i.e., temperature TSA, vacuum VSA or combined VTSA) were analysed to determine the efficiency of the adsorption/desorption cycle through working capacities and the purity of the recovered CO$_2$. It was shown how VTSA outperforms the selected TSA and VSA cycles in both properties, especially at low % of SO$_2$ in the flue gas mixture. High amounts of SO$_2$ reduce the working capacity of CO$_2$ as well as its purity at the outlet, making unpractical CO$_2$ recovery with Mg-MOF-74.

References

Empirical Valence Bond Methods for Probing Dynamics in the Condensed Phase

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In my talk, I will describe work carried out in my group using the empirical valence bond (EVB) method to describe the potential energy surfaces of reactive chemical systems, and to describe the dynamics of such reactions in condensed phases [1]. In the EVB method, the potential energy surface is obtained as the lowest eigenvalue of a pseudo-Hamiltonian matrix, whose diagonal elements are formed by traditional forcefields, and the off-diagonal terms are resonance coupling terms.

A first focus will be the dynamics of hydrogen fluoride in acetonitrile, for which we have used a variety of different EVB models. As well as previously published work [2] I will present new results.

A second topic will be dynamics of organic reactions in solution, in which I will present unpublished work.

References


Are electrostatic properties of proteins the origin of enzyme catalysis?

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The origin of enzyme catalysis remains a question of debate despite much intense study. The biggest challenge is to define the common property responsible for speeding up chemical reactions in active sites of enzymes. In this presentation we focus on three not related enzymatic models i.e protease of HIV-1 (PR),[1] glycine N-methyltransferase (GNMT)[2] and HG.3 and HG3.17, de novo design enzyme Kemp eliminase [3],[4] in order to investigate their common features crucial for catalysis.

Herein, we report results of QM/MM theoretical studies for (a) peptide bond cleavage in multi-step reaction catalysed by HIV-1 PR, (b) the S\textsubscript{N}2 methyl transfer reaction catalysed by GNMT, and (c) kemp elimination catalysed by two de novo enzymes, HG3.17 and HG.3. In general, our studies indicate the importance of the electrostatic properties of the protein in the active site. Thus, in the multi-step reaction catalysed by HIV-1 PR, the electric field created by the protein in the active site of the enzyme emerges as being critical for the electronic reorganization required during the chemical process. Additionally, the decomposition of the electrostatic forces generated by the protein in the scissile peptide bond on the rate limiting transition state would favour the peptide bond cleavage.

In the case of GNMT, compression cannot explain the experimental variations of KIEs in the wild-type and several mutants. On the contrary, electrostatic properties in the active site correlate with the catalytic activity of the different versions of the enzyme. And finally, in Kemp reaction, the higher reactivity of the most evolved protein, HG3.17, is related with a better electrostatic preorganization of the environment that creates a more favourable electrostatic potential for the reaction to proceed. The limitations of the less active HG- 3 can be related to a lack of flexibility, a not well- fitted active site, and a lack of protein electrostatic preorganisation, which decrease the reorganisation around the oxyanion hole.

References

Theoretical Mass Spectrometry: from Organic to Biological Molecules

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Mass spectrometry (MS) is a widespread technique with applications ranging from fundamental studies to the so-called omics sciences, like proteomics, metabolomics etc… Since such experiments give very accurate information on the mass of the species but not on their structure, theoretical chemistry is often coupled to them. In particular, in the case of collision induced dissociation (CID) MS the product fragments are obtained without information on their structure neither mechanisms.

In last years, we have developed an approach based on chemical dynamics to obtain fragmentation products by modelling, in different ways, the collisional activation [1]. In particular chemical dynamics simulations have pointed out some crucial insights:

1) Some of the fragments are obtained by a fast, non-statistical, mechanism, called shattering, which cannot be predicted by statistical theory based on potential energy surface calculation. A clear evidence was obtained in the fragmentation of [Ca-formamide]\textsuperscript{2+} cluster [2].

2) The tautomerization process is a key aspect which must be considered to understand fragmentation. This is important not only in peptide fragmentation, both positively [3] and negatively charged [4], but also in other molecules, like steroids [5] and nucleic acids [6].

3) Semi-empirical Hamiltonians can be employed in several cases, thus allowing a relatively important statistical sampling.

Finally, we will show the overall way of iteratively generate different tautomers and obtain the full reaction network by combining graph theory analysis with simulations. This approach was able to reproduce also high-resolution mass spectroscopy results.

Example from the recent literature of our group will be discussed.

References

A computational approach to the structural toxicity of aluminum with biomolecules

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Although, aluminum is the most abundant metal and the third most abundant element in the Earth’s crust it has no essential role in any biochemical system in any extant organism[1]. The increased bioavailability of aluminum due to human intervention, raises concerns on the toxic effects that this so far “excluded from biology” metal might have on living organisms. Unfortunately, there is increasing evidence that aluminum could be behind of a variety of toxic effects, with significant risks for human health[2-3]. Consequently, the bioinorganic chemistry of aluminum has emerged as a very active field of research. However, the experimental determination of structure and affinities of Aluminum-Bioligand complexes is not without difficulties and theoretical methods have emerged as a fundamental tool to unveil aluminum biochemistry.

In the present talk I will review some of the recent advances made by our group on this field[4-7]. We will show how computational methods (DFT, QM/MM and classical molecular dynamic simulations) can be combined to determine the relative affinity of aluminum towards potential biological chelators. This can shed light on the type of biological compounds responsible for the so-called structural toxicity mechanism of aluminium.

References

Reactivity of hydrofluoropolyethers towards OH: a cost-effective implementation of multiconformer transition state theory

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The adverse environmental impact of CFC release into the atmosphere [1,2] has led to an international effort to replace them with acceptable alternatives. The Montreal Protocol led to the phase out of CFCs in industrialized countries because of their elevated ozone depletion and global warming potentials (ODP and GWP). Development of environmentally friendly replacements with lower tropospheric lifetimes (reaction with OH) became urgent, with HCFCs, HFCs and PFCs being selected as first- and second-generation replacements. However, non-zero ODP (HCFCs) and high GWP was still an issue with these compounds, with the latter two classes targeted by the Kyoto Protocol because of their high GWP. The design and development of useful alternatives continued, with hydrofluoropolyethers (HFPEs) appearing as promising third-generation replacements because of their zero ODP and even lower GWP.

Here, we will provide a detailed insight behind the computational strategies used in predicting the reactivity of different HFPEs towards the OH radical. Having a general formula of \( R - (OCF_2CF_2)\_p(OCF_2\_q - OR) \) (\( R = CF_2H, CH_3, CH_2CH_3, CH_2CH_2CH_3, CH(CH_3)2 \)), we have calculated nine rate constants: all five possible cases for \( p0q1, p1q0 (R = CF_2H, CH_3) \), \( p0q2 (CH_3) \) and \( p2q0 (CH_3) \). In the absence of any reported theoretical results, the quality of our cost-effective approach [3] (with M08-HX/aug-pcseg-2//M08-HX/pcseg-1 DFT calculations and using Eckart tunneling) based on multiconformer transition state theory (MC-TST) [4] will be assessed by comparison with four experimental rate constants [5,6]. Our investigations yield rate constants averaging a factor of \( \approx 0.7 (k_{MC-TST}/k_{exp}) \) of experimental data.

The good agreement with experimental results provides a valid framework for present and future calculations, where this cost-effective approach will prove essential in our objective of understanding the atmospheric chemistry of HFPEs. Hopefully, the gained theoretical knowledge will serve as an important tool in the design and development of new greener CFC alternatives.

References
Theoretical study of aromatic esters

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The study of acetylation of alcohols is of great interest by the utility of its products of reaction, esters, and is one of the most frequently used transformations in organic synthesis as it provides an efficient means for protecting hydroxyl groups in a synthetic process [1].

Geometric parameters of esters products: phenyl acetate, p-methylphenyl acetate and p-nitrophenyl acetate were performed in the gas phase using the DFT/B3LYP density functional quantum mechanical method and was adopted the 6-31+G* basis set. Enthalpies of formation were determined using the AM1 method. Experimental studies [2] and theoretical work [3] were carried out.

The Table 1 lists the energies, lengths and angles values obtained.

<table>
<thead>
<tr>
<th>Esters Structures</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
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Table 1. Energies, lengths and angles of esters structures

References

Giant barocaloric effects in multiferroic solid solution BiFe\textsubscript{0.5}C\textsubscript{0.5}O\textsubscript{3}

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The persistent miniaturization of modern electronic devices requires developing new refrigerant techniques such as solid-state cooling. In solid state cooling, high efficient cooling cycles can be achieved at the unit cell scale by applying external stimuli (either stress or electro-magnetic fields). First-order pressure-induced phase transitions involving a large change of volume should lead to huge changes in temperature, \(\Delta T\) (see equation below, \(C\) is the heat capacity). For practical applications, this phenomenon, known as barocaloric effect, should occur at conditions as close as possible to ambient \((T \sim 300\, \text{K}; \, p_t \sim 0\, \text{GPa})\).

\[
\Delta T = \frac{T}{C} \int_0^{p_t} \left( \frac{\partial V}{\partial T} \right)_p \, dp = -\frac{T}{C} \Delta V \left( \frac{dp}{dT} \right)_{p_t}, \quad C \equiv \text{heat capacity}
\]

According to both experimental and theoretical studies [2,3], a phase transition in the multiferroic material BiCoO\textsubscript{3} (BCO) involving a giant volume change of \(\sim 11\%\) occurs between a tetragonal phase (T) P4mm and an orthorhombic (O) Pbmn. In the 0 K limit, the critical pressure is around 3-3.5 GPa whereas at room temperature drops down to 2-2.5 GPa, a value that still is too high for solid-state applications. A possible way to reduce this transition pressure, as recently proposed by Cazorla et al. [3], is chemical substitution: similar phase transitions involving similar volume changes might occur in the solid solution BiFe\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{3} (BFCO) at a much lower pressure.

We have carried out a quasi-harmonic DFT-PBE study on BFCO to determine the thermodynamic stability among several energetically competitive polymorphs [4]. In agreement with the experimental results by Azuma et al. [5], we have found that the ground state of the solid solution is a tetragonal structure with a \(c/a\) ratio around 1.3. Our results also predict a zero-temperature a phase transition to a rhombohedral (R) phase, analogous to the ground-state of pure BiFeO\textsubscript{3}. The change in volume for this phase transition is close to 10\% (see Table 1). Our preliminary calculations show an inverse barocaloric effect of \(\Delta T \sim -10\, \text{K}\) at room temperature, suggesting that BFCO is a highly promising material for solid-state cooling applications.

<table>
<thead>
<tr>
<th>System</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>(\Delta V) (%)</th>
<th>(p_t) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCO</td>
<td>T</td>
<td>O</td>
<td>11</td>
<td>3.5</td>
</tr>
<tr>
<td>BFCO</td>
<td>T</td>
<td>R</td>
<td>9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1. Comparison between phase transitions for BCO and BFCO in the limit of 0 K. Phase transitions involving a similar change in volume can occur at lower pressure in BFCO.

References
Fostering the basic instinct of boron in B-Be interactions

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The ability of boron to behave as a Lewis base has recently attracted much attention, subverting its traditional Lewis acid role [1,2]. For a neutral boron compound to act as an electron donor a certain accumulation of charge is needed to foster its basic character, being equally important the good acceptor character of its counterpart in the Lewis pair. Beryllium is a powerful Lewis acid in closed-shell interactions, as revealed by the strength of beryllium bonds when compared to other closed-shell interactions [3].

Figure 1. Two electron-deficient atoms (B and Be) form strong Lewis base-Lewis acid pairs. ELF (0.85) for the (NH₃)₂HB···BeH₂ complex, V(B,Be) = 1.98e.

Boron-beryllium bonds, formed by two electron-deficient atoms that usually behave as Lewis acids, were not described until 2015 [1] (and, as the authors of this finding claimed, old neighbours finally shook hands). In this work [4] we explore a series of L₂HB···BeX₂ complexes where L are small neutral ligands (L = CNH, CO, CS, N₂, NH₃, NCCH₃, PH₃, PF₃, PMe₃, H₂O; X = H, F) at the M06-2X/6-311+G(3df,2pd)//M06-2X/6-31+G(d) level of theory. Not only interact B and Be, but they also can reach binding energies up to -283.3 kJ/mol (L=H₂O). We analyse how the strength and nature of this B-Be interaction is modulated by the ligands using different methods (QTAIM, ELF, DFT-SAPT, NBO).

References

Efficient fuzzy community detection in chemical space complex networks

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The concept of chemical space (CS) has been around for decades being a recurrent topic in nowadays cheminformatics and medicinal chemistry. As it is now understood the chemical space is defined as the set of all possible small organic molecules [1]. Applying the structure-based drug design point of view of [2] we obtain a lower bound estimate for the CS size of $10^{60}$ compounds.

A new and powerful way to describe the CS is to resort to the structure-activity relationship hypothesis, which states that structurally similar molecules should exhibit similar behavior [3]. Thus, it is possible to describe the CS (or a subset of it) as a network of molecules interrelated by a similarity measure [4]. This concept of Chemical Space Networks (CSNs) allows for an easy visualization of chemical space and opens the possibility of using the arsenal of methods and techniques developed by network scientists.

Complex network, or network science, is a modern interdisciplinary field that focuses in the structural and dynamic study of complex systems under the prism of a networked set of interrelated elements [5]. In a network, a problem of key importance is the determination of communities of elements more densely connected among them than with the rest of the network. Finding groups (clusters) of alike elements in a set is not a new problem in the pattern recognition and machine learning fields. However, for relational systems where the elements are interrelated in form of a network, the topology of the problem imposes a restriction not considered in classical clustering algorithms.

An interesting approach to community detection in networks is the fuzzy one, where each network node has a fractional participation in every community. This allows quantifying the different roles the nodes play in the network. The fuzzy approach represents the general case of community detection since the individual membership coefficients allow the adscription of each node to a single community or to a reduced set of them.

In this work, we adapt and determine the capacity of a new fuzzy community detection algorithm, TRIBUNE [6], to deal with large similarity-based networks. Thus, a TRIBUNE version tailored to similarity weighted, undirected networks is presented and parallelized on multicore environments. The performance of the new algorithm is analyzed as a function of the network size. In addition, the maximum network size tractable in a reasonable time frame is also determined.

References

Using the Reaction Force and the Reaction Electronic flux on carbenoid cyclopropanations

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We present an MP2/6-311G** study of Li and Mg carbenoid cyclopropanations. Carbenoid cyclopropanations have been studied at experimental and theoretical level due to the stability of the reacting systems, the efficiency and their stereospecificity. We have found that all the reactions proceed in a concerted, low barrier and exothermic way. The reaction force analysis indicates that the energy barriers are mostly composed by structural rearrangements which corresponds to the approach of the carbenoid to ethylene. The products form complex structures among the formed cyclopropane and the metal salt confirmed by NCI calculations, indicating that there are attractive forces between a cyclopropane single bond and the metal, that lowers with the ionic character of the salt which composes the system.

![Figure 1. NCI interactions for cyclopropane and magnesium salts.](image)

References

Macroscopic $pK_a$ prediction of polyprotic acids from DFT calculations: the case of acetohydroxamic acid

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The accurate calculation of $pK_a$ values in solution is a current challenge in computational chemistry and many computational approaches have been proposed to tackle this problem. In particular, it is especially difficult to estimate macroscopic $pK_a$ values of polyprotic acids from DFT-derived microscopic $pK_a$ values due to the errors of the latter. The goal of this study is to account for the existence of all the acid-base equilibria in acetohydroxamic acid (AHA) and come up with the methodology that best yields its macroscopic $pK_a$ in water. DFT calculations were combined with pure continuum and cluster-continuum approaches, which were used to model the solvent effects.

AHA is a drug used with antibiotics and/or surgery to treat certain types of bladder infections. It is also used as a chelating ligand for organometallic compounds. AHA exists in an equilibrium involving four main isomers (the amide and imide forms in their Z and E conformations, see Figure 1) each of which possesses two acid sites. Hence, each neutral form can dissociate in aqueous solution and exists in equilibrium with its corresponding anionic forms. These multiple dissociation equilibria contribute to the relatively low overall $pK_a$ of this compound.

Figure 1. Neutral forms of AHA.
Exploring the dynamics of α-synuclein with replica-exchange coarse-grained molecular dynamics simulations

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Intrinsically disordered proteins (IDPs) are not well described by a single, stable 3D conformation but by an ensemble of such conformations. This makes their structural characterization especially challenging, both experimentally and computationally. Most of the popular all-atom force fields were designed to model folded proteins and, when applied to IDPs, tend to give too compact conformations in comparison to the experimentally observed ones. Some corrections addressing this issue have been proposed, yielding force fields that can reproduce the experimental dimensions of some small IDPs.

α-synuclein is a well-known IDP because of its relation to Parkinson’s disease (PD). To understand the role of this protein in PD at the molecular level, it is necessary to have a methodology for generating an ensemble of structures that properly describes it. Moreover, it is desirable for this methodology to be extensible to modified forms of the protein (like the ones resulting from its glycation or its combinations with metal ions) so that the effects of these modifications on the structural ensemble of α-synuclein (and therefore on the development of PD) can be assessed.

In this work, we have applied the Replica Exchange with Solute Scaling methodology (REST2) [1] combined with the coarse-grained force field SIRAH [2] to the structurally unbiased exploration of the conformational dynamics of α-synuclein at the microsecond scale. We have found that a 30% increase in the standard strength of protein-water interactions yields a much better reproduction of the experimental radius of gyration of the protein. Furthermore, this methodology is readily extensible to the study of α-synuclein modifications, given that SIRAH uses the position of real atoms to place coarse-grained beads, allowing the nearly atomistic identification of functional groups establishing interactions, and therefore the introduction of modified amino acids [2].

Figure 1. Primary structure of α-synuclein.

References
The role of Metal-Organic Frameworks in Cobalt-Catalyzed Hydroformylation of 1,2-Hexane

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Based on Cobalt and Rhodium catalyst, via metal-phosphine complexes, the hydroformylation of alkenes is one of the most important applications in transition metal catalysis. A big problem for the industrial process is that, under hydroformylation conditions, these metal-phosphine complexes show low thermal stability and low regio-selectivity. Metal-organic frameworks (MOFs) could provide a solution to this problem. In fact, an interesting property of MOFs is the possibility to tailor-made their internal pore surface. The idea is to create the desired active site on the MOF’s internal surface (i.e. a phosphine group where to attach the catalyst) tuning the electronic and steric properties of the active site (e.g. functionalising the organic ligand) for enhancing the regio-selectivity and increasing the stability of the metal-phosphine complex.

Amongst the several types of MOFs, UMCM-1 particularly suits the purpose of catalysis since its large pores allows olefins diffusion and the featured terephthalic acid linker can be easily functionalised with phosphines exhibiting different electronic and steric properties without modifying the topology. These phosphine derivatives will act as coordination site for the catalyst (i.e. Cobalt Carbonyl).

In this work, first-principles simulations have been performed for investigating how, by different phosphine groups, the reaction mechanism of the alkenes hydroformylation process can be switched from linear to branched.
Modelling the repair of damaged proteins by antioxidants

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Free radicals are very reactive species that can damage proteins and other biomolecules. One of the first products of these reactions are carbon-centred protein radicals, which may subsequently become other species. Certain molecules, known as antioxidants, can scavenge free radicals by several mechanisms, including hydrogen atom transfer (HAT) and single electron transfer. This way antioxidants could also repair damaged proteins.

A particularly interesting group of antioxidants are those with thiol groups in their structure. Dihydrolipoic acid (DHLA) and glutathione (GSH) are examples of these antioxidants in which the S-H bond is weak enough to efficiently repair protein carbon-centred radicals by the HAT mechanism. GSH is a natural tripeptide (L-glutamate, L-cysteine and L-leucine) which takes part in many biochemical reactions that regulate the levels of free radicals. Phenolic compounds, such as α-tocopherol (vitamin E) or its water soluble analogue Trolox, are also known for their antioxidant activity. Trolox is commonly used as a reference molecule against which the antioxidant capacity of other species and mixtures is assessed.

In this work, we have used the M06-2X functional with the 6-31+G(d,p) basis set and the SMD solvation model to study the thermodynamics and the kinetics of the HAT repair reactions between the antioxidants GSH and Trolox and four N-formyl leucinamide radicals (centred at the α, β, γ and δ carbons). Calculations have been performed in water and in pentyl ethanolate, to mimic the effect of the microenvironment (hydrophobic or hydrophilic) of the damaged amino acid within the protein. The protein model N-formyl–leucinamide was recently used to study the antioxidant capacity of DHLA following a similar repair mechanism [1,2]. The results obtained in this work allow the antioxidant activity comparison between Trolox, GSH and DHLA.

Figure 1. Antioxidants used in this study: GSH (left) and Trolox (right).

References
Molecular Orbital Analysis of Local Current Distributions in Quantum Transport Through Single Molecular Junctions

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We developed a simple molecular orbital analysis of local current distributions inside single molecular junctions.[1,2,3] Using the first-order perturbation theory and non-equilibrium Green’s function techniques in the framework of tight-binding approximation, we show that the leading contributions to local current distributions are directly proportional to the off-diagonal elements of transition density matrices. Under the orbital approximation, the major contributions to local currents mainly come from a few dominant molecular orbital pairs which are mixed through the interactions between the molecule and electrodes, which leads to a simple molecular orbital picture for understanding current distributions inside a molecule under a bias potential. A few simple molecular junctions consisting of single- and multi-ring conjugated systems are used to demonstrate that local current distributions inside molecular junctions can be decomposed by partial sums of a few leading contributing transition density matrices.

![Figure 1. Local current distributions inside a coronene molecular junction.](image)

References

Theoretical study of the initial steps in the reaction of toluene with the hydroxyl radical

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Toluene is one of the main anthropogenic aromatic molecules in the atmosphere, due to cars exhaust, solvent use and biomass burning. Its reactions with the hydroxyl radical contribute to ozone depletion and aerosol forming in the atmosphere.

There is a general consensus in that the most important reactions are addition to the benzene ring, leading to cresols, and H-abstraction from the methyl group, leading to the benzyl radical which can further react with O2, eventually producing benzaldehyde. Several experimental and theoretical studies, however, differ about the structure of the products and their relative abundance. The present work, part of a larger systematic study on all the possible reaction mechanisms of toluene with the hydroxyl radical and the oxygen molecule, addresses the initial steps of such reactions, namely H-abstraction and ring addition.

Ab initio (MP2, CCSD(T)), composite model chemistry (CBS-QB3, G4) and density functional calculations (M06 with the 6-31+G(d,p), 6-311++G(3df,2pd) and cc-pVQZ basis sets) have been performed on reactants, intermediates, transition states and products of the C7H8 + HO● reaction. The accuracy and precision of the methods was judged by comparison to the experimental enthalpies of formation of several reactions intervening in the full mechanism. In the process, new enthalpies of formation are predicted for several radical and closed shell derivatives of toluene.

Table 1. Comparison of theoretical and experimental enthalpies of formation (in kcal/mol).

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis Set</th>
<th>Phenyl Radical</th>
<th>Benzylic Radical</th>
<th>Benzyl Radical</th>
<th>Phenolic Radical</th>
<th>Benzoic Acid</th>
<th>Alcohol</th>
<th>Average±2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>6-311+G(3df,2pd)</td>
<td>23.8</td>
<td>21.4</td>
<td>5.8</td>
<td>23.8</td>
<td>4.4</td>
<td>1.7</td>
<td>2.9</td>
</tr>
<tr>
<td>CBS-QB3</td>
<td>6-31+G(d,p)</td>
<td>1.7</td>
<td>1.1</td>
<td>2.3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>G4</td>
<td>6-31+G(d,p)</td>
<td>0.2</td>
<td>1.4</td>
<td>1.8</td>
<td>2.8</td>
<td>0.4</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>M06</td>
<td>6-311++G(3df,2pd)</td>
<td>4.7</td>
<td>0.4</td>
<td>1.6</td>
<td>4.1</td>
<td>2.8</td>
<td>3.3</td>
<td>5.8</td>
</tr>
<tr>
<td>cc-pVQZ</td>
<td>6-311++G(3df,2pd)</td>
<td>6.1</td>
<td>1.7</td>
<td>1.3</td>
<td>6.3</td>
<td>4.2</td>
<td>5.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>81±2</td>
<td>49.7±0.4</td>
<td>27.2±0.2</td>
<td>13.2±1.1</td>
<td>8.83±2.6</td>
<td>27.7±11.4</td>
<td>23.0±0.2</td>
</tr>
</tbody>
</table>

It was shown that thermochemically and kinetically there is no reason for hydroxylated products to be formed more abundantly than products derived from the benzyl radical. Classical TST and VTST rate constants were calculated at several levels of theory. The conclusion obtained, comparing the theoretical and experimental values is that the third body (normally He) is essential for the ring addition reaction mechanism. The theoretical results fit nicely in the rate constant vs pressure experimental curve when He pressure tends to zero. Atmospheric chemistry consequences are discussed.
Low-barrier hydrogen bonds in enzymes: a static or a dynamic concept?

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Allosteric regulation and cooperativity phenomena are ubiquitous in protein function. Many enzymes are known to change their activity in response to a chemical stimulus from the substrate itself. Binding of the latter to allosteric regulation sites or to the active site in enzymes can lead to a change of the global tertiary and quaternary structure. Recently, it was discovered that enzymes utilizing the vitamin B1 cofactor thiamin diphosphate (ThDP) such as e.g. pyruvate dehydrogenase feature a communication channel between the two remote active sites of the obligate functional dimers [1,2]. The atomic structures suggested that a ‘proton wire’ consisting of numerous acidic amino acid residues and water molecules synchronizes the catalytic events at the two active sites by reversibly shuttling a proton through this channel in a Grothuss-type mechanism thereby chemically activating the bound cofactors in reciprocal manner [2]. In this work we focus on the human transketolase (pdb code: 4kxw) also a ThDP-dependent enzyme. X-ray diffraction experiments at an unprecedented 0.8 Å resolution identify a proton sitting in between two Glu residues (E366’ and E160), Figure 1. Through the combination of molecular dynamics and quantum mechanics/molecular mechanics (QM/MM) calculations, we have found a viable mechanism of transport and are able to link the experimental assignment of the “proton density” to the latter pathway. The delocalization of the proton is confirmed by alchemical QM/MM runs, shifting the proton density in/out of an active site, and solving the proton wave function equation for the respective model potentials.

The system enables a unique opportunity for the study of the strongly disputed concept of low-barrier hydrogen bonds (LBHB). Our calculations show that such labile protons are better understood considering the dynamics of the full system, instead of regarding a single potential well for an individual hydrogen bond.

Figure 1. Left side: a QM/MM model showing a minimum structure with the proton located between two Glu residues. Right side: the corresponding potential energy surface and proton 1D wave function.

References

Gas adsorption on graphene: Introducing flexibility in the graphene sheet

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Graphene and derived products have shown great promise in the context of gas adsorption, possible applications range from environmental protection over gas sensing to energy storage. An important issue in the understanding of the involved principles, will be the movement of graphene itself. We have performed molecular dynamics calculations on the adsorption of different gases like methane, hydrogen, nitrogen, water and carbon monoxide including an intramolecular force field for graphene [1]. More specifically we have used and compared three different force fields found in the literature [2][3][4], one of which was originally developed for carbon nanotubes, while the other two were constructed specifically for graphene. Two of the force fields include stretch, bending and torsional terms, while the third one only uses stretch and bending terms. We have thus compared the behavior of a flexible graphene sheet to a more conventionally used rigid graphene sheet within the context of gas adsorption.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecule.png}
\caption{Adsorption of methane on a rigid (left) and flexible (right) graphene sheet.}
\end{figure}

References

Acknowledgement
The project leading to this application has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 642294.
The Entry of CoA into Enzymes: A Case Study with Pyruvate Formate-Lyase

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Coenzyme A (CoA) is an important coenzyme required, for example, in fatty acid synthesis and the citric acid cycle in aerobic organisms, where it is crucial for the oxidation of pyruvate. CoA also participates in pyruvate metabolism in anaerobic organisms, whereby pyruvate and CoA are transformed to formate and acetyl-CoA (AcCoA) in the presence of Pyruvate formate-lyase (PFL).[1] PFL is a glycyl radical enzyme requiring activation by a member of the radical SAM enzyme superfamily.[2] Such radical enzymes are receiving increased interest because of their possible applications in biotechnology.[3] The mechanism of PFL is thought to be initiated by the formation of a radical at Gly734, which is subsequently shuttled to Cys418 via Cys419. The addition of radical Cys418-S∙ to pyruvate leads to C-C bond dissociation, resulting with formation of formyl radical and acetyl-Cys418. The latter species acts as a temporary acetyl carrier and a reactant in the subsequent half-reaction with the second substrate CoA to produce acetyl-CoA. Formation of AcCoA, the final product, closes the catalytic cycle of PFL.[4]

The investigated aspect of this mechanism concerns the process that allows CoA to enter the active site, which is a prerequisite for the second half-reaction. The problem with this step is that the binding site of CoA is located at the protein surface, while the active site is buried in the protein interior.[5] In search for possible solutions to this problem the models representing the PFL system before and after the first half-reaction with pyruvate were subjected to long unrestrained molecular dynamics (MD) simulations, to examine the possible effect that acetylation of the enzyme has on the necessary conformational changes. The PFL systems were also subjected to the free energy calculations used to estimate potential of mean force (PMF) for the process of CoA approaching the active site before and after the pyruvate cleavage.

References
Computational Prediction of the Chemical Reactivity Properties of the Therapeutic Peptide of Marine Origin Parasin I through the Calculation of Conceptual DFT Descriptors

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In this computational study, eight density functionals, CAM-B3LYP, LC-ωPBE, M11, MN12SX, N12SX, ωB97X, and ωB97XD, related to the Def2TZVP basis sets, are assessed together with the SMD solvation model for calculation of the molecular properties and structure of the therapeutic peptide of marine origin Parasin I. All the chemical reactivity descriptors for the system are calculated via Conceptual Density Functional Theory (CDFT). The active sites suitable for nucleophilic, electrophilic, and radical attacks are selected by linking them with the Fukui function indices, electrophilic Parr functions, and condensed Dual Descriptor ∆f(r), respectively. The study reveals the MN12SX and N12SX density functionals are the most appropriate density functionals for predicting the chemical reactivity of the molecule under study.

Additionally, the relative pKa values for the several Lys residues present in the peptide are predicted with great accuracy as well as the ability of the studied molecule in acting as an efficient inhibitor of the formation of Advanced Glycation Endproducts (AGEs), which constitutes a useful knowledge for the development of drugs for fighting Diabetes, Alzheimer and Parkinson diseases.
The challenge to describe six-porphyrin nanoring’s aromaticity

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Porphyrrin nanorings are interesting compounds because they offer an end-free π-conjugated system with remarkable properties such as photophysical and guest-encapsulating.[1] Aromaticity is a multifold property[2] that is useful to understand the electronic structure of such belt-shaped π-systems. Herein we focused in BLA, BOA, FLU, HOMA as well as the recently introduced AV1245[3] and AVmin[4,5] to provide an electronic structure assessment of these hoop structures.

In this project, the aromaticity of a six-porphyrin nanoring in four different oxidation states (neutral, tetracationic, hexacationic and dodecationic species)[6] has been studied. Aromaticity indices reveal the local and global changes of aromaticity among the different studied species of the nanoring as well as the key role of the connectors between the porphyrins.

Figure 1. Local Aromaticity is useful to explain the Global Aromaticity of the Nanoring.

References
Catalytic systems for CO and CO\textsubscript{2} transformations studied by experimental and computational complementary methods

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The energy and chemical industry is nowadays very much dependent on oil, which production is in decline since 2008 and there are concerns about their future availability. Carbon oxides (CO and CO\textsubscript{2}) are increasingly seen as attractive potential feedstocks for fuels and chemicals. Furthermore, the need of decreasing the emissions in the atmosphere of a greenhouse effect gas such as CO\textsubscript{2} is promoting the research in the area of CO\textsubscript{2} transformation. The main drawback is its thermodynamic stability and kinetic inertness. To overcome this problem the use of catalysts or highly reactive substrates is required. For example, epoxides react with CO\textsubscript{2} in the presence of a catalyst to form cyclic carbonates or polycarbonates (Scheme 1).

![Scheme 1](image)

The cost in time and resources of the synthesis and trial of new catalysts make worth the use of all possible tools to ensure the success of any proposal. The state of development of computational chemistry makes it a very useful tool to help in the development of catalysts for specific needs. It can provide information about the structure of the active catalyst and about the mechanism of the reaction of interest, and this knowledge can be used to predict the most promising catalysts prior to their synthesis. In spite of the size of the systems and the complexity of the reactions this filed has to deal with, Density Functional Methods (DFT) provide a very satisfactory results.

We present here some examples of the synergy of experimental and computational methods in the development of catalysts for CO and CO\textsubscript{2} utilization. They will comprise some examples of organometallic catalysts to obtain polyketones and organic carbonates [1-3], and some results on natural organic catalysts that present promising potentialities to obtain cyclic carbonates from CO\textsubscript{2} by one-pot reactions from alkenes. They have the added advantage of being obtained from vegetable wastes, in particular from sugar cane bagasse, what provides a green route highly interesting.

References
On the nature of $\pi-\pi$, $\sigma-\pi$, and $\sigma-\sigma$ stacking in extended systems

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Non-covalent interactions involving $\pi$ systems are a frequent and crucial motif in a variety of fields in chemistry, biology and materials science. Extended $\pi$ systems mostly interact by means of $\pi$ contacts, so the behaviour of systems as fullerenes, carbon nanotubes, graphene and graphene nanoflakes and nanoribbons is mainly controlled by these interactions.

Stacking interactions have been widely studied in aromatic systems, especially in the prototypic benzene dimer. However, it has been shown that the stabilization in cyclohexane dimer is similar to that in benzene dimer, and the interaction between cyclohexane and benzene is in fact stronger than that in benzene and cyclohexane dimers.$^{[1]}$ Therefore, since $\pi-\pi$, $\sigma-\pi$ and $\sigma-\sigma$ contacts can provide similar stability to the systems, all three motifs can be important for explaining their behaviour, as well as for engineering new supramolecular receptors or functional molecules.

The interactions in aromatic-aromatic ($\pi-\pi$), aliphatic-aromatic ($\sigma-\pi$), and aliphatic-aliphatic ($\sigma-\sigma$) dimers formed by linear acenes of different size and their hydrogenated counterparts have been evaluated by applying symmetry-adapted perturbation theory SAPT(DFT) in order to reveal their nature.

References

Theoretical study on the nature of several non-covalent interactions involving π systems

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The nature of the interaction in complexes containing π systems was theoretically investigated using the Symmetry Adapted Perturbation Theory method with intra-monomer correlation effects described at the DFT level (DFT-SAPT). This approach allows splitting the interaction energy in contributions with physical meaning: repulsion, electrostatic, induction and dispersion. The complexes studied include several non-covalent interactions: X:···π (electron lone pair – π cloud); XH···π (hydrogen bond-like interactions) both with X = O, S, N, P and C; and also X(+)···π (cation–π complexes) with X = ammonium cation, and X(−)···π (anion–π complexes) with X = chloride and fluoride. Except with the halides, the effect of the progressive methylation of X was also studied. The π systems selected comprise an electron rich π cloud (benzene), an electron deficient π cloud (1,3,5-triazine), and an intermediate case (1,3,5-trifluorobenzene). The SAPT(DFT) analysis shows that dispersion contribution dominates the interaction between neutral fragments (the X:···π and XH···π contacts) even when the fragments are non-methylated. The relative weight of electrostatics increases in complexes with ions, although it never dominates the interaction. It has been observed that the complexes between triazine and the cations can be stable even with a repulsive electrostatic, refuting the accepted idea that the cation–π interaction is controlled by just electrostatics. The methodology used allows to rationalize in a unified way various types of non-covalent interactions, and emphasizes the importance of using in this type of study an appropriate level of calculation, capable of correctly describing the dispersive effects.

Figure 1. Contribution of Electrostatics, Dispersion and Induction to Eint, the interaction energy of the complexes studied. The contributions are computed relative to the sum of the absolute values of these three components of Eint. Dispersion and Induction are always attractive but there are some complexes with Elec > 0. Among the systems with repulsive Electrostatic contribution are the cation–π complexes of triazine (▲).
Fullerenes or endofullerenes inside nanorings, the importance of the size

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During the last few decades fullerenes and their wide range of properties have attracted a lot of attention. For this reason, a method that allows to discriminate between the different types of fullerenes is crucial. In this process macromolecular chemistry has an important role that allows to catch and release fullerenes. These complexes are formed by non-covalent interactions, and in particular nanorings are one of the most interesting hosts due the concave surface of their hole and their tuneable size.

In order to understanding the interactions that allows to encapsulate the fullerene inside the nanoring, a study of different pristine fullerene (C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78}) as well as cluster and metallic endofullerenes (Sc\textsubscript{3}N@C\textsubscript{80}, Y@C\textsubscript{82}, Y\textsubscript{2}@C\textsubscript{82}, Tm@C\textsubscript{82}, Lu\textsubscript{2}@C\textsubscript{82})\textsuperscript{1} with the [11]Cycloparaphenylene ([11]CPP) nanoring was performed. In this research we found that the size of the fullerene is the main factor to store them inside the [11]CPP. When the fullerene fills the cavity, the dispersion interaction is maximized and the complexation energy is similar for the different guest, fullerenes or endofullerenes.

References

Theoretical Self-Healing Capacity of Polymers with Disulfide Cross-Links

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Self-healing materials are a very promising kind of materials due to their capacity to repair themselves. Among others, diphenyl disulfide-based compounds (R₂Ph₂S₂) appear to be among the best candidates to develop materials with optimum self-healing properties. Based on Ab Initio calculations, we proposed a [2+1] radical mediated mechanism to be the responsible for such self-healing properties [1], which was later confirmed experimentally [2] (see Figure 1). In addition to this, non-covalent interactions between the polymeric chains are very important, since they keep disulfides closed enough for reaction. These non-covalent interactions have been studied by means of Classical Molecular Dynamics (see Figure 1 for system models), and show that hydrogen bonding play a much more important role than π-π stacking. Combining both Classical Molecular Dynamics and Ab Initio results, we conclude that there are two main factors that are relevant in the self-healing properties of disulfide-based materials. Firstly, the capacity to generate sulfenicyl radicals by breaking the disulfide S-S bond and, secondly, the ability of these radicals to attack neighboring disulfides. The former is dominated by the bond dissociation energy of the S-S bond, while the latter is strongly influenced by two other factors. On the one hand, the hydrogen bond interactions established between chains, and on the other, the energy barriers for the attack of sulfur radicals to neighbor disulfides.

We have defined three new parameters to estimate the influence of these features, and with them, we have defined a theoretical self-healing capacity [3]. In this vein, a novel theoretical parameter has been defined to predict the self-healing capacity of disulfides and related materials, which will help experimentalists in the development of improved materials.

Figure 1. Left: radical mediated mechanism. Right: system model for non-covalent interactions.

References

Electrostatic and Steric Effects on Chorismate Mutase Reactivity

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One paradigmatic example for the analysis of the origin of the catalytic efficiency of enzymes is Chorismate Mutase. This enzyme catalyzes the unimolecular conversion of (-)-chorismate to prephenate. The 2-million rate acceleration achieved by this enzyme results from a combination of Transition State (TS) stabilization and the displacement of the conformational equilibrium of reactants towards reactive conformations. These two enzymatic effects on the reaction are due to a combination of electrostatic and steric effects, which can be conveniently dissected performing mutations in the active site[1]. In this work we use multiscale QM/MM methods in combination with free energy[2] and TS optimization methods[3] to study the effect of different mutations. In particular we focus our attention on the consequences of the mutation of a positively charged arginine to the isosteric neutral residue citrulline. We have analysed the consequences that this mutation has on the characteristics of the TS ensemble and on the reaction minimum free energy path, including the reactants conformational equilibrium. The results of our simulations are compared to the available experimental data[1].

References

Second-Principles Density Functional Theory: A systematically improvable multi-scale method including electrons and lattice degrees of freedom

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During the last two decades first-principles methods, particularly Density Functional Theory (DFT), have become an indispensable tool in the study of solid-state systems. However, interpreting or predicting the results of experiments requires, in many cases, to go beyond the length and/or time scales allowed by current computational power. Based on the idea that not all electrons play a relevant role in the determination of the physical magnitudes under scrutiny, we present[1] a systematically improvable approximation to DFT based on a rigorous separation of these active electrons and holes from those of a reference electron density. Using a similar expansion to that found in Tight-Binding DFT methods we obtain a large term containing the energy of the reference system, and a second, much smaller one, associated to the active part of the electron density. By employing a well-tested model potential[2] to reproduce the energy surface associated to the reference system and representing the active electrons with a small but accurate localized (Wannier) function basis-set we obtain an efficient simulation method that can be used to calculate systems with tens of thousands of atoms with approximations that are systematically improvable towards DFT-quality. We provide several examples of its application[1,3] using the newly implemented SCALE-UP code[4] in complex oxides involving magnetism, metallic states and ferroelectricity.

Figure 1. Second-Principles DFT smoothly bridge simulations performed with a force-field and first-principles simulations.

References
First Principles Study of Palladium and Platinum complexes with 1,3-dithiole-2-thione-4,5-dithiolate ligands as Model Photosensitizers.

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Titanium dioxide has attracted huge interest in recent years, motivated by the important applications in solar energy conversion processes (photocatalysis and solar cells), gas sensors and biomaterials[1]. The surface of the oxide layer is the material for photoanode DSSCs, and responsible for the chemisorption of organic dye which acts as a sensitizer. The most important advantage of TiO$_2$ is optical stability, low toxicity, and appropriate band structure[2].

DSSCs differ from conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport and arise as an inexpensive and environmentally friendly alternative to the conventional silicon based photoelectric conversion device. In addition, compared with organic dyes, inorganic metal complex dyes have high thermal and chemical stability. In this way, other metal complexes have been investigated with respect to their applicability as sensitizers in DSSCs, in particular metals comprising nickel[3], platinum[4]. In addition, metal complexes with 1,3-dithiole-2-thione-4,5-dithiolate ligand is an important class of functional materials[5].

In this works, we perform DFT periodic calculations using the Vienna Ab initio Simulation Package (VASP). Adsorption of [CH$_3$]$_2$[M(DMIT)$_2$] complex on the TiO$_2$ (101) surface was done in three different adsorption configurations: linked by S$_{thione}$ S$_{thiole}$-S$_{thiolate}$ and plane, and M = Pd and Pt. The adsorption energies of complexes are negative and indicate that the process is exothermic except for palladium complex on S$_{thione}$ adsorption mode. The plane adsorption was the most stable form with -1.37 eV and -2.24 eV for Pd and Pt respectively.

Analysis of the density of states (DOS) demonstrated that the lowest unoccupied molecular orbital (LUMO) of metal complex lies below the conduction band of TiO$_2$. Thus, it is not favorable for an efficient electron injection from the complexes into the semiconductor surface. Modifying or exchange one of the ligand at [CH$_3$]$_2$[M(DMIT)$_2$ complex was an alternative strategy to raise the energetic position of the LUMO.

References

Can Supported Reduced Vanadium Oxides form H₂ from CH₃OH? A Computational Gas-Phase Mechanistic Study

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A detailed density functional theory study is presented to clarify the mechanistic aspects of the methanol, dehydrogenation process to yield molecular hydrogen, and formaldehyde. A gas-phase vanadium oxide cluster is used as a model system to represent reduced V⁰⁺ oxides supported on TiO₂ catalyst. The theoretical results provide a complete scenario, involving several reaction pathways in which different methanol adsorption sites are considered, with presence of hydride and methoxide intermediates. Methanol dissociative adsorption process is both kinetically and thermodynamically feasible on V-O-Ti and V=O sites, and it might lead to form hydride species with interesting catalytic reactivity. The formation of H₂ and CH₂O on reduced vanadium sites, V⁰⁺, is found to be more favorable than for oxidized vanadium species V⁵⁺, taking place along energy barriers of 29.9 kcal/mol and 41.0 kcal/mol respectively.

References

Computational Study of Boron Insertion Reaction into Benzofuran’s C-O Bond

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Products of borylation reaction are important for organic synthesis, functional materials and bioagents\textsuperscript{1}. Recently, Yorimitsu and coworkers\textsuperscript{2} presented a boron insertion reaction into the C-O bond of benzofuran. This reaction is catalysed by Ni(0) complex bearing a NHC ligand in the presence of Cs\textsubscript{2}CO\textsubscript{3}. In the classical transmetalation-like mechanism, the role of the salt is not clear, neither it is clear the sequence of the reaction steps.

In this communication, we present the results of a computational study carried out using DFT based methods (B3LYP-D3, M062X, and wB97XD). We have found that the reaction follows a cross-coupling like mechanism. Also, we have proved the formation of the B\textsubscript{2}nip\textsubscript{2}-Cs\textsubscript{2}CO\textsubscript{3} adduct. Furthermore, the most favourable reaction path is the one where there is a boron insertion into Ni-C bond which results from the oxidative addition. And then, the B-O bond formation gives the desired product directly. The reactivity of other substrates is explored.

Figure 1. Most favourable mechanism.

References

Separation of the Coulomb Hole into Dynamic and Nondynamic Contributions

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The account of electron correlation in quantum calculations is a most important challenge in current computational chemistry. Whereas the \textbf{dynamic} (also known as \textit{weak}) part of electron correlation accounts for the interactions due to the movement of the electrons, \textbf{nondynamic} (or \textit{strong}) correlation is important in systems where the ground state cannot be described by a single determinant.

The wavefunction includes information regarding electron-electron interactions. However, it becomes more intuitive to use the pair probability density (or \textit{reduced two-electron density matrix}). The \textbf{intracule density} \cite{1}, a contraction of the pair probability, is the probability function for the interelectronic vector that retains the information of electron correlation, but with the advantage of working with functions of lower dimensionality.

The introduction of electron correlation decreases the probability of finding two electrons close to each other, and in turn the probability of finding them in longer interelectronic distances increases. This consequence of electron repulsion can be easily assessed by means of the \textbf{Coulomb hole}, defined as the difference between the exact or FCI (correlated reference) and the HF (uncorrelated reference) intracule densities \cite{2}. In our approach, we use the Hartree-Fock-like (HFL) density matrix functional as a qualitative separator between the weak and strong correlation parts \cite{3, 4}.

In this context, a systematic study over a group of diverse diatomic molecules has been performed with the aim to assess the magnitude of the electron correlation and to reveal the nature of the type of correlation present in the molecule.

References

Rechargeable calcium batteries as a potential alternative for lithium-ion batteries: a DFT-screening of cathode materials

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Lithium-ion batteries are at the present the main electrochemical energy storage system in electronic devices and in the ground field of transportation. However, sources of lithium are limited, raising the need of designing alternative secondary batteries that could satisfy the increasing demand for enhanced energy density. Calcium is an attractive candidate due to its low cost, natural abundance and low reduction potential. The feasibility of reversible calcium plating/stripping using conventional alkylcarbonate electrolytes opens prospects of developing a new calcium based rechargeable battery technology [1]. While Ca metal is suitable as anode material, the identification of potential cathode materials able to reversibly intercalate Ca ions at high voltage is a current challenge on the field.

First-principles calculations are an invaluable tool in designing new electrode materials based on the intercalation reaction of monovalent (Li, Na, K) and multivalent (Mg, Ca, Al) cations. Numerous achievements in predicting relevant properties (including voltage, crystal structure stability, electronic structure and ionic mobility) of electrode materials for Lithium ion batteries using Density Functional Theory has been reported in the last two decades [2]. In the same line, we are performing a Density Functional Theory (DFT) investigation of the Ca-intercalation reaction and the physical properties of potential cathode materials based on 3d-transition metal ions. The DFT-screening of oxides, silicates, sulphides and carbonates points to a low Ca- mobility as the critical parameter.

References
Tuning the radical character of small graphene fragments

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It is well known that triangular graphene substructures hold an open-shell structure in their ground state, with radical character increasing with the number of fused benzene rings. Despite that the spin multiplicity of these systems can be systematically predicted through the simple Ovchinniko’s topological rule \cite{1}, the fine characterization of their electronic structure is a real challenge from a theoretical and computational point of view \cite{2}.

In this work we undercover to a great detail the intricacies of the ground and low-lying states of the two smallest members of this family, i.e. phenalenyl and triangulene (Figure 1), by combining different calculations within the density functional and (multiconfigurational) wave function theories. These results allow us to rationalize and design phenalenyl and triangulene derivatives with different ground state spin multiplicities by applying chemical modifications in selective positions: (i) N-doping, (ii) B-doping and (iii) saturation of edge carbons, as was proposed by Malrieu et al. \cite{3}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_1.png}
\caption{Molecular representation of phenalenyl (left) triangulene (right).}
\end{figure}

References

The role of tunneling in gas-grain reactions in diffuse molecular clouds

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Molecular clouds are objects in the interstellar medium (ISM) in which the particle density and the interstellar radiation field are high and low enough respectively to allow the formation of molecular species. They can be classified as diffuse or dense depending on the attenuation of the radiation field [1]. In particular, in diffuse molecular clouds wavelengths giving rise to dissociation of simple molecules and radicals (H₂, OH, NH, CH) are filtered to some extent. In these regions, atom addition reactions involving hydrogen are enhanced by the "catalytic" effect (storage effect) of siliceous and carbonaceous dust grains. This chemistry is driven by diffusion of the hydrogen atom on the surface, following a Langmuir-Hinshelwood mechanism [2]. However, diffusion over these surfaces is linked to the interaction of both the hydrogen atom and the heavy atoms with the surface itself, giving rise to kinetic barriers that vary depending on the physical state of the adsorbate. At the low temperatures of the ISM, between 10 and 50 K, thermal hopping is an unlikely mechanism to explain hydrogen mobility, being quantum tunneling the most plausible explanation.

This communication presents our results on the topic of quantum tunneling of hydrogen on siliceous forsterite (010) surface, which has been proven to be a successful surface when mimicking crystalline and amorphous silicates in the ISM [3]. The study of the tunneling has been carried out in the framework of instanton theory, a path integral method for determining non-classical crosses of potential energy barriers [4]. Both purely diffusion barriers and diffusion+radical recombination barriers are considered for the main interstellar heavy atoms (C,N,O) for the formation of radicals CH, NH and OH respectively. Moreover the first results on the influence of exact tunneling in the formation of molecular hydrogen, the most important astrochemical molecule, will be presented. Thermal effects in the diffusion are also included via ab-initio molecular dynamics simulations.

References

Anion–π catalysis on fullerenes: A combined DFT and experimental study

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Anion–π interactions on fullerenes are poorly explored because theoretical understanding and synthetic accessibility are more demanding. However, the localized π holes on its surface promise unique selectivities, particularly with regard to anion–π catalysis (see Figure 1). To elaborate on this promise, tertiary amines are attached nearby to turn on anion–π interactions as soon as the negative charge is injected into the substrate. Critically dependent on the precision of this positioning, the resulting stabilization of anionic intermediates and transition states on fullerenes is shown to selectively accelerate disfavored enolate addition and exo Diels–Alder reactions [1].

The observed selectivities are fully consistent with computational simulations, particularly with regard to the discrimination of differently planarized and charge-delocalized enolate tautomers by anion–π interactions. In the presence of chiral interfacers, anion–π catalysis on the π sphere occurs with high enantioselectivity.

References

The triplet state in PDI

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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 the triplet state. Despite that the triplet manifold is not initially accessible through photoexciitation, recent studies have identified spin triplets as the final photoproduct states upon exciton decay processes in PDI dimers [3] and in the crystal [4].

In the present work we aim to unravel the properties of the lowest triplet state (T\textsubscript{1}) in molecular and crystal PDI. We describe in great detail the electronic structure of T\textsubscript{1} and rationalize the particularities of the triplet manifold in the crystal structure by means of computed vertical energy gaps, exciton delocalization, interchromophoric interactions and charge transfer contributions. To that end, we make use of a variety quantum chemistry methods and computational tools within the density functional theory (DFT).

References


Figure 1. PDI molecule studied in this work.
Frustrated Lewis pairs as dynamic cross-links for self-healing materials

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The combination of Lewis acids and bases, defined as electron pair donors or acceptors, usually results in the formation of strong Lewis acid-base adducts. Nevertheless, when bulky acids and bases are combined, their steric demands may preclude these classical donor-acceptor interactions, giving rise to the so-called frustrated Lewis pairs (FLP)[1], which lead to unique and unprecedent reactivity[2]. In particular, these species can activate various small molecules or bonds[3].

The activation of diethyl azodicarboxylate (DEAD) by a FLP has been recently exploited for the production of a dynamic cross-link[4]. Thus, the addition of DEAD to a FLP-functionalized polystyrene promotes network formation, cross-linking the reactive polymer chains, and produces a dynamic, self-healing and heat-responsive gel.

The aim of this work is to explore computationally this process to get a deeper understanding of the nature and reversibility of the interaction between the FLP and DEAD. The knowledge achieved will allow us to pursue new FLPs combined with small molecules that may be useful for the experimental community as a first step towards new self-healing materials.

References
Activity and Selectivity of Cobalt Catalyst in Hydroformylation of Propene

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Alkene hydroformylation by homogenous catalyst is an important industrial process. It is used in the synthesis of aldehydes from alkenes and syngas (H₂ and CO).

During the course of the studied reaction a propene substrate, under high pressure of hydrogen and carbon monoxide, reacts at high temperature to give two products, linear n-butyraldehyde and branched iso-butyraldehyde. The ratio of the amounts of these two products depends on the conditions of the reaction (temperature, initial catalyst and propene concentrations, pressure). The reaction is catalyzed by unmodified cobalt catalyst.

The computational workflow developed by our group previously [1] consists of accurate calculations (DFT, CCSD(T)) of electronic structures of the compounds involved in the catalytic cycle and kinetic modelling based on transition state theory.

We propose the mechanistic model that is able to reproduce quite accurately the experimentally measured kinetics and selectivity [2-3] of propene hydroformylation by unmodified cobalt catalyst at an operating temperature of 150º C (Figure 1).

Reference
Chemical fragments in real space as open quantum systems

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Although partitions of the physical space into chemical fragments are now common in the theory of chemical bonding, e.g. the quantum atoms defined in the Quantum Theory of Atoms in Molecules (QTAIM) [1], not so many works have tried to deal with a chemical fragment as truly open quantum systems. Here we show how the partial trace over the environment degrees of freedom can be defined in real space. The subsystem reduced density operators so defined are shown to be intimately linked to the Electron Distribution Functions (EDF) formalism devised years ago [2]. Several examples will show the power of this approach.

References

New diagnostic tool for the analysis of the nonlinear optical properties

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While most of the theoretical works in the field of nonlinear optical properties (NLOPs) have been devoted to the search of the most effective quantum chemical methodology for the electronic contribution to NLOPs, the number of tools to analyze their nature is still limited. For example, in the experimentally oriented studies, atomic-type partitionings of NLOPs based on the Mulliken-type [1] and the real-space electron density [2] analyses are usually adapted, though hitherto they have showed limited utility in NLOP benchmarking of quantum chemical methods. In the pioneer work of Chopra et al. [3], the possibility of an orbital partitioning of the polarizability was proposed and years later was expanded in the analyses of Nakano [4] and Ye and Autschbach [5].

In this work, we present a new Partitioning of NLOPs into (natural) Orbital Contributions (PNOC). The response of natural orbitals is properly captured via changes in the one-particle reduced density matrix, overcoming the approximations of the commonly used uncoupled sum-over-states partition of the NLOPs. The implementation of this decomposition is straightforward and can be implemented for all computational methods available. Furthermore, such obtained overall NO contributions to the NLOPs can be used directly in the local description of these properties (i.e. as functions of the position in a real-space). Besides demonstrating the main features of the PNOC scheme, the important question about the importance of different type of electron correlation, namely static and dynamic correlation, in the computations of the NLOPs will be discussed. With the aid of our analysis, we obtain more insight on that using two different chemical model systems, chain-like conjugated and radical systems (both possess high values of NLOPs). Due to both the simplicity and the orbital consistency of the PNOC scheme, PNOC is an excellent tool for benchmarking the performance of quantum chemical methods in the NLOPs computations and for designing new molecular systems with enhanced NLOPs.

References
A new ab initio interaction potential based on the Hydrated Ion Concept has been developed to obtain the structure, energetics and dynamics of the hydration of uranyl in aqueous solution. It is the first force field that explicitly parameterizes the interaction of the uranyl hydrate with bulk water molecules to accurately define the second-shell behavior. The $\text{[UO}_2\text{(H}_2\text{O})_5\text{]}^{2+}$ presents a first hydration shell U-O average distance of 2.46 Å and a second hydration shell peak at 4.61 Å corresponding to 22 molecules using a coordination number definition based on a multisite solute cavity. The second shell solvent molecules have longer mean residence times than those corresponding to the divalent monatomic cations. The axial regions are relatively depopulated, lacking direct hydrogen bonding to apical oxygens. Angle-solved radial distribution functions as well as the spatial distribution functions show a strong anisotropy in the ion hydration. The $\text{[UO}_2\text{(H}_2\text{O})_5\text{]}^{2+}$ solvent structure may be regarded as a combination of a conventional second hydration shell in the equatorial and bridge regions, and a clathrate-like low density region in the axial region. Translational diffusion coefficient, hydration enthalpy, power spectra of the main vibrational modes and EXAFS spectrum simulated from molecular dynamics trajectories agree fairly well with experiment. The extension of the potential has also been extended successfully to other actinyls (Np(V,VI), Pu(VI), Am(VI)). These other species require NEVPT2 quantum chemistry calculations due to their open shell electronic structure.
Can standard DFT calculations correctly describe the physical properties of AlOOH under pressure?

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The behavior of AlOOH under pressure has been the object of many experimental studies. Under ambient conditions, AlOOH is stable in the α phase (diaspore, fig. 1). The δ phase (fig. 2) becomes the stable phase at about 17 GPa, while a third phase (called γ phase or bohemite) is metastable.

AlOOH equations of state have been reported in various papers, but, even when the p-V data collected by different researchers agree quite well, the bulk moduli obtained by fitting the data with Birch-Murnaghan or other analytical equations of state are very different. Quite strangely, large discrepancies are also found among the theoretical results, even if the calculations have been done using the same approximations.

I will discuss the origin of these uncertainties by mean of DFT calculations. Furthermore, I will show that the use of GGA for solids (like PBEsol or TCAsol) is mandatory to obtain a satisfactory and quite accurate description of this system [1, 2]. I also discuss the symmetrization of the hydrogen bond in the δ phase. There is a long-standing debate about the pressure at which the symmetrization of the hydrogen bond takes place. I will show that PBEsol and TCAsol allow one to come to a quite convincing and well defined conclusion [2].

References
Design of New Disulfide- and Diselenide-Based Organic Compounds for the Improvement of Self-Healing Materials

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Self-healing materials are a very promising kind of materials due to their capacity to repair themselves. Among others, diphenyl disulfide-based compounds (Ph₂S₂) appear to be among the best candidates to develop materials with optimum self-healing properties at room T. Recent theoretical and experimental studies [1,2] have shown that the mechanism leading to this process is a [2+1] radical-mediated mechanism (Figure 1. Left). Given that the formation of sulfenyl radicals strongly depends on the S-S bond strength, which can be modulated chemically by the use of proper derivatives, a wide set of different disulfide compounds, both aromatic and aliphatic, were studied, with amino derivatives appearing to be the most promising ones. Further work showed that hydrogen bonding between disulfide chains is also a relevant factor since it favours the contact among disulfide units (Figure 1. Right), which is crucial for the reaction to take place [3]. Taking this into account, the authors were able to establish a theoretical protocol based on the obtained results, offering a systematic way for predicting the theoretical self-healing capacity of materials. The protocol consists in three parameters, namely $\rho$, the probability of radicals to be formed, $k$, the exchange reaction rate constant, which accounts for the influence of the activation barrier of the reaction and $\omega$, which takes into account the number of disulfides or diselenides lying in the reactive region. This protocol has been used in order to study the theoretical self-healing capacity of different disulfide and diselenide materials including few of the most commonly used in polymer science such as urea, urethane, polyester and polyglycol.

References
Understanding substrate preference in alcohol dehydrogenases. A combined theoretical and experimental approach

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The origin of substrate preference in promiscuous enzymes has been investigated by enzyme isotope labeling of the alcohol dehydrogenase from Geobacillus stearothermophilus. Alcohol dehydrogenase from *Geobacillus stearothermophilus* strain LLD-R (BsADH) is a promiscuous thermophilic enzyme that warrants extensive mechanistic investigations.[1,2] The reversible conversion of alcohols to their corresponding carbonyl counterparts by alcohol dehydrogenase (ADH) has crucial importance in cell metabolism and has also been exploited in the food, fine chemical and pharmaceutical industries for chemical processing and chiral alcohol production.

Significant insights into the role of enzyme motions in catalysis have recently been gained from investigations of isotopically labelled enzymes, in which the non-exchangeable atoms $^{13}\text{C}$, $^{15}\text{N}$ and $^2\text{H}$ were replaced with $^{13}\text{C}$, $^{15}\text{N}$ and $^2\text{H}$, respectively.[3,4]. Further, the process of electrostatic preorganization can be promptly probed by testing substrates with different physical properties, thus facilitating the mechanistic elucidation of dynamic coupling.

We have employed experimental and computational simulation to compare the effect of dynamic coupling in BsADH catalysis by using different substrate in protein isotope labelling studies. For “good” substrates with high catalytic turnover, enzyme kinetics remain largely unaffected by protein isotope labelling, whereas for “bad” substrates with low catalytic turnover significant extent of dynamic coupling was observed.[5]

From our analysis, at physiological temperature, protein dynamic coupling to the reaction coordinate was insignificant. However, the extent of dynamic coupling was highly substrate-dependent at lower temperatures. For benzyl alcohol, an enzyme isotope effect larger than unity was observed, whereas the enzyme isotope effect was close to unity for isopropanol. Frequency motion analysis on the transition states revealed that residues surrounding the active site undergo substantial displacement during catalysis for sterically bulky alcohols. BsADH prefers smaller substrates, which cause less protein friction along the reaction coordinate and reduced frequencies of dynamic recrossing. This hypothesis allows a prediction of the trend of enzyme isotope effects for a wide variety of substrates.

References

The hydration structure of the heavy-alkalines through molecular dynamics and X-ray absorption spectroscopy: surface clusters and eccentricity

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Physicochemical properties of the heaviest stable alkaline cations, K, Rb and Cs in water have been examined from classical molecular dynamics (MD) simulations. Alkaline cation–water intermolecular potentials have been built from ab initio interaction energies of [M(H₂O)ₙ]⁺ clusters. The exchangeable hydrated ion model has been used to build the interaction potentials.[1,2] For Rb⁺ and Cs⁺ unlike the case of other monatomic metal cations, the sampling needed the inclusion of surface clusters to properly describe the interactions.[3] The first coordination shell is found at an average M–O distance of 2.72 Å, 2.87 Å and 3.12 Å for K, Rb and Cs, respectively, with coordination numbers of 7, 8 and 10. Structural, dynamical and energetic properties are discussed on the basis of the delicate compromise among the ion–water and water–water interactions. These contribute almost on the same foot to the definition of the solvent structure around the two heaviest cations, Rb⁺ and Cs⁺ whereas the ion–water interactions are dominant in the lightest ones. K⁺ represents a midway between them. A significant asymmetry is detected in the Rb⁺ and Cs⁺ first hydration shell. The structural and dynamical evolution of this property along the group is analyzed. In relation with the structure, the O–H RDF has been revealed as a significant structural parameter to establish differences in the closest solvation around the metal cations, as shown in Figure 1.

Reorientational times of first-shell water molecules for Cs⁺ support a clear structure-breaking nature for this cation, whereas the Rb⁺ and K⁺ values do not differ from pure water behavior and those of Li⁺ and Na⁺ are longer than the water values, supporting their structure-making nature. Experimental EXAFS and XANES spectra [4,5] have been compared to simulated ones, obtained by means of application of the FEFF code to a set of statistically significant structures taken from the MD simulations. Due to the presence of multi-excitations in the absorption spectra, theoretical–experimental agreement for the EXAFS spectra is reached when the multi-excitations are removed from the experimental spectra.

References
"Dynamic" and Quantum Effects in Enzymatic Catalysis

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Understanding of enormous catalytic efficiency of enzymes is hindered by the complex dynamic behaviour of enzymatic active sites. Multiple motions happen at timescales ranging from femtoseconds to microseconds, affecting the reactivity in non-trivial way. The case of enzymatic proton and hydride transfer is complicated even further, due to possible importance of nuclear quantum effects, particularly tunnelling. Not surprisingly, this complexity raised question about the validity of the Transition State Theory (TST) for enzymatic processes, because some of its assumptions may be oversimplistic.

We have applied a generalized hyperplanar transition state optimization technique \cite{1} combined with statistical reweighting procedure to calculate the intrinsic error of TST in the hydride transfer reaction catalysed by human dihydrofolate reductase \cite{2}. Hydride transfer is coupled to breaking/forming of two large conjugated systems, involving multiple substrate degrees of freedom and making the reaction coordinate particularly complex. We show that poor results obtained in previous studies are due to the use of an inadequate reaction coordinate and not to the limitations of TST. We also show that the non-equilibrium “dynamic” effects actually have smaller impact on the enzymatic reaction compared to the reaction in solution. Finally, we apply Ring-Polymer Molecular Dynamics technique to estimate the impact of nuclear quantum effects on the transition state geometry. Particularly we analyse the fluctuations of the donor-acceptor distance, which might facilitate the hydride tunnelling and, therefore, act as a promoting vibration.

References

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Unusual fragmentation mechanisms of excited doubly-positively charged amino acids in the gas phase

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Radiation damage of biological tissues starts at the femtosecond timescale, where ionization processes lead to the production of numerous secondary particles (electrons, ions, radicals). An important research activity focuses on the understanding of these processes at the molecular level [1]. In this context, ion-biomolecule collisions have become a fundamental technique to study radiation damage at the physical stage [2,3].

We have recently implemented a strategy based on the combination of experimental and theoretical studies to successfully disentangle the complicated fragmentation dynamics of complex molecular systems after ionization and excitation in collisions with energetic multiply charged ions [4]. Experimentally, we obtain the data in the gas phase for neutral molecules in collisions with low-energy highly charged ions. State-of-the-art multi-coincidence detection mass spectrometric techniques are used to determine the charge state of the molecule before fragmentation. The experimental data are analyzed by means of quantum chemistry calculations. In particular, *ab initio* molecular dynamics simulations of the excited and charged species provide valuable information on the fragmentation mechanisms; further exploration of the potential energy surfaces with the density functional theory calculations allows us to obtain energetic and structural information on the most populated dissociation channels.

In this communication we present our results obtained by applying this methodological approach to study the fragmentation dynamics of small lineal amino acids, doubly-positively charged in the gas phase, NH2(–(CH2)n−COOH; n=1 glycine [4]; n=2 β–alanine [5] and n=3 γ–aminobutyric acid GABA [6,7]. Our results have shown that in competition with the expected Coulomb explosion, the doubly-positively charged lineal amino acids present several de-excitation mechanisms. In particular, hydrogen migration and hydroxyl group migration, together with ring formation, are mechanisms that appear in the femtosecond timescale, and lead to unusual fragmentation products.

References
The design of new organic compounds to be used in the fabrication of electroluminescent devices requires a theoretical study of photophysical and electronic properties at both the molecular and the supramolecular level, along with an analysis of their charge transport properties. Butterfly-shaped molecules are interesting π-conjugated compounds that could be good candidates as materials for OLEDs, because of their high fluorescence efficiencies in solid state, which are related to the cross-stacking mode that they adopt in the aggregated state [1, 2]. Cross-stacking in the crystalline state restricts the free rotations of pendant groups in these molecules, causing the excited state to decay via radiative channels. Although their twisted structures prevent undesirable cofacial π-stacking, they could also provoke a higher separation between adjacent molecules hindering charge transport. Therefore, it could be necessary to reach a compromise solution between an intense fluorescence emission and semiconducting behaviour for butterfly-shaped compounds.

We have chosen a set of four butterfly-shaped molecules (see Figure 1), with known crystal structure, to study their photophysical properties in solution and solid phase using Density Functional Theory (DFT) calculations. DFT has been employed to analyse the main geometric changes that occur in both the ground and excited states when going from solution to solid phase, and also after the ionization process. Reorganization energies have also been calculated for both electronic excitation and ionization processes to elucidate which normal modes assist the relaxation process from both the excited charged state and the excited neutral state. The efficiency of charge injection and transport from a molecular point of view has also been analysed. Our results point out that the selected compounds could be good candidates as materials for optoelectronic applications.

![Figure 1. Chemical structure of the set of studied butterfly-shaped molecules.](image)

References

Assessment of sulphur-gold bonding in the adsorption of monosubstituted thiourea derivatives on Au(111) surface

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Capped nanoparticles are hybrid inorganic-organic systems formed by a metal nanoparticle protected with an organic molecule. Recent studies have demonstrated the potential applications of these capped nanoparticles in fields like sensing, drug delivery and antibacterial control\cite{1}. Gold nanoparticles and organosulphur compounds have been widely employed in the formation of capped nanoparticles due to the strong chemical affinity between sulphur and gold\cite{2}. In addition, gold nanoparticles exhibit a high level of biocompatibility which highlights its stability on biological systems\cite{3}. Thiourea derivatives are organosulphur compounds with a special attractive as capped agents owing to its catalytic, ionophore, luminescent and biological properties. In the present computational study we assessed the strength and stability of sulphur-gold bonding during the adsorption of different monosubstituted thiourea derivatives on Au(111) surface (see Figure 1).

The adsorption of monosubstituted thiourea derivatives isomers on the Au(111) surface was modelled in the framework of DFT employing the PBE functional implemented in the VASP code\cite{4}. The density dependent dispersive correction was included to take into account van der Waals interactions\cite{5}. According to our calculations the strength of electron donating/withdrawing groups affected the final arrangement of thiourea derivatives. In addition, we obtained significant differences in the deposition of the thiourea derivatives isomers on Au(111) which was attributed to interactions of different nature between the molecule and the metal surface. The strengthening or weakening of sulphur-gold bonding was also a consequence of the electron donating/withdrawing groups within the thiourea derivatives. Using atomic polarizabilities we were able to address the changes occurred in the thiourea derivatives-Au(111) interface during adsorption. These results allowed us to establish, under a simple approach, rules for the prediction of adsorption geometry in functionalized thioureas.

How Do London Dispersion Interactions Impact the Photochemical Processes of Molecular Switches?

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In the last two decades, linear-response time-dependent density functional theory (LR-TDDFT) has become one of the most widely used approaches for the computation of the excited-state properties of atoms and molecules[1]. Despite its success in describing the photochemistry and the photophysics of many molecular systems, its domain of applicability has been limited by several substantial drawbacks. In particular, the most commonly underlined problems of LR-TDDFT comprise the correct description of Rydberg states, charge transfer excited states, doubly excited states and nearly degenerate states[2]. In addition to these shortcomings, the approximate functionals used in TDDFT are unable to fully describe London dispersion interactions. In this work, we aim at understanding the impact of van der Waals interactions on the properties of chemical systems beyond their electronic ground state. For this purpose, we performed excited state and molecular dynamics computations on the prototypical cis-stilbene molecule (A) and compared the results with its 3-3',5-5'-tetra-tert-butyl derivative(B). While the explicit treatment of London dispersion interactions results in negligible changes for the cis-stilbene, we show that these attractive forces have a substantial influence on the energetics and structural evolution of its substituted derivative. In the latter case, intramolecular dispersion interactions impact the outcome of the simulation qualitatively, leading to an increased preference for the photocyclization pathway. The methodological consequences of this work are not uniquely applicable to the illustrative stilbene case. In fact, this molecule is representative of a whole class of chemical situations, where dispersion dominates the interactions between the unexcited substituents of a photoexcited chromophore. This is, for instance, a common situation in organic photovoltaics where donor molecules are usually functionalized with long alky l side chains to improve solubility and assembly[3].

Figure 1. Energy profiles (in electronvolts) of molecules A (left) and B (right).

References
Electron Counting in Position Space: From Quantum Fragments to Lewis Structures to Multicenter Bonds

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An electron counting technique to generate Lewis structures from position space partitioning procedures is proposed. We base our approach on reformulating the adaptive natural density partitioning (AdNDP) algorithm proposed by Zubarev and Boldyrev (Phys. Chem. Chem. Phys. 10, 5207 (2008)) in real space through the use of domain-averaged cumulant densities, which take into account many electron correlations. Averages are performed over the basins provided by the quantum theory of atoms in molecules (QTAIM). The decomposition gives rise to a set of n-center, two-electron orbitals which describe the dominating Lewis structures of a molecular system, and is available both for single- and multi-determinant wavefunctions. As shown in several examples, chemically intuitive descriptions, in close correspondence to those obtained through the AdNDP recipe, are now available from fully invariant position space descriptors.
Intramolecular Rearrangements of [Re(4,4′-NMe$_2$-2,2′-bipy)(CO)$_3$(N-RIm)]: R=Mes vs R=Me. Effect of the dispersion energy

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Dearomatization of pyridines and other six-membered N-heterocycles is a challenging task that can provide a route to the synthesis of functionalized molecules present in many natural products and pharmaceuticals[1]. Organometallic reagents of the early transition and f-block metals typically metalate the ortho C-H bond of pyridine to afford $\eta^2$-(C,N)-pyridine complexes. Experimental studies on the dearomatization of related transition metal-coordinated 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands under mild conditions, prior to our work, were unknown[2]. Particularly, it has been reported that the addition of the equimolar amount of KN(SiMe$_3$)$_2$ to a solution of [Re(bipy)(CO)$_3$(N-RIm)]OTf (R=Mes, Me) in THF at -78 ºC led to the deprotonation of the central CH group of N-RIm (C$_{im}$), and to the subsequent attack of C$_{im}$ on the H-bonded carbon atom in ortho position (C6) of the bipy ligand[2]. The effect of different substituents at the para positions (4 and 4′) of the bipy ligand on the deprotonation reaction of such Re complexes has recently started to be studied both experimentally and computationally. Interestingly, the experimental deprotonation of [Re(bipy)(CO)$_3$(N-RIm)]OTf (R=Mes, Me) in THF at -78 ºC led to the deprotonation of the central CH group of N-RIm (C$_{im}$), and to the subsequent attack of C$_{im}$ on the H-bonded carbon atom in ortho position (C6) of the bipy ligand[2]. The effect of different substituents at the para positions (4 and 4′) of the bipy ligand on the deprotonation reaction of such Re complexes has recently started to be studied both experimentally and computationally. Interestingly, the experimental deprotonation of [Re(4,4′-NMe$_2$-2,2′-bipy)(CO)$_3$(N-MesIm)]OTf leads to the formation of the C$_{im}$-C6 coupling product as happened in the absence of substituents at the positions 4,4′. However, the replacement of Mes by Me at the imidazole ligand leads to a different product, the C$_{im}$-Re coupling product. This prompted us to computationally investigate the different reactivity pattern experimentally observed. Based on our broad computational experience on the intramolecular rearrangements of similar and related metal complexes, we initiate our investigation using the level of theory PCM(UFF)-B3LYP/6-31+G(d)(LANL2DZ + f for Re)[3-5]. However, this computational protocol could not confirm the products experimentally found. Specifically, the C$_{im}$-C6 coupling with a Gibbs energy barrier of 13.8 kcal/mol is the predicted product for R=Me, while the C$_{im}$-Re coupling with a Gibbs energy barrier of 15.4 kcal/mol should be obtained when R=Mes. The correction of the B3LYP energies by adding the dispersion energy does not change these results either. Then, several density functionals with and without including the dispersion energy correction during the structure optimizations were tested. The best agreement with experiment was found with the B97D functional. Herein, we present these results as well as a comparison with the B3LYP ones.

References
Second-principles study of topological properties of ferroelectric nanodomains

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Nowadays, the study of magnetic structures with nontrivial topological properties is very important as they may open the door to novel nanotechnologies with huge potential impact. The interest of the scientific community in such structures has been growing in the last few years, with many studies reporting skyrmions in magnetic systems [1]. In this context, some authors have discussed electric skyrmions, whereby an exotic arrangement of electric dipoles would yield skyrmion-like structures in ferroelectric materials. Indeed, the recent experimental discovery of a dipole vortices in PbTiO3/SrTiO3 superlattices [2] has added to earlier theoretical predictions of skyrmions in ferroelectric nanocomposites [3] and Bloch-like structures in ferroelectric domain walls [4], and the possibility of stabilizing and manipulating electric skyrmions currently attracting a lot of attention.

Following these ideas, we have used a novel first-principles-based (second-principles) force field developed for PbTiO3 [5,6] to investigate the behavior of ferroelectric nanodomains immersed in a big domain of opposite polarization. Our simulations yield the first prediction of an electric skyrmion in a single-phase material. We have also found that these dipole structures can be controlled applying an epitaxial strain or external electric fields, which may open the door to interesting applications.

References
Understanding the effect of aggregation on the photophysical properties of phenylenevinylenes

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Absorption and emission spectra in organic compounds depend on the intrinsic characteristics of molecules (chemical structure, shape, substituents, side chains, etc.) as well as on the polarity of the solvent in solution and the packing in solid state [1]. The intriguing aggregation-caused quenching (ACQ) and aggregation-induced emission (AIE) are phenomena which could dramatically change the photophysical properties when going from isolated to aggregate state. Thus, the study of the effect of aggregation on the absorption and emission spectra is mandatory and previous to any search for technological and/or biomedical applications of new compounds.

From our previous experience in phenylenevinylene derivatives [2], we have applied both absorption and emission electronic spectroscopic techniques and Density Functional Theory (DFT) calculations to get insight into the effects of the molecular aggregation on the photophysical properties of this fascinating luminescent family of compounds. Vertical electronic transitions have been calculated by using Time-Dependent (TD) DFT for the isolated monomer (in different solvents) and for a model cluster to mimic the aggregated state (see Figure 1). In addition, the molecular geometry of both ground and excited states has been calculated to discuss about the electronic mechanisms responsible for the electronic relaxation process.

References
Study and comparison of de novo design enzymes by QM/MM theoretical studies

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Nowadays it is possible to generate new proteins from scratch on the basis of our understanding of protein biophysics. [1] Even though the computational design of new enzymes is still at an early stage, being the first example of de novo protein design published in 2008, it has rapidly earned a place in biochemistry. Among the first reactions used as benchmark to de novo design of enzymes [2] stand out the retro-aldolase reaction. It presents the mechanistically most complex process designed to date [3]–[5]. This novel catalysts design have to catalyse a carbon-carbon bond cleavage in a non-natural (not found in biological systems) substrate: 4-hydroxy-4-(6-methoxy-2-naphthyl)-2-butanone, via covalent Schiff base intermediate[4]. Over the course of the evolution, alternative protein scaffold and active-site cavities have been investigated.

The aim of this work is to study the reaction mechanism of the two best variants of retro-aldolase de novo designs, the RA95.5-8 and RA95.5-5 (whose experimentally measured [6] $k_{\text{cat}}/k_{\text{uncat}}$ values are $2.6\cdot10^7$ and $1.1\cdot10^7$ respectively) and to understand the origin of their catalytic power. Our theoretical studies have been based on the analysis of potential energy surfaces employing hybrid QM/MM potentials, with the QM subset of atoms initially described by the semiempirical Hamiltonian AM1; followed by correction with the M06-2X functional with the 6-31+g(d,p) basis set. QM/MM Molecular dynamics simulations have been employed later to generate the free energy surfaces for each step of the mechanism in terms of on-the-fly string methodology[7] and potential of mean forces (PMFs), obtained through the combination of WHAM+US techniques. Our findings will pave the way to propose mutations that could enhance the activity of this complex multi-step catalyzed reaction.

References
A Computational Kinetics Study of the Antioxidant Activity of Tryptamine

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A computational kinetics study of the antioxidant activity of tryptamine toward HO• and HOO• radicals in water at 298 K has been carried out. Density functional methods have been employed for the quantum chemical calculations and conventional transition state theory was used for rate constants evaluation. Different mechanisms have been considered: radical adduct formation (RAF), single electron transfer (SET), and hydrogen atom transfer (HAT). For the reaction of tryptamine with the hydroxyl radical nearly all channels are diffusion controlled, and the overall rate constant is very high, 6.29 x 10¹⁰ M⁻¹ s⁻¹. The RAF mechanism has a branching ratio of 55%, followed by the HAT mechanism (31%), whereas the SET mechanism accounts just for 13% of the products. The less hindered carbon atom neighbor to the nitrogen of the indole ring seems to be the preferred site for the RAF mechanism, with a branching ratio of 16%. The overall rate constant for the reaction of tryptamine with the HOO• radical is 3.71 x 10⁴ M⁻¹ s⁻¹, suggesting that it could be a competitive process with other reactions of hydroperoxyl radicals in biological environments. For this reaction only the HAT mechanism seems viable. Furthermore, only two centers may contribute to the HAT mechanism, the nitrogen atom of the indole ring and a carbon atom of the aminoethyl chain, the former accounting for more than 91% of the total products. Our results suggest that tryptamine could have a noticeable scavenging activity toward radicals, and that activity is mainly related to the nitrogen atom of the indole ring.

Figure 1. Structure of TRA in aqueous solution [1] with numbering of atoms employed in the present work.

References

The influence of multiple conformations and paths on rate constants and product branching ratios.  
The thermal decomposition of 1-propanol radicals

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The potential energy surface involved in the thermal decomposition of 1-propanol radicals was investigated in detail using automated codes (tsscds2018 and Q2DTor). From the predicted elementary reactions, a relevant reaction network was constructed to study the decomposition at temperatures in the range 1000 – 2000 K. Specifically, this relevant network comprises 18 conformational reaction channels (CRCs), which in general exhibit a large wealth of conformers of reactants and transition states. Rate constants for all the CRCs were calculated with the TheRa program, using two approaches within the formulation of variational transition state theory (VTST). The simplest, one-well (1W) approach considers only the most stable conformer of the reactant and that of the transition state. In the second, more accurate approach, contributions from all the reactant and transition state conformers are taken into account using the multipath (MP) formulation of VTST. In addition, kinetic Monte Carlo (KMC) simulations were performed to compute product branching ratios. The results show substantial differences between the values of the rate constants calculated with the two VTST approaches. On the other hand, the KMC simulations carried out with the two sets of rate constants indicate that, depending on the radical considered as reactant, the 1W and the MP approaches may lead to significantly different results.
Hydrolysis Reaction on Metal Bound ATP: Effect of the Metal on the Reaction

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Adenosine triphosphate (ATP) is a very important molecule in biology, and the hydrolysis reaction of ATP is one of the main sources of energy for living cells. ATP is also involved in protein phosphorylation, a very important reaction in cellular regulatory mechanisms.

ATP contains a triphosphate group that can bind Mg(II) but also other cations. It is well established that Mg(II) catalyzes the hydrolysis of a monophosphate, but interestingly it was demonstrated experimentally[1] that trivalent cations such as Al(III) in turn catalyze the triphosphate hydrolysis in which the entire triphosphate group is transferred to the target amino acid.

In the present study, we employ DFT cluster models to characterize all possible hydrolysis reaction pathways in ATP interacting with either Mg(II) or Al(III). In overall, the results are in agreement with the experimental observations and they provide a comprehensible explanation why the nature of the cation determines the hydrolysis reaction of ATP.

References

Predicting and Understanding the Reactivity of Aza[60]fullerenes

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The Diels–Alder reactivity and selectivity of the simplest azafullerene C₅₉NH and cyclopentadiene have been computationally studied by applying the Activation Strain Model (ASM) [1] of reactivity in conjunction with the Energy Decomposition Analysis (EDA) [2] method [3].

A significant decrease of the Diels–Alder reactivity is found for the azafullerene system compared to the C₆₀ from both kinetic and thermodynamic points of view for the 16 chemically different [6,6] bonds. This finding suggests that the heteroatom strongly influences the entire fullerenic cage. Also, a low regioselectivity for the cycloaddition involving the heterofullerene is predicted.

According to the ASM, the higher energy barrier computed for the azafullerene systems can be mainly ascribed to the lower interaction energy between the deformed reactants along the entire reaction coordinate. By decomposing the interaction energy with the EDA method, this less stabilizing interaction energy for the reaction involving C₅₉NH is mainly the result of lower orbital and electrostatic interactions. In addition, by means of the EDA-NOCV method [4] this less stabilizing orbital interaction to a weaker π(diene)–π(fullerene) interaction for the C₅₉NH system (see Figure 1).

**Figure 1.** Plot of the deformation densities (∆r) of the pairwise orbital interactions between CP and C₆₀ (a) and C₅₉NH (b) and associated stabilization energies (∆E, in kcal/mol).

**References**

Non-adiabatic fragmentation of H$_2$O$^+$ and HDO$^+$

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In a recent work [1], we performed a calculation to study the fragmentation of H$_2$O$^+$ in its state, produced by a sudden ionization of the water molecule. There, we showed that the fragmentation dynamics requires to consider the three lowest electronic states, and the non-adiabatic couplings between them, and it involves a fast (in the femtosecond timescale) transition at the conical intersection between and states, and a slow (picoseconds) relaxation of the wave packet between the and states through a Renner-Teller transition at linear geometries.

In this work, we explore how the fragmentation dynamics changes with the initial conditions. In particular, we simulate the experiment of Harbo et al [2], who used a 532 nm laser to excite stable H$_2$O$^+$ ions, and found a branching ratio for production of H$^+$ and OH$^+$ of, in contrast to 0.31 found in the experiment without laser excitation of Tan et al [3]. Figure 1 shows our preliminary results for the fragmentation of H$_2$O$^+$ starting from a excited vibrational state 2.3 eV above the ground state; we find qualitative agreement with the result of Harbo et al.

We have also considered the isotopic dependence of the fragmentation branching ratios by running a simulation with the isotopomer HDO$^+$. Here we find that the probability of breaking the OH bond is twice that of braking OD, in agreement with experiments of Sayler et al [4].

![Figure 1. Ion production probability, as a function of time, in the fragmentation of H$_2$O$^+$ ( ) with initial conditions as in [2].](image)

References
Theoretical approach for predicting the color of anthraquinones dyes in solution

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Anthraquinones (Fig.1) are a class of industrial dyes, either from synthetic origin or found in nature. Although several theoretical studies have clarified the accuracy, at the ab initio level, of the prediction of the maximal absorption wave length[1], this parameter alone is not sufficient for simulating the color and the color intensity[2]. This is the reason why we have developed a computational approach based on DFT and TD-DFT in conjunction with a vibronic treatment for band shape prediction and a polarizable continuum model for solvent description. This approach, that computes the λ.max values of the absorption spectra, linked to the hue, and the shape of the absorption band linked to the chroma, is shown to provide good accuracy in perceived colors for the anthraquinones and thus contributes to fill the gap between the color chemistry and the optic physics of materials.

Figure 1. Schematic representation of anthracene-9,10-dione (Anthraquinones).

References
Azide anion confined inside carbon nanotubes: quantum chemical and molecular dynamics study

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The exceptional energetic difference between single, double and triple nitrogen-nitrogen bonds makes polynitrogen compounds promising candidates as high energy-density materials.

Recent discoveries[1,2] have shown that the synthesis of such molecules is now a reality, although the difficulty for their storage still remains an issue.

Indeed, such compounds are generally highly volatile, in particular at ambient conditions, and a major challenge is to find ways to improve their stability.

A possible approach is their confinement inside nanostructures of various types, e.g. carbon nanotubes, such that the restricted space within the cavity and the host-guest interactions favour stabilization.

In this work we present an in-depth investigation of the confinement of the azide anion, a common precursor in the synthesis of larger nitrogen clusters, inside carbon nanotubes of different sizes and lengths.

In particular, quantum chemical calculations (using both wave function and density functional methods) of interaction energies, relaxation effects and an analysis based on natural bond orbitals will be presented along with a study of the effects on these properties with respect to the diameter and length of the nanotubes[3].

Moreover, the results of molecular dynamics simulations will also be presented, in particular highlighting the implementation of the improved Lennard-Jones potential[4] in the DL POLY 4 program package.

A specific model potential will also be introduced, which treats explicitly the induction effects due to the presence of the excess charge on the nitrogen species, which allows for an analysis of the interaction types involved between the nanotube and the azide anion and a direct comparison to the quantum-chemical study.

![Molecular Electrostatic Potential](image)

**Figure 1. Molecular electrostatic potential of a CNT(5,5) perturbed by the presence of the azide anion.**

**References**


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What Controls Photocatalytic Water Oxidation on TiO$_2$?
A Photochemical Perspective

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In the photocatalytic oxidation of water by TiO$_2$, excitation of the semiconductor generates a hole-electron pair that oxidizes and deprotonates adsorbed water molecules, leading to generation of oxygen. This process, also known as the oxygen evolution reaction (OER), is one of the main bottlenecks that prevents the use of water photoelectrolysis on TiO$_2$ for fuel generation, since it has a low efficiency. To determine the reasons behind this, we have studied the mechanism with theoretical methods[1]. Our approach considers the reactivity of the hole and electron as a correlated exciton pair. We centre on the first step, where hydroxy radicals are generated after a coupled proton and electron transfer (PCET) step:

$$\text{H}_2\text{O}@\text{TiO}_2 + h\nu \rightarrow \text{HO}@\text{TiO}_2 + \text{H}^+ + e^-$$

Our calculations show that the reaction is exothermic and almost barrierless. This is in contrast to previous studies which do not consider the excitonic character explicitly and blame the low efficiency on the energy barriers for the PCET. In our model, the low efficiency is due to the high probability of charge recombination, which regenerates the reactant. In turn, the charge recombination is associated to crossings between electronic states with different charge configurations.

References
From computation to experiments: prediction and validation of the pre-catalytic conformation and the reaction mechanism of a DNAzyme

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Although the catalytic power of RNA (ribozymes) has been broadly studied over the past 20 years, less is known about the catalytic features of DNA. In the past years DNA acting as a catalyst (DNAzymes) has emerged as a blooming field in biomedicine and biotechnology.[1] DNAzymes were first developed as a therapeutically tool to silence genes through the cleavage of mRNA targets although DNAzymes for other reactions have been also designed.[1]

It has not been till recently that the first structure of a DNAzyme was resolved.[2] This structure sheds light into the pseudoknot type folding of the 44-nucleotide DNA strand in complex with the already ligated 15-nucleotide RNA strand. The 9DB1 DNAzyme catalyzes the ligation reaction of two RNA strands in the presence of Mg²⁺ or Mn²⁺ cations. However the structure of the 9DB1 was crystalized in its post-catalytical state, making it difficult to establish which is the Michaelis Complex that undergoes catalysis, the correct positioning of the reactants and the reason for the transition state stabilization. Moreover, the role of metal ions necessary for catalysis could not be understood as no ions were found near the linkage site.

In order to unravel the mechanistic features of the 9DB1 DNAzyme we have performed classical molecular dynamics (MD) simulations to simulate the post-catalytical state and to construct the pre-catalytical active state. With the use of Molecular Interaction Potential (CMIP) calculations and classical MD simulations we were able to predict the binding site of the cations and to obtain a catalytically competent structure. We have also made use of the hybrid DFT/MM methodology to perform MD simulations to unravel the most preferred mechanism in terms of free energy which resembles that of polymerases. Moreover, in order to validate our mechanistic proposal biochemical experiments have been performed to validate our theoretically proposed mechanism and cation binding. We were able to confirm that our simulations were able to predict where the cations are placed in the DNAzyme and their role in catalysis. These mechanistic insights could be used to understand how the first crystalized DNAzyme works, to enhance its catalytic power as well as to clarify the role of cations in catalysis.

Figure 1. X-Ray structure of the 9DB1 DNAzyme.

References
Gentlest Ascent Dynamics combined with the Shrinking Dimer Method and Newtonian Dynamics: an efficient way to explore Potential Energy Surface

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We have revisited the Gentlest Ascent Dynamics (GAD) method to find saddle points in multi-dimensional PESs and we propose an implementation of the method by combining it with an optimization-based version of the Steepest Descent method due to Zhang and Du [1]. The GAD-SD algorithm in combination with dissipative Newton dynamics can be seen as a novel “metadynamics” for PESs. The idea is simple, we already know that the solution of the GAD-SD equations of motion represent the fastest (variational) way to reach a saddle point starting from a given position in the multiconfiguration space. Hence, if we are able to concatenate this technique with a dynamics that brings us from a saddle point to a minimum then we could already envision a numerical technique for the exploration of PESs. The GAD-SD equations are

\[
\begin{align*}
\dot{x}_{ci+1} &= \dot{x}_{ci} - \Delta t_i \left[ 1 - 2 w_i w_i^T \right] g(x_i) \\
\dot{w}_{ci+1} &= \dot{w}_{ci} - \Delta t_i \left[ 1 - w_i w_i^T \right] (g(x_{ci+1}) - g(x_i)) / d_i
\end{align*}
\]

(GAD-SD Equations)

where \( x_i \) is the position, \( w_i \) is the control vector, \( g(x_i) \) the gradient vector at \( x_i \), \( d_i \) and \( \Delta t_i \) parameters at the step \( i \), and \( x_{ci} = (1-p_i) x_i + p_i x_{ci+1} \), where \( 0 < p_i < 1 \). These equations are combined with a dissipative Newton equation of the type,

\[
\frac{d^2 x}{dt^2} = -g(x) - \gamma \frac{dx}{dt}
\]

(D-N Equation)

where \( \gamma > 0 \) is a friction coefficient. The friction removes energy from the system until the trajectory reaches the minimum of the PES. The general algorithm works as follows: The dynamics always starts with the GAD-SD Eqs., and the initial conditions for a given trajectory are chosen randomly (both for the initial position and the control vector). As soon as the GAD-SD trajectory reaches a saddle point (which we identify by defining the threshold condition \( |g(x)|^2 < \text{th} \)), the algorithm switches from GAD-SD to dissipative Newtonian dynamics. After a small random boost (\( \Delta x \)) on the position of the trajectory, the Eqs. (GAD-SD) are substituted by Eq. (D-N), and the trajectory starts to fall into a neighbouring (local or global) minimum. Once a minimum is reached (which we identify by checking the two conditions \( \det (\nabla_x \nabla_x^T V(x)) > 0 \) and \( |g(x)|^2 < \text{th} \)), the algorithm switches back from Newtonian to GAD-SD dynamics. A random boost is applied again on the trajectory and after an initial random control vector is chosen, the algorithm continues until all minima and saddle points have been sampled.[2]

References
SAPT Study of the Rg – propylene oxide system, with Rg = He, Ne or Ar

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We present the SAPT study of the most stable, among fourteen different configurations, of ab initio energy of the system Rg – propylene oxide, with Rg = He, Ne or Ar. We have calculated the potential energy surface for these systems at CCSD(T)/aug-cc-pVDZ, with the geometry of propylene oxide frozen, for the most stable one, we optimized the geometry at MP2/aug-cc-pVDZ with all parameters free. For the Helium and Neon, the most stable one is the E\textsubscript{4} configuration (Fig. 1(a)), with distance of center of mass (CM) of Oxygen and CM of CH\textsubscript{2} with Helium of 3.2825Å and for Neon of 3.3066Å. For Argon, the most stable one is the F\textsubscript{3} configuration (Figure 1(b)) with distance of Neon with CM of the face CH\textsubscript{2}–CH\textsubscript{3}–O of 3.5074Å. All calculation was performed using BSSE correction\textsuperscript{1}.

SAPT\textsuperscript{2} is designed to calculate the interaction energy of a dimer, where the interaction energy is expressed as a sum of perturbative corrections, each correction resulting from a different physical effect. This decomposition of the interaction energy into distinct physical components is a unique feature of SAPT which distinguishes this method from the supermolecular approach, which only holds the total interaction energy, the results are presented in Figure 2.

Figure 1. Leading configuration for the Rg – propylene oxide, with Rg = He, Ne or Ar, systems, (a) E\textsubscript{4} configuration used for Helium and Neon, (b) F\textsubscript{3} configuration for Argon.

Figure 2. (a) SAPT decomposition energy for He, (b) for Ne, (c) for Ar

References
Origin-independent decomposition of nonlinear optical properties

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Rational strategies of non-linear optical (NLO) materials benefit from evaluating the partial contributions from individual atoms or groups of atoms to the total NLO response. Accordingly, significant efforts have been done to recover global linear and non-linear optical properties (NLOP) from the additive contributions of molecular fragments. There are several examples in the literature of such type of decompositions for the polarizability ($\alpha$). The problem is that the fully additive atomic contributions obtained are origin-dependent, while the global NLOP is not.

In 1990, Bader [1] showed that in the framework of QTAIM $\alpha$ could be decomposed into two origin-independent terms (intrinsic and charge-transfer). The charge-transfer term typically accounts for 60-90% of the total value of $\alpha$. [2] The intrinsic term can be decomposed into origin-independent atomic contributions, but the individual atomic contributions of the charge-transfer term are not origin-independent. This problem was partially circumvented by Keith,[3] by devising a strategy where the atomic contributions are connectivity-dependent. The practical realization of Keith’s scheme has been recently utilized by several authors, [4] but has also received some recent criticism.[5] Certainly, a better solution to this age-old conundrum is yet to be found.

In this talk we discuss for the first time how the NLOP in general can be exactly decomposed into strictly additive one- and two-center contributions (atoms or groups). [6] The one-center terms are somewhat related to Bader’s intrinsic contributions, whereas the two-center ones naturally account for the interplay of the atoms/groups to enhance or decrease the overall NLOP. The transferability of the terms obtained is explored for a set of molecules, and is compared with that obtained with previous decomposition strategies.

We are confident that this new scheme solves a long-standing riddle and paves the way for truly predictive rational design of NLO materials.

References
Aggregates of Curcuminoid-BF₂ Dyes

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We will present a theoretical investigation of dimers of borondifluoride complexes of curcuminoid derivatives¹. We will show that the absorption character of these complexes is attributed to an intramolecular charge transfer process, stemming from the combination of electron donor (D) and acceptor (A) units in a D-A-D quadrupolar like architecture, in which A is the central dioxaborine ring and D is the terminal aromatic moiety². Three different monomers have been studied (Figure 1).

![Figure 1. The structure of the borondifluoride curcuminoid monomers studied.](image)

We have also investigated several covalent homodimers of these chromophores (Figure 2). Our results reveal that the electronic structure and photophysical properties of these curcuminoid covalent dimers cannot be explained by the conventional Kasha’s model since their π-stacking structure results in significant interchromophoric charge transfer interactions in the excited state manifold. The nature of such interactions has been rationalized in terms of intra and inter chromophoric diabatic states.

![Figure 2. The structure of the closed borondifluoride curcuminoid covalent dimers.](image)

References

Polyfluorinated Dendrimeric Phthalocyanines as Potential Photosensitizer in Photodynamic Therapy: A Computational Study

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Over the past two decades, phthalocyanine compounds have been extensively used as photosensitizers for photodynamic therapy of cancer [1]. Photodynamic therapy is a promising tumor treatment in which visible light is used in conjunction with a non-toxic photosensitizer in an oxygen rich environment [2]. To destroy the living cells, singlet oxygen must be activated by energy transfer mechanism from the photosensitizing compound; phthalocyanines are good candidates for this treatment due to their strong absorption in the red region of the visible spectrum and high singlet oxygen quantum yield [3].

Besides, there may be predominant reasons which may improve the photosensitizer’s singlet oxygen generation efficiency such as solvent effect, electron donating character of substituents and interactions between macrocyclic rings [4]. These parameters influence the triplet state energy, and hence intersystem crossing probability, and ultimately determine phthalocyanine propensity to activate the singlet oxygen. Additionally, they may cause the shift of the Q-Band in electronic spectra.

Time-dependent density functional (TDDFT) approaches allow the extension of the accurate ground state DFT efficiency to excited states [5]. We have thus undertaken the computational task of investigating the optical properties of pentafluorobenzoxy- substituted phthalocyanines [6] as well as of their unsubstituted analogues to foresee whether they might be used as photosensitizers in photodynamic therapy (Figure 1).

![Figure 1. Unsubstituted (R₁) and pentafluorobenzoxy- substituted (R₂) metallophthalocyanines and their free base analogues.](image)

References

Novel Tetrakis 4-(1-(pyridin-4-yl)ethoxyl) Substituted Phthalocyanine Derivatives: Synthesis and DFT/TD-DFT Calculations

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There are many studies focused on reducing the cost of electrocatalyst by different strategies. In last decades, the macrocyclic complexes with metallic inner core and their pyrrolyzed materials have gained attention as electrocatalysts for polymer electrolyte membrane fuel cells[1,2].

In this regard, we recently synthesized novel tetrakis 4-(1-(pyridin-4-yl)ethoxyl) substituted metallophthalocyanines (Pcs) carrying pyridine nitrogen in the N-doped carbon materials with Fe(II), Co(II) and Zn(II) metal center by using the previously used experimental procedure[3] (Figure 1). The substituents on the peripheral positions have chiral centers which result in diastereomeric isomers. Because of difficulties for the isolation of stereoisomers, their spectral properties are usually measured in stereoisomeric mixtures. Therefore, the main focus of this study is to investigate the influence of diastereomeric character of Pcs on their spectral properties.

Time-dependent density functional (TDDFT) approaches which allow us to extend of the accurate ground state DFT efficiency to excited states were employed[4] via oB97XD/6-31G(d). Geometry optimizations of RRRR, RRSS, RSRS, RSSS, SRRR diastereomers were performed. In addition to spectral properties, HOMO-LUMO energy gaps and charge transfer potencies will be discussed. We expect that this approach will be useful to understand the effect of stereochemical differences on the optical properties of Pcs that are candidates to become electrocatalysts.

![Figure 1. Tetrakis 4-(1-(pyridin-4-yl)ethoxyl) substituted metallophthalocyanines.](image_url)

References

From the discovery of benzene in 1825 to the present day, the concept of aromaticity has experienced several revolutions that have fueled the interest of both theoretical and experimental chemists. Very recently, several works[1-3] have highlighted the importance of aromaticity in excited states. Aromaticity is essential to understand and predict many photochemical processes. This renaissance of excited state aromaticity represents an important revolution in the field of aromaticity. Although aromaticity is a property usually linked to the ground state of stable molecules, certain excited states are unquestionably aromatic. This is especially the case of annulenes in the lowest-lying triplet states whose aromaticity follows the 4N Baird rule.[4] In this work, we apply this rule to discuss the aromaticity of all-metal clusters,[5] we discuss the existence of Hückel-Baird hybrid aromatic species,[6] and we show how Clar’s rule can be extended to the lowest-lying triplet excited states of certain polycyclic conjugated hydrocarbons (PCHs).[7] In this last work, we show that the lowest triplet energy is observed for that isomer among a set of isomeric PCHs which in its T1 state hosts the largest number of aromatic cycles, i.e., Clar π-sextets and Baird π-quartets/octets combined (Figure 1).

**Figure 1.** The three central 4nπ-electron units considered in the PCHs studied.

**References**

Non-orthogonal Configuration Interaction for the Calculation of Electronic Couplings

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In singlet fission, the energy of a molecule in one of its excited states is split over two molecules, each then being in their first triplet state (Figure 1) [1]. This process can adequately be described in ensembles of molecules in terms of molecular states. For this purpose, we have developed a non-orthogonal configuration interaction method that allows the description of a molecular crystal, using the (embedded) cluster approach, in terms of many-electron basis functions (MEBFs), each describing a particular electronic state of a molecule in the ensemble. The MEBFs can be constructed as antisymmetrised products of molecular wavefunctions of the MCSCF-type [2,3]. The advantage of this approach is that we can calculate the diabatic excited states in the ensemble, and the coupling between excited states localised on different molecules, such as the electronic coupling matrix element relevant for singlet fission, $\langle S_0 S_1 | H | ^3T^T \rangle$ [1]. In this presentation, an overview of the method will be given, and we show different applications of this method for the calculation of the relevant matrix elements for singlet fission in solids like tetracene and cibalackrot.

![Figure 1](image.png)

\textbf{Figure 1.} The singlet fission process. The rate of energy transfer is governed by the matrix element $\langle S_0 S_1 | H | ^3T^T \rangle$.

\textbf{References}

Towards the understanding of the excited-state decay of Fe(II) complexes

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The use of iron-based metal-organic complexes for the design of optical devices would represent a paramount technological improvement given the natural abundance, low cost and weak toxicity of this metal. Unfortunately, iron-based complexes tend to deactivate at the subpicosecond scale after irradiation due to the population of metal-centred (MC) states. Recent highly remarkable advances have been carried out to increase the absorption capacities [1] and the metal-to-ligand charge-transfer (MLCT) state lifetimes [2], however, the full understanding of the excited-state deactivation of these species is not completely achieved from a theoretical point of view. The main reason is the large size of the systems, which often leads to tedious and demanding theoretical treatments hampering a satisfactory mapping of the relevant potential energy surfaces (PESs) involved in the photoresponse. This problem can be however gradually solved making use of efficient methodologies for the excited-state modelling in conjunction with the growing computational power of modern computers.

In this contribution we present [3], for the first time, the full mapping of the triplet PESs of a family of Fe-NHC compounds presenting \textit{facial} (\textit{fac}) and \textit{meridional} (\textit{mer}) isomerism. The photochemical landscapes have been built computing the minimum energy paths (MEPs) of the triplet states, which have allowed the connexion between the different minima that mediate the excited-state decay. Thereby, the relative competition between the different photochemical routes has been assessed, identifying the Fe-N bond stretching as the main coordinate driving the decay, and discarding any relevant contribution of the quintet state. A striking influence of the \textit{fac}/\textit{mer} isomerism in the topology of the triplet PESs is unveiled, predicting significant differences in the excited-state lifetimes of the two isomers.

References

A novel caspase-1 mechanism of reaction

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Caspase-1 is an enzyme that catalyzes the hydrolysis of the proinflammatory cytokine Interleukin 1-beta into its active form. Caspase-1 is involved in inflammatory and apoptotic process and, for this reason, a detailed molecular description of the caspase-1 mechanism has a great pharmacological interest. In spite of this, there are no clear experimental evidences that can support the mechanism proposed, so far for the acylation step[1,2], based in a mechanism previously reported for the papain family, another class of cysteine proteases[3]. Whose active site differs from that of caspase-1.

We have performed a study using a Constant pH Molecular Dynamic Simulation (CpHMDS)[4] in order to determine the most probable protonation state of Cys285 and His237 in the active site of the enzyme. We found that in the Michaelis complex these residues should be found in its neutral state. The mechanism accepted for the acylation step involves the cysteine deprotonation by the δ-nitrogen of histidine. However these residues are separated by more than 5 Å in the 29 available crystals in the Protein Data Bank for the caspase-1 enzyme, preventing the proton transfer between them. In contrast, we found that Cys285 can be deprotonated by the oxygen in the carbonyl backbone of the aspartate of the peptide substrate, which facilitates the formation of the carbon sulfur bond in the acylation process (see Figure 1).

![Acylation step proposed for caspase-1.](image)

References


CO₂ Adsorption on TiO₂ Surfaces Promoted by Potassium

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Carbon dioxide is one of the main chemicals responsible for the greenhouse effect, thus contributing to the global warming. A way to lower CO₂ emissions is to deploy it as recourse in catalytic reactions using soft conditions. However, it is well-known that CO₂ is very stable and shows low reactivity as the first step in any chemical transformation involves a bending of the O=C=O bond, i.e. an activation. Alkali metals act as promoters of heterogeneous catalysts in a very wide range of important chemical processes in which CO₂ participates; notorious examples are the water-gas shift (WGS) reaction or alcohol synthesis. In this work we use potassium atoms in order to increase the catalytic activity of catalysts previously developed by our group [1], based on TiO₂ as support, as well as the CO₂ activation.

Single potassium atom deposition on TiO₂(110) results in reduction of the substrate and the formation of loosely bonded potassium species which can move easily on the oxide surface, in agreement with experimental results [2], to eventually promote catalytic activity everywhere. The results of density functional calculations show a large adsorption energy (~3.6 eV) with a small barrier (~0.25 eV) for diffusion on the oxide surface (Figure 1a). Moreover, simulations of different potassium coverages indicate a decrease of adsorption energy as potassium coverage increases, and point to a limiting value for substrate reduction.

Deposition of Cu atoms shows a similar reduction of the substrate, with high adsorption energy, although lower than that of potassium (~2.45 eV). Using a model of catalyst consisting of a copper cluster, Cu₈, supported on TiO₂(110) we study the effect of the promoter on the CO₂ adsorption. Our DFT calculations reveal that CO₂ molecule anchors and gets activated only in the presence of potassium (Figure 1c).

References
DFT calculations and Structure–Activity Relationship research of Pyrazoloaxizin-2-Ones and Pyrazoloaxizin-2-Thiones: activity evaluation

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In the present work, we are interested in the qualitative study of a series of 14 pyrazolooxazine derivatives to research the structure-activity relationship.

The DFT / B3LYP // 6-311 ++ G (d, p) type calculations are performed in the gas phase in order to determine and analyze the equilibrium geometries of the pyrazolooxazine derivatives. The principle of HSAB (Hard and Soft Acids and Bases) was first used to determine the centers of activity of a molecule and the effects of substitution on its systems. Then, the multi-parameter optimization (MPO) methods and the study of the structure-activity properties were applied to the compounds using the HyperChem 8.0.6 software. The results of the analysis frontier orbitals show that pyrazolooxazine-2-thiones, which have a HOMO-LUMO energy gap (2.961 eV) lower than that of pyrazolooxazine-2-ones (3.211 eV), are therefore the most reactive and they have a nucleophilic behavior. The highest absolute hydration energy is that of the compound (f\textsubscript{1}) in the presence of the 2-ethylthiophene group (6,013 kcal / mol) and the compound (g\textsubscript{2}) in the presence of the phenyl group (7,253 kcal / mol). The LogP values of the pyrazolooxazine derivatives show that these compounds will have a low permeability across the cell membrane. Finally, the compound (f\textsubscript{1}) has the highest LipE value (4.196) for the data set, so it is considered the most optimal compound.

Keywords: QSAR, DFT, HSAB Principle, HyperChem.
DFT study on the radical scavenging activity of thiamine

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Imbalance of oxygen radicals, such as aroxyl (·OR) and peroxyl (·OOR) radicals, is related to chemical impairment of proteins, nucleic acids and other biomolecules. The concentration of free radicals in the organism is regulated by specific enzymes but also by small molecules like glutathione and some vitamins. The present works provides a detailed study of the radical scavenging capacity of vitamin B1 or thiamine.

The reactions between thiamine and methoxy (·OCH₃), methyl peroxy (·OOCH₃) and hydroperoxyl (·OOH) radicals have been calculated. Three possible reaction mechanisms were considered for each radical, namely the Single Electron Transfer, the Radical Adduct Formation, and the Hydrogen Atom Transfer, in aqueous and lipid environment.

The thermodynamic and kinetic feasibility of each reaction pathway were calculated with the M05-2X functional [1] and the 6-311+G(d,p) basis set in combination with the SMD solvent model [2] to account for effects of the aqueous or lipidic (modelled with pentyl ethanoate) environments. These data were used to build a model of the macroscopic antioxidant capacity of thiamine from which the main reaction pathways were identified.

References
Theoretical Kinetic Study of the Keto−Enol Tautomerism Propen-2-ol + HO$_2$ ↔ Acetone + HO$_2$. Implications in the Combustion of 2-Butanol

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The keto-enol tautomerism is an important process in the pyrolysis and combustion of biofuels, as well as in atmospheric systems. We conducted multi-structural torsional variational transition state theory calculations [1] of the keto−enol tautomerism propen-2-ol ↔ acetone, which may occur unimolecularly or catalysed by radicals like HO$_2$ and H. Our goal is to update the kinetic models of important biofuels in which this tautomerism may play a role.

To ascertain the role of the studied reactions, we implement our new kinetic information into previously developed kinetic models for the pyrolysis and combustion of butanol isomers, and perform simulations of the combustion and pyrolysis processes by using ANSYS CHEMKIN-PRO 18.1 software. [2]

In this work, we investigated the HO$_2$-catalyzed tautomerism propen-2-ol + HO$_2$ ↔ acetone + HO$_2$ and compared its role, in the combustion of the 2-butanol isomer, to that of the unimolecular process propen-2-ol ↔ acetone and other reactions consuming propen-2-ol. The radical HO$_2$ promotes a double hydrogen atom transfer reaction through a concerted mechanism, significantly reducing the enthalpy barrier to the keto-enol process to 7.2 kcal mol$^{-1}$, which is 44.9 kcal mol$^{-1}$ lower than that to the unimolecular process. [3]

We ran premixed laminar flame, perfectly stirred reactor, and closed batch reactor simulations using a recently updated version [3] of the kinetic model for butanol isomers developed by Sarathy et al., [4] hereafter referred to as former model, to simulate the combustion of 2-butanol. The same simulations were also run with an updated model which resulted from the implementation of our calculated rate constant for propen-2-ol + HO$_2$ ↔ acetone + HO$_2$ into the former one, which instead includes the HO$_2$-assisted kinetic information by means of an analogy to the reaction ethenol + HO$_2$ ↔ acetaldehyde + HO$_2$. Results of species concentration profiles, flame speeds, and ignition delay times obtained with both kinetic models were compared. The updated model predicts a slightly slower consumption of propen-2-ol and a lower yield of acetone than the former model. This is due to the lower magnitude of the rate constant obtained in our calculations than those from the analogy. However, despite the pronounced kinetic enhancement exerted by the HO$_2$ radical, the tautomerism propen-2-ol + HO$_2$ ↔ acetone + HO$_2$ is not as prominent in the consumption of propen-2-ol as the reactions propen-2-ol ↔ acetone, propen-2-ol + HCOOH ↔ acetone + HCOOH, and H-addition into the double bond. Both kinetic models predict very similar flame speeds and ignition delay times.

References

Theoretical Kinetic Study of the Keto-Enol Tautomerism Propen-2-ol + H ↔Acetone + H: Pressure Effects and Implications in the Pyrolysis and Combustion of tert- and 2-butanol

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Alternative fuels, including alcohols, are considered promising because they can be derived from biological material and their physicochemical properties are compatible with the requirements of modern engines [1] preferably from renewable sources, include alcohols with up to five or even more carbon atoms. They are considered promising because they can be derived from biological matter via established and new processes. In addition, many of their physical-chemical properties are compatible with the requirements of modern engines, which make them attractive either as replacements for fossil fuels or as fuel additives. Indeed, alcohol fuels have been used since the early years of automobile production, particularly in Brazil, where ethanol has a long history of use as an automobile fuel. Recently, increasing attention has been paid to the use of non-petroleum-based fuels made from biological sources, including alcohols (predominantly ethanol. However, the chemistry of alcohols, like that of butanols, is not fully understood. In this work, we carried out a theoretical kinetic study of the H-assisted propen-2-ol tautomerism, which was found to proceed in two steps. The first step involves H radical addition to the double bond of the propen-2-ol to form an intermediate radical, i-C₃H₅OH+H⇒CH₃ĊOHCH₃. In the second step, the H atom of the O−H bond of the intermediate is released and acetone is formed, CH₃ĊOHCH₃⇒CH₃COCH₃+H. In our study, the forward and reverse rate constants of both steps were computed. Ab initio calculations were performed at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level. Rate constants were determined taking into account variational principles, multistructural torsional anharmonicity, and pressure effects.

Current kinetic models of butanol isomers include some of the H-assisted tautomerism reactions using kinetic data of analogies. Therefore, to investigate the effect of the computed rate constants, the kinetic model developed by Sarathy et al. [2] for butanol isomers and previously updated by Grajales-González et al., [3] hereafter called former model, was further upgraded, and then called henceforth updated model, to carry out pyrolysis and oxidation simulations of tert- and 2-butanol isomers. Pyrolysis closed batch reactor simulations with both models do not show any essential differences in the concentration profiles of key species in virtue of the persistent low concentration of H radicals that prevents the first step of the studied tautomerism from happening. For oxidation closed batch reactor simulations, same concentration profiles were obtained; nonetheless, scarcity of differences was attributed to the abundant H radicals occurrence once all propen-2-ol has been consumed by other reactions, such as the unimolecular tautomerism, which becomes the main source of acetone. On the contrary, in premixed flame simulations, the concentration of H radicals is substantially high while propen-2-ol is still available; as a result, this alcohol is the main channel to the intermediate radical formation. With the updated model, the concentration of this radical turns out to increase and decrease during the oxidation of tert- and 2-butanol, respectively; however, due to the low concentration of this species, the changes linked to related substances are subtle.

The computed rate constants helped to improve the existing kinetic models and give new insights into the chemistry of different species involved in the overall propen-2-ol tautomerism.

References

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Isotopic fractionation is a widely used to explore environmental processes. For instance, the relative $^{13}\text{C}/^{12}\text{C}$ and $^{2}\text{D}/^{1}\text{H}$ ratios can be used to identify the source of methane, an abundant atmospheric gas with several sources, each with a unique isotopic fingerprint. One source is hydrogenotrophic methanogenesis, an archaeal process whereby hydrogen and carbon dioxide are converted to methane in a process involving seven reaction intermediates and nine different enzymes. My experimental collaborators (Dr. Itay Halevy, Department of Earth and Planetary Sciences, Weizmann Institute of Science) are working on a model to understand how each step affects the overall isotopic fractionation. For this purpose, they need equilibrium isotopic fractionations calculated as part of this project, used in conjunction with some assumptions for the kinetic isotopic fractionations.

Isotopic fractionation can be calculated using the vibrational frequencies of each species:

\[
\alpha = \frac{\beta_{\text{CH}_4}}{\beta_{\text{CO}_2}}; \quad \beta = \frac{Q_H}{Q_L} = \frac{\sigma_H}{\sigma_L}, \quad \prod_{i=1}^{3N-6} \frac{u_{H_i}}{u_{L_i}} \cdot \frac{\exp\left(-\frac{u_{H_i}}{2}\right)}{\exp\left(-\frac{u_{L_i}}{2}\right)} \cdot \frac{1 - \exp\left(-u_{L_i}\right)}{1 - \exp\left(-u_{H_i}\right)}
\]

where $N$ is the number of atoms, $\sigma$ is the rotational symmetry number, $H$ and $L$ denote the heavy and light isotopes, respectively, and $u_i = \frac{h\omega_i}{k_B T}$. [1] In this study, density functional theory is used to estimate the isotopic fractionations. While the reactant and product molecules are small, the reaction proceeds through several intermediates that are much larger in size, making DFT a reasonable compromised between cost and accuracy. In addition to estimating the fractionations, key factors influencing the accuracy of the calculations are considered.

References

Location of Optimal Bond Breaking Points on Potential Energy Surfaces.

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The reaction path of a mechanically induced chemical transformation changes under stress. It is well established that the force-induced structural changes of minima and saddle points, can be described by a Newton Trajectory (NT), which describes the movement of the stationary points on the original or stress-free potential energy surface. Given a reactive molecular system, a well-fitted pulling direction, and a sufficiently large value of the force, the minimum configuration of the reactant and the saddle point configuration of a transition state collapse at a point on the corresponding NT trajectory. This point is called barrier breakdown point or bond breaking point (BBP). The Hessian matrix at the BBP has an eigenvector with eigenvalue zero, \( \det H(x) = 0 \), being \( H(x) \) the Hessian matrix at a BBP point. The gradient vector and its norm at this point indicate which force (both in magnitude and direction) should be applied to the system to induce the reaction in a barrierless process. Within the manifold of BBPs, there exist optimal BBPs indicating what is the optimal pulling direction and what is the minimal magnitude of the force to be applied for a given mechanochemical transformation. In this optimal BBP the eigenvector of null eigenvalue coincides with the gradient vector, thus this point is also on a Gradient Extremal [1]. Thus, the gradient vector is an eigenvector of the Hessian matrix of eigenvalue zero,

\[
\begin{vmatrix}
H(x)g(x)[g(x)]^\top - 0 \\
g(x) \neq 0
\end{vmatrix}
\]  
\text{(Optimal BBP Condition)}

where \( g(x) \) is the gradient vector at BBP point. Since these special points are very important in the context of mechanochemistry and catalysis, it is crucial to develop efficient algorithms for their location. We have proposed a Gauss-Newton restricted step algorithm [2] that is based on the minimization of a positively defined function, the so-called \( \sigma \)-function,

\[
\sigma(x) = \frac{g^T(x)H^2(x)g(x)}{g^T(x)g(x)} = s^T(x)s(x) 
\]  
\text{(Sigma Function)}

where \( s(x) = H(x)g(x)||g(x)||^2 \) to locate these type of points. The function \( \sigma(x) \) is a sum of squares of nonlinear functions, \( s(x) \); thus, it is a non-negative function. It is clear that a minimum \( x_{\text{min}} \) of the function \( \sigma(x) \) for which \( \sigma(x_{\text{min}}) = 0 \) is a desired solution since this can only arise if \( x_{\text{min}} \) satisfies \( s(x_{\text{min}}) = 0 \), which is the Optimal BBP Condition and thus \( x_{\text{min}} \) is the optimal BBP. The algorithm shows stability and efficiency during the location process of optimal BBPs.

References

Simple bond patterns predict Diels–Alder selectivity of empty fullerenes

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Cycloaddition reactions play an important role in the functionalization of empty and endohedral fullerenes. In particular, Diels–Alder (DA) cycloadditions are a powerful tool for the introduction of a six-membered ring to a fullerene cage enabling the preparation of many derivatives with applications in material and biological sciences[1,2].

Since there exist different types of C–C bonds on a fullerene cage, regioselectivity is commonly exhibited. Taking C$_{60}$ as an example, the DA addition prefers to take place on the [6,6] bonds over the [5,6] ones, as revealed by experiments and computations. For larger and less symmetrical cages, a great number of possible regioadducts may be formed. To understand the DA selectivity of fullerenes, various models as distortion/interaction and several descriptors based on different arguments such as bond lengths, pyramidalization angles and HOMO-LUMO interactions have been commonly applied, but there are no clear and universal rules that allow making reliable predictions[3].

In this work[4], we present a systematic study on the DA additions to empty fullerenes from C$_{60}$ to C$_{180}$. We found that activation barriers and reaction energies obtained from DFT calculations correlate well with each other. The latter energies can be well reproduced by a Hückel-based simple model[5,6], which indicates that the π electronic effect is the key factor governing the relative stability of cycloadducts. We further show that DA cycloadditions to empty fullerenes occur preferentially at a few simple bond patterns, which can be used as a visual guide for approximate prediction of the DA reactive sites. Moreover, we suggest two quantitative descriptors that have a direct chemical interpretation in terms of bond forming and breaking ability and in terms of local aromaticity. Based on the latter criterion, the bond pattern preference can be naturally understood.

References

Biomass fractionation by ionic liquids

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The problems derived from the use of oil as raw material for obtaining the chemical compounds basic for our economy has boosted the creation of the so-called biorefineries, in which biomass is used as raw material instead of fossil fuels.

The most abundant biomass, the lignocellulosic biomass (LCB), is composed of cellulose, hemicellulose and lignin, which can be transformed into a set of chemical products similar to those derived from oil \cite{1}. The first step for a successful processing of the LCB is its dissolution, in order to separating the three polymers (fractionation). Ionic liquids (ILs), particularly imidazolium-based ILs, have successfully been employed for the dissolution of LCB as a more sustainable alternative to the most commonly used fractioning processes. Besides, thanks to the easy tuneability of their physicochemical properties, it is possible to adequate their chemical structure to an specific application.

The solvent properties of ILs are based on the Coulomb and dispersion interactions they establish with both polar and non-polar solutes \cite{2}. Accordingly, experimental data suggests that the ability of the IL to establish hidrogen bonds and the nature of the anion is a determining factor of the ability of the solvent to dissolve the LCB \cite{1,3}. The thorough understanding of the solvation mechanism of BLC is fundamental for optimizing the IL-based fractionation process, a basic step if the widespread use of BLC as raw material is aimed.

This work addresses the solvation of cellulose and lignin in methylimidazolium chloride (MIMCl), by means of ab initio molecular dynamic methods. CP2K calculations are carried out to describe the solvation patterns and affinity of the IL for the biomass, in order to identifying the basic properties that define the solvation ability of the material. The difference between cellulose and lignin model systems is addressed, as the main objective of the fractionation process is to separate both polymers. This data provides not only the knowledge for suggesting new materials with improved properties, but also the necessary reference data to design reliable calculation procedures at a smaller computational cost.

References

Transition metal complexes to activate or insert alkynyl compounds

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Gold(I) complexes are very efficient catalysts for the electrophilic activation of alkynes under homogeneous conditions[1]. Alkynes are the preferred gold(I) target even in presence of oxygen-containing nucleophiles, which, in turn, readily attack gold-activated alkynes to form new C-O bonds. When several oxygen-nucleophiles are simultaneously present in the reaction media competitive additions to the C≡C triple bond are possible. In this work we consider the simplest alkyne, acetylene, to comprehensively study all reaction routes with water and the cetal 2,2-dimethyl-1,3-dioxolane (DMDO), as a representative of OR nucleophiles, activated by [Au(PH₃)]⁺. If water wins an alcohol or, eventually, acetaldehyde may form, whereas if the cetal wins the first round a new net of reaction paths becomes available.

On the other hand, the insertion of unsaturated molecules into transition metal-alkoxide bonds requires a vacant site or a labile ligand in the metal sphere to favour the coordination of the substrate adjacent to the bond that undergoes the insertion. However, the presence of lone pairs of electrons on the oxygen atom and the high polarity of the M-O bond open the possibility of a nucleophilic attack on the uncoordinated substrate by the undissociated alkoxo ligand. Actually, it has been experimentally checked that [Re(OR)(CO)₃(bipy)] (R = Me, Et, ‘But; bipy = 2,2’-bipyridine) complexes are able to react with activated alkynes such as dimethyl acetylenedicarboxylate, DMAD, yielding the insertion of the alkyne into the Re-O bond[2]. In this work the reaction of [Re(OR)(CO)₃(bipy)] (R = Me) with the alkyne HC≡COCOMe, HMAD, is theoretically studied. Among three potential final species, thermodynamic stability clearly points to the insertion one as the preferred product.

References
Rationalization of the Activity of the Lactone form of Topotecan towards the DNA/TopoI Complex

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Topotecan (TPT) is a non-toxic anti-cancer drug characterized by a pH dependent lactone/carboxylic acid equilibrium.¹² TPT acts on the covalently bonded DNA/Topoisomerase I (DNA/TopoI) complex by intercalating between two DNA bases at the active site, which turns TopoI into a DNA-damaging agent and inhibits supercoil relaxation. Although only the lactone form of the drug is active and efficiently inhibits TopoI, both forms are found to be good binders that are co-crystalized at the same location within the DNA/Topo1 complex. To gain further insights into the pH dependent activity of TPT, the differences between two TPT:DNA/TopoI complexes presenting either the lactone (acidic pH) or carboxylic (basic pH) form are studied by means of molecular dynamics together with interaction energy using QM/MM method and topological analysis. We identify two specific amino acid residues which have direct relationship with the activity of the drug: i.e., lysine 532 (K532) and asparagine 722 (N722). K532 forms a stable hydrogen bond bridge between TPT and DNA only when the drug is in its active lactone form. The presence of the active drug triggers the formation of a stable network between protein residue N722 and DNA increasing the binding affinity of DNA towards TopoI and further slowing down the release of DNA. Overall, our results yield a clear understanding of the activity of TPT-like class of molecules and can help future design of new anti-cancer drugs targeting Topoisomerase enzymes.³

References


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Kohn–Sham density functional theory (KS-DFT)[1] is the most widely used method for the electronic structure calculations of systems of interest in both chemistry and solid-state physics, but its applicability to very large systems is limited by its scaling with system size ($N^2$ in the best case, $N^3$ usually). Orbital-free density functional theory (OF-DFT)[2,3] represents a very attractive alternative to KS-DFT for large systems because of its simple implementation and an almost linear scaling with system size ($N$ in the best case, $N\log N$ usually), but its accuracy is still lacking for most of chemistry applications.

In this context, we will show that the quantal density functional theory (Q-DFT) equations of the density amplitude[4-6] represent an important link between KS-DFT and OF-DFT, and they can be used to map the complex interacting system to a fictitious one of non-interacting bosons with the same density (either in its ground or some convenient excited state). Since the non-interacting system is composed of bosons, it is completely described with just one orbital—the square root of the total density i.e., the density amplitude—and the KS equations reduce to just one equation, with important similarities to the one of OF-DFT. The treatment of the kinetic energy of the non-interacting system and of the exchange-correlation potential in Q-DFT and OF-DFT, however, are crucially different. In this study we aim to explain those differences using accurate atomic densities[7,8]. The ultimate goal of this project is to use information from Q-DFT to improve the kinetic energy functionals used in OF-DFT: an important step to bridge the gap in accuracy between OF-DFT and KS-DFT.

References
Session 1 (Tuesday)

Computational Study of the Affinity of Polychlorinated Dibenzofurans for Graphene Surface

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Polychlorinated dibenzofurans exhibit a high degree of toxicity, and are frequently included within the dioxin-like compounds, a well-known family of pollutants. A great effort is currently done to develop efficient methods of detection and extraction of these compounds from the environment. The first step is to look for proper materials that exhibit a large affinity for these dioxin-like compounds in order to immobilize them for further detection/extraction. Recent experimental studies using graphene have shown this material may be a good alternative to activated carbon for elimination of dioxins. Moreover, the unique properties of graphene and graphene related materials make them useful also for chemical detection. In this study, quantum chemical calculations were carried out to investigate the stability of different polychlorinated dibenzofurans adsorbed on a model graphene sheet formed by ninety-six carbon atoms. The calculations were done using Density Functional Theory (DFT), with the exchange-correlation functional M06-2X and the Pople basis set 6-311G+(d). An interaction energy decomposition analysis was performed using a recent approach based on electron deformation densities in order to characterize the nature of the interaction. Finally, the results obtained for graphene were confronted with those obtained for white graphene, a structure where carbon is replaced by boron and nitrogen. White graphene could be a promising material for elimination of hydrocarbon pollutants due to the large affinity of these molecules for its surface.

FIG. 1. 2,3,7,8-tetrachlorodibenzofuran (TCDF).

FIG. 2. Graphene sheet model (C96).

References:
Molecular dynamics of hTK1 – a first step on the way to understand the enzyme action

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Human thymidine kinase 1 (hTK1) is crucial for salvage pathway phosphorylation of thymidine. The enzyme, found especially in dividing cells, maintains sufficient dTTP for DNA replication.[1] Despite its importance, the mechanistic details of its reactions still remain a question. Mixed Quantum Mechanics and Molecular Mechanics (QM/MM) calculations could be a method of choice to provide answers.

In order to conduct reliable QM/MM studies, a realistic 3D structure of the enzyme has to be constructed. Usually this is achieved with the use of experimentally-determined data, but currently available hTK1 structures are not suitable for reaction mechanism studies. Among other problems, there is no structure containing proper substrates of the reaction in the enzyme, which is essential for QM/MM studies. Usually, this could be overcome with docking, but hTK1 is changing its quaternary structure upon binding substrates[2] (i.e. “opening”) and only closed-forms of enzyme, unable to fit both substrates, were experimentally observed and reported. This last trait makes it impossible to dock the substrates correctly without prior preparation.

In this work, we obtained hTK1 in its active, opened form using over 500 ns Molecular Dynamics (MD) simulations provided by GROMACS software with AMBER99SB*-ILDN all atom force field and the TIP3P water model and ions (physiological conditions) in cubic box. In order to have full enzyme structure, homological modeling and some substrate overlapping were required – these were prepared with Maestro (Schrodinger) software.

During the simulations we observed a set of structural changes in the quaternary structure, leading to an open state of an enzyme. The thorough analysis of results, comparing with literature reports and control simulations of hTK1 docked with closed-form promoting substrates was conducted. These allow us to state, that the structure is now ready for further QM/MM studies and we managed to obtain the opened form of the enzyme. Moreover, the changes observed during the simulations already provide us with some insight into the enzyme operating, especially the active site binding scheme and the most important amino acids that will be involved in the enzymatic reaction.

Acknowledgements

The calculations were performed in GRNET during PRACE SoHPC 2016. The replicas are performed with PL-Grid Infrastructure grant (S.M) and with the support of the Polish National Science Center (NCN) under the Grant No. UMO-2014/14/A/ST4/00405 (J.R.)

References

Calibration of TD-DFT methods to simulate the emission spectra of organoborans in the Red-NIR region

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Organoborans constitute an enormous family of chemicals with interesting luminescent applications either in optoelectronics or in the biological/biomedical field [1,2]. Among them, the group of derivatives of the 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, BODIPY, has achieved great popularity due to their interesting spectroscopic properties, namely, they usually exhibit strong absorption in the UV range as well as sharp emission bands what, in addition to their small size and ease of structure modification, provides them with powerful capabilities to produce materials of use in organic electronics [1] and bio-fields as for instance, probes for bioimaging [2].

In this research, the attention is focused on those BODIPYs emitting in the red-NIR region. Red as well as NIR emitters are highly emissive, specially in solution and find interesting applications in a large assortment of fields.

Thus, the main objective of the current investigation is to perform a calibration of TD-DFT methods addressing the simulation of the emission spectrum in solution of red-NIR emitting BODIPYs. To allow for further structural variability, organoborans showing other patterns of boron complexation are included. Therefore, the spectral range (600.870) nm has been divided in 9 segments of 20 nm but for the region >800 nm which is considered as only one of them. For each segment 5 emission wavelengths have been considered belonging to 33 organoborans. 8 solvents covering a diverse polarity range have been taken into account, namely, c-hexane, toluene, C₂H₂Cl₂, CHCl₃, dibutyl ether, THF, HOCH₃ and NCCH₃.

As concerns the theoretical methods, the selected density functionals are reported in Table 1. They are implementing the 6-31G(d,p) basis set along with others that are going to be tested as 6-31+G(d,p) and 6-311G(d,p). Thus, as preliminary results, first simulations of the emission spectrum with M06-2X/6-31G(d,p) approximation yield systematic overestimations of the experimental values around 20-25%. In addition, some low performance behavior has been observed for the couple of density functionals N12/N12SX that requires further testing.

<table>
<thead>
<tr>
<th>NGA</th>
<th>Hybrid</th>
<th>Range separated hybrid</th>
<th>+ Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N12</td>
<td>M06-2X, M08-HX</td>
<td>N12SX, LC-wHPBE</td>
<td>wB97XD</td>
</tr>
<tr>
<td></td>
<td>PBE1PBE, HSEh1PBE</td>
<td>CAM-B3LYP, wB97X</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Selected density functionals.

References
Insights into the role of Aryl-Co(III) intermediates in C–H Activation: from Alkyne Annulations to Aryl-Co(III) Masked-Carbenes

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The selective annulation reaction of alkynes with substrates containing inert C–H bonds using cobalt as catalyst is currently a topic attracting significant interest. However, the mechanism of this transformation was poorly understood. Recently it has been provided crystallographic evidences of an organometallic aryl-Co(III) intermediate proposed in 8-aminoquinoline-directed Co-catalyzed C–H activation processes.[1] Subsequent insights obtained from the application of our new organometallic aryl-Co(III) compounds in alkyne annulation reactions are also disclosed. We have provided evidence from DFT studies that indicates that a mechanism involving an organometallic aryl-Co(III)-alkynyl intermediate species is preferred for terminal alkynes, in contrast to the generally accepted migratory insertion pathway [1).

The synthesis of a family of aryl-Co(III)-carboxylate complexes and their reactivity with ethyl diazoacetate have been also recently achieved. [2,3] Theoretical evidence of unique C-metalated aryl-Co(III) enolate intermediates is provided, unravelling a carboxylate-assisted formation of aryl-Co(III) masked-carbenes.[2,3] DFT results complete agree with the subsequent crystallographic characterization. Moreover, additional evidence for an unprecedented Co(III)-mediated intramolecular SN2-type C–C bond formation in which the carboxylate moiety acts as a relay is disclosed. The key role of Lewis acids unveiling a Li-mediated carboxylate activation that triggers the C–O bond cleavage/C–C bond formation event. This novel strategy is key to tame the hot reactivity of a metastable Co(III)-carbene and elicit C–C coupling products in a productive manner.

References
Electronic analysis of DMIT and DMIO complexes of Sn(IV) and Sb(V)

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Over the last few decades, dithiolate ligands and its metal complexes have been studied extensively. The 1,3-dithiole-2-thione-4,5-dithiolate (dmit) and 1,3-dithiole-2-one-4,5-dithiolato (dmio) have a especial highlight due to theirs characteristics of conductivity, ferromagnetism and nonlinear optic [1]. Although, the spectroscopy of the metal complexes of these ligands is not well described in literature as IR-Raman and UV-Vis spectra being the main features found in experimental reports [2]. A more advanced study of the electronic structure has not yet been done. Therefore, our objective is to enhance the comprehension of $[\text{Sb}(L)_3]^{-1}$ and $[\text{Sn}(L)_2]^{-2}$ complexes structure using dmit and dmio ligands and the interaction between the metal cation and the ligand, by applying the Energy Decomposition analysis (EDA), Quantum Theory of Atoms In Molecules (QTAIM) and Natural band Orbital (NBO).

Theoretical study was performed with the density functional theory (DFT) method CAM-B3LYP/6-311G(d,p) for light elements (C, S, O) and ECP-SBKJC basis set for Sb and Sn atoms, using Gaussian 09 for optimization, GAMESS, for EDA and NBO, and MultiWFN for QTAIM analysis. The EDA was made to describe the electrostatic and covalent components of the metal-ligand interaction, aligned with the QTAIM analysis that could show the critical points between bonds and rings presented in the molecule. The NBO analysis allowed evaluation the hybridization and donor-acceptor energy of the metal-ligand interaction.

The Sb⁵⁺ and Sn⁴⁺ forms a charge octahedral complex with dmit and dmio, with a T form for antimony and tin complex and a Y form for the tin complex as well. EDA, associating the metal ion and two ligand with another ligand, shows a predominant covalent interaction in all cases, besides the electrostatic component of the metal-ligand interaction was unfavourable, mainly due to high Pauli repulsion term. The QTAIM calculation shows a good analysis of all interaction of the complex, presenting the bond’s energy that corroborate with experimental data.

![Figure 1. QTAIM analysis of $[\text{Sb(dmit)}],^{-1}$](image)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Gap Energy (eV)</th>
<th>Orbital Híbrizdad</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMIT</td>
<td>-4.38</td>
<td>Sb($s^{16.27%}$, $p^{51.48%}$; $d^{32.19%}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S($s^{9.02%}$, $p^{99.94%}$)</td>
</tr>
<tr>
<td>DMIO</td>
<td>-4.66</td>
<td>Sb($s^{16.27%}$, $p^{51.48%}$; $d^{32.19%}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S($s^{9.02%}$, $p^{99.94%}$)</td>
</tr>
</tbody>
</table>

Table 1. Hibridization and gap energy values of Sb complex from NBO analysis

References

Topology as a tool for constructing energy models

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Theoretical chemistry is nowadays routinely used for the development of rigorous models and concepts that facilitate the understanding, design and control of novel processes. Its main goal is understanding the relationship between the quantum structure and the macroscopic properties of matter. This holds the key for the development of the rational design of compounds addressing a tag property.[1] The link between the electronic structure of a system and its energy is the main bridge when trying to explain macroscopic properties from their geometrical structure, as energy enables to understand the behavior of systems against changes in thermodynamical properties.

Within this context, in this work, we propose a topological energy model that accounts for interactions between electron pairs. As we are interested in electron pairs we used the Electron Localization Function (ELF) topology and coupled it with Interacting Quantum Atoms (IQA) energy partition for obtaining a real space picture of different energy terms.[2] In particular, our model presents two classical terms: kinetic and electrostatic, and an exchange-correlation one. Interestingly, we see that the ELF-IQA energetic partition recovers very well the DFT-computed system energy and that energy terms present a similar behaviour as those proposed in the Bond Charge Model (BCM) [3]. Noteworthy, a very good agreement of kinetic term against \(1/R^2\) and electrostatic one against \(1/R\) was found, exchange-correlation contribution being almost negligible, see Figure 1. This paves the way towards the first construction of an energy model and force fields based on topology which recovers classical models while enabling to connect them to quantum mechanics and thus improve them progressively.

Figure 1. ELF basins and energy model terms for ethane molecule.

References

Accurate CCSD(T) and SAPT Comparisons of R-X⋯π Interactions to other Common Noncovalent Binding Motifs with Applications to Protein-Ligand Complexes

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Bonds involving an aromatic moiety as an acceptor, otherwise known as R-X⋯π interactions, have increasingly been recognized as being important in materials and in protein–ligand complexes. [1,2] These types of interactions have been the subject of many recent investigations, but little is known about the ways in which the strengths of R-X⋯π interactions vary as a function of the relative geometries of the interacting pairs. Here we discuss accurate CCSD(T) and SAPT2+3dMP2 computations investigating the potential energy landscapes for systems of HBr and NCBr complexed with benzene, fluorobenzene, and toluene. Similar calculations were used for R-H⋯π, halogen bonding, and hydrogen bonding complexes, and are also discussed in order to put the energetic and directional characteristics of R-X⋯π interaction into a larger context. The strength, character, and directionality of R-X⋯π interaction found in protein-ligand complexes derived from the protein data bank are also discussed.[3]

It is found that R-X⋯π interactions can be comparable in strength to conventional halogen bonds, hydrogen bonds, and R-H⋯π interactions. In terms of the dependence of these interactions on geometric parameters, here it is found that only the separation between the complexed molecules have a strong effect on interaction strength while other geometric parameters, such as tilting and shifting R-X⋯π donor relative to the aromatic plane, affect these interactions only mildly. Importantly, it is found that the C$_{6v}$ (T-shaped) configuration is not the global minimum for any of the dimers investigated.

Figure 1. Schematic representation of R-X⋯π contact involving benzene and BrCN.

References
How to reduce NO₂ computationally by pincer based metal catalysts

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The hydrogenation of nitrous oxide by pincer ruthenium complexes supposes a promising way to functionalize a hazardous gas and reduce the greenhouse effect, generating dinitrogen and water. The particular P<sub>Csp2</sub>P ligand (see Figure 1a), which is not a simple spectator, but it directly assists in the formation of a characterized epoxide complex, affording the N₂ release if N₂O is used as a reactant.[1,2] Next the hydrogenation is undertaken with H₂ as a reactant, generating water as a main product. All these statements are discussed mechanistically, by means of Density Functional Theory (DFT) calculations.[3] The stoichiometric nature of the reaction described here is rationalized by the competition between N₂O and H₂ to react with the PCP iridium pincer complex. And the role of water is predicted in silico to be a non innocent product and could be the solution to assist, facilitating a catalytic performance.

![Figure 1. (a) PC<sub>Csp2</sub>P ligand–pincer Ir based catalyst. (b) Hydrogenation of N₂O by the PNP-pincer Ru based catalyst (P = P(iPr)₂).](image)

On the other hand, the whole reaction mechanism for a PNP pincer based catalyst has also been undertaken, see Figure 1b.[4,5] The possibility of a water autocatalysis at the initial stages of the reaction was determined, while it would be hindered as time progresses and water is formed as a product of the hydrogenation of N₂O. In complete absence of water, a peculiar bond cleavage of any of the Ru–P bonds in order to form a Ru–O–P moiety has been computationally highly stable, and we consider it a plausible catalyst poisoning due to the high energy required in order to continue the mechanism and close the catalytic cycle. Between the three studied ligands on P atoms, iPr is indeed the best one, with tBu having increased bulkiness and Ph gaining some conjugation between the phenyls and the pyridine, thus, requiring more energy to overcome the upper barrier of the whole mechanism. Further studies are planned to in silico predict a modified PNP pincer Ru-based catalyst that does not need the presence of any water molecule, together with the control of the potential Ru–P bond cleavage that here has been demonstrated to lead toward the decomposition of the catalyst.

References

Tuning resonance assisted hydrogen bond strength by increasing the number of fused six-membered rings

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Intramolecular Resonance Assisted Hydrogen Bond (RAHB) brings extra-stabilization to a molecule due to the creation of a quasi-ring, which resembles a benzene ring. In a recent review[1] it was highlighted the involvement of RAHB as a driving force in the synthesis of organic, coordination and organometallic compounds. The extra-stabilization of the quasi-ring depends on different factors, being the availability of π electron within the new quasi-ring one of the more important ones. Thus, when RAHB is linked to one or more benzene rings (sharing a CC bond) the ipso-ring aromaticity influences the RAHB distance: the lower the aromaticity of benzene ring the shorter the HB distances, so stabilizing the system.[2,3]

Following Clar’s aromatic π rules, polycyclic aromatic hydrocarbons (PAH) have quite different aromaticity if they are in a linear or a kinked topology,[4] so presenting more or less available π electron for sharing with a quasi-ring. The goal of this work is to design materials with different HB distance (different HB strength) based on the addition of two RAHB to PAH that have different linear or kinked structure. Recently it was demonstrated[5] that substituents at the ipso-ring change the RAHB distances, so addition of an extra ring (adding two different substituent, HC=O and OH) is modifying HB distances. In that sense, another goal of this work is to analyze how many consecutive benzene rings are needed to eliminate the two RAHB quasi-rings communication. General rules can be written down in order to tailor PAH with RAHB presenting particular hydrogen bond distances. These rules will be based in the number of rings added as well as the particular topology they present, not only linear or kinked but also the relative position of HC=O and OH in the quasi-rings.

![Diagram of PAHs with two quasi-ring having different number and topology.](image)

**Figure 1.** PAHs with two quasi-ring having different ring number and topology.

**References**

Magnetism in hybrid organic-inorganic systems: the giant ferromagnetic $\pi$-d interaction in iron-phthalocyanine molecule

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In this contribution we analyze the magnetic interaction between itinerant $\pi$- and localized $d$-electrons in metal-phthalocyanines, a representative example of magnetic hybrid systems. Metal-phthalocyanine molecules have been extensively studied for a long time due to their versatility and wide range of applications as dyes, gas sensors, solar cells, biomimetic catalysts, optical and electronic devices, quantum information,... If the metal atom has a non-null magnetic moment, the interaction between the Pc $\pi$ and metal $d$ electrons, i.e., between the itinerant $\pi$-electrons and localized magnetic moments on the metal atom, modifies the transport properties of the molecular conductor. This interaction is at the origin of many interesting phenomena with remarkable importance in the field of molecular electronics and spintronics, such as the giant negative magnetoresistance observed in several phthalocyanine-based conductors, among many other important physical properties. Despite the fundamental and technological importance of this on-site intramolecular interaction, its giant ferromagnetic nature has been only recently demonstrated by the experiments conducted by Murakawa et al. in the neutral radical $[\text{Fe(Pc)(CN)}_2]\cdot2\text{CHCl}_3$ [1].

In this contribution, we present a multiscale study of the magnetic interactions in $[\text{Fe(Pc)(CN)}_2]\cdot2\text{CHCl}_3$ combining wavefunction-based electronic calculations on isolated $\text{Fe(Pc)(CN)}_2$ molecules and density functional theory-based periodic calculations on the crystal. Our calculations confirm the ferromagnetic nature of the $\pi$–$d$ interaction, with a coupling constant as large as $J_{\pi d}/k_B = 570$ K, in excellent agreement with the experiments, and the presence of intermolecular antiferromagnetic interactions driven by the $\pi$-$\pi$ overlap of neighboring Pc molecules. The analysis of the wavefunction of the ground state of the $\text{Fe(Pc)(CN)}_2$ molecule provides the clues of the origin of this giant ferromagnetic $\pi$–$d$ interaction.

(a) (b)

Figure 1. (a) Magnetic 3d Fe and $\pi$ Pc orbitals. (b) Spin density map for the ground state of the 211 supercell.

References
Understanding the gas solubility behaviour in ionic liquids combining different molecular modelling tools: soft-SAFT and COSMO-RS

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Ionic Liquids (ILs) are defined as salts that remain liquid at a temperature below 100 ° C, as a consequence of the asymmetry between the cation and the anion. The network of hydrogen-bonding and other highly directional association interactions occurring in these compounds define their physicochemical properties. In fact, the possibility of tuning an IL for a particular application by an appropriate choice of the cation-anion pair, converts them in good candidates for gas separation and CO₂ capture applications. However, there is still a need for a further understanding of the dependence of the gas behaviour on the ionic liquid microscopic structure in order to enhance their design for ad-hoc applications. Due to the large amount of cation-anion combinations, molecular modeling and quantum mechanics techniques provide an excellent framework to progress on this field.

In this contribution, some ILs, which may be potential candidates for CO₂ capture and separation, will be studied. This will be carried out using two different computational tools. From one side, the Statistical Association Fluid Theory (SAFT) molecular-based equation of state [1] will be used to develop coarse-grained molecular models for the ILs and to characterize these solvents and the gas interactions. This equation, based on Wertheim’s first-order thermodynamic perturbation theory (TPT1), provides a framework in which the different physical effects of the molecule are considered in a coarse-grained approach. From the other side, the COnductor like Screening MOdel for Realistic Solvents (COSMO-RS) [2] will also be used to study the molecules charge density distribution. The idea behind COSMO-RS is to create a virtual conductor embedding the molecule using continuum solvation models to determine the charge distribution of the molecule. Afterwards, DFT calculations are used to estimate the chemical potentials, from which other thermodynamic properties, such as the activity coefficients or the solubility, are predicted. Using both, SAFT and COSMO-RS, the thermodynamic properties and the solubility of CO₂ and other gases in the selected ILs will be studied from a molecular point of view, in order to gain insight on the mechanism facilitating the absorption. All this information will be used to address the best IL for gas separation and presented at the meeting.

References
Carbon dioxide is the primary greenhouse gas generated by human activities, mainly from the combustion of fossil fuels for energy and transportation. Despite the development of alternative renewable energy sources, fossil fuels still dominate in almost all near future projections [1]. Therefore, many efforts have been addressed to the development of cost-efficient technologies for separation and capture of carbon dioxide. Solid adsorbents like zeolites or metal-organic frameworks are promising candidates [2].

In the present work, Grand Canonical Monte-Carlo (GCMC) simulations are used to assess optimum faujasite structures (Figure 1), the well-known family of zeolites, in CO$_2$ capture processes. Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) and Temperature Swing Adsorption (TSA) procedures have been considered to evaluate purity, selectivity, working capacity and isosteric heat in ten faujasite structures with different Al content. Results indicate that faujasites with high Al content are the most effective for TSA whereas intermediate Al content structures perform better at VSA conditions and ultimately, low Al content faujasites are more suitable for PSA process [3,4].

References

Aluminium Ion Promoted DPPH· Scavenging Reaction of the Hydroquinone

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Aluminium is the most abundant metal on the earth crust, being for a long time unavailable to biological systems due to geo-chemical cycles with silicic acid. Human intervention, like soil acidification, increased the bioavailability of aluminium. Unfortunately, this small and highly charged ion can cause important deleterious effects in biological systems. Among them, it has been suggested that aluminium can display a significant pro-oxidant activity. In general, the possibility that aluminum affects redox reaction equilibria has been confirmed by Fukuzumi et al. [1], which recently reported the effect of the aluminium ion in the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH·) scavenging reaction using methylated derivatives of the hydroquinone (MeₙQH₂, n = 0–4) in a hydroalcoholic medium. They found that the rate constant significantly increased by the addition of Al³⁺, a fact ultimately related to the ability of aluminium to stabilize the reduced form of DPPH·.

Figure 1. Optimized structures of DPPH· and QH₂ containing aluminium complexes.

In this work, we have used Density Functional Theory to obtain different coordination structures of aluminium with solvent, DPPH·, QH₂, and their redox counterparts. The visualization of the spin densities allowed to localize the radical and to characterize the conditions in which the electron-transfer from DPPH· to hydroquinone is facilitated by aluminium. Our results are in agreement with the experiments and allow us to provide for a rationalization of the effect of aluminium in these reactions.

References
Complex Organic Molecules Formation through the Gas-Phase Reaction between HNO and CH$_2$CHOH$_2^+$

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Knowing how the molecules present in the interstellar medium can evolve to ones that are more complex is an interesting topic in astrochemistry. The study of possible reactions between detected species can help to understand the evolution in complexity of the interstellar matter and also allows knowing the formation of new molecules which could be candidates to be detected. We focus our attention on two molecules detected in space, vinyl alcohol [1] and azanone [2,3]. The viability of formation of COMs that could lead to prebiotic species from these reactants is reported.

In the present work, we carry out a theoretical study of the ion-molecule reaction between protonated vinyl alcohol and azanone [4]. Stationary points on the potential energy surface (PES) are characterized at the second-order Moller-Plesset level in conjunction with the aug-cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis set. In addition, the electronic energies were refined by means of single-point calculations at the CCSD(T) level (coupled cluster single and double excitation model augmented with a non-iterative treatment of triple excitations) with the same basis set.

From a thermodynamic point of view, twelve products, composed by carbon oxygen, nitrogen, and hydrogen, which could be precursors in the formation of more complex biological molecules, can be obtained from this reaction. Among which we can stand out ionized glycine and two of its isomers. The analysis of the PES shows that only formation of cis- and trans-O-protonated imine acetaldehyde, CH$_2$NHCOH$^+$ and CHNHCHOH$^+$, are viable under interstellar conditions. Our results suggest that imine acetaldehyde could be a feasible candidate to be searched for in space.

In addition, we carried out a computational study of the four conformers of imine acetaldehyde in order to report, at “spectroscopic” accuracy, stabilities, molecular structures, as well as spectroscopic parameters for the imine acetaldehyde conformers that could help in their laboratory or astronomical detection.

References
Structural Trends in Monoboronyl Compounds

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A computational study of the monoboronyl compounds of the second-row elements Na, Si, P, S and Cl has been carried out. It has been shown that [NaBO] exhibits a rather flat PES. Three minima were characterized, linear NaBO, linear NaOB and an L-shaped structure with a $\angle$NaOB angle of 92.3°. The NaBO isomer and the L-shaped structure are nearly isoenergetic, the former lying slightly lower in energy (0.26 kcal/mol) at the highest level of theory. Linear NaOB is located 2.11 kcal/mol above linear NaBO. The barrier for the conversion of the L-shaped structure into linear NaBO is about 5.1 kcal/mol. Therefore it seems that both species could be potential targets for experimental detection. In the case of silicon monoboronyl only two minima, linear SiBO and linear SiOB, are found. the latter lying about 13 kcal/mol above SiBO.

For the rest of second-row monoboronyls the preference for the XBO arrangement is much clearer. In fact, for monoboronyls of phosphorus, sulphur, and chlorine the linear XOB species is shown to be a transition state, because in all cases imaginary frequencies are found for the degenerate bending mode. Non-linear minima are found in these cases, although all of them lying quite high in energy above linear XBO: 46.45 (P), 80.96 (S) and 119.5 (Cl) kcal/mol, respectively. Furthermore, in all cases small barriers for their conversion into the XBO isomer are found, suggesting that quite likely the linear XBO isomer should be the main experimental target.

Dissociation energies of monoboronyls tend to increase when moving from left to right of the second row. Linear XBOs, which are the most stable isomers for the different [XBO] species, have moderate dissociation energies for Na (69.8 kcal/mol), Si (79.24 kcal/mol) and P (78.97 kcal/mol). On the other hand, relatively large dissociation energies are found for SBO (97.55 kcal/mol) and ClBO (118.98 kcal/mol).

An analysis of the bonding for second-row monoboronyls has been carried out, emphasizing the different characteristics of the X-B and X-O bonds along the second-row.

Figure 1. Scans obtained through optimizations at different fixed $\angle$XBO angles. The relative energies (taking the XBO isomer as reference) at the CCSD/aug-cc-pVTZ level of theory are given in kcal/mol.
A Universal Footprint of Dispersion Interactions

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Dispersion or van der Waals (vdW) interactions are ubiquitous in nature, governing the stability of molecules and materials and having an essential role in molecular recognition, the double-helical structure of DNA, molecular adsorption on surfaces, and the adhesion of micromachined surfaces [1]. They are so important in physics, chemistry, and biology, that even the most simple electronic structure methods consider corrections for vdW interactions. vdW forces arise from the electrostatic interaction between fluctuations in the electron density, and the pairwise effect in the energy shows a well-known leading $1/R^6$ decay, where $R$ is the interaction distance between fragments. This fact is often exploited in the construction of effective pairwise potentials that enter the expressions of various methods, including the typical ad hoc corrections of many density functional approximations [2]. Conversely, the effect of vdW interactions in the wave function or related quantities has been less discussed in the literature. This knowledge could shed some light in the design of computational approaches including vdW interactions in ab initio manner, which are essential to account for density-dependent dispersion effects, such as those occurring in excited states.

In this work [3], we use perturbation theory to find the leading term in the expansion of the intracule pair density in terms of $R$, the interatomic distance. Our results reveal a universal $1/R^3$ dependency that is confirmed by numerical calculations in various noble gas dimers. Upon integration of the vdW contribution to the intracule, we recover the vdW energy that follows the established $1/R^6$ decay.

![Figure 1. Dependency of the energy and the intracule of the pair density with the fragment distance (R).](image)

To our knowledge, this is the first universal fingerprint of dispersion interactions that can be directly employed to model the shape of the pair density and, therefore, it can be used as a stringent constraint in the judicious design of new methods and approximations in electronic structure theory including vdW interactions.

References

Atomic Decomposition of the Electrostatic Solvation Energy Using the Interacting Quantum Atoms Approach

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Basing on the first- and second-order density matrices, the interacting quantum atoms (IQA) method[1] decomposes the total energy of a molecular system in terms of one- and two-center (atomic) contributions within the context of the quantum theory of atoms in molecules. IQA is able to process wavefunctions derived from several electronic-structure methods (HF, CCSD, CASSCF), but also admits DFT charge densities by defining \textit{ad hoc} additive exchange-correlation energies. [2] IQA quantifies both intra- and intermolecular interactions, characterizing unambiguously many aspects of chemical bonds and intermolecular forces. Here we incorporate electrostatic continuum solvent effects into the IQA energy decomposition. To this end, the interaction between the solute electrostatic potential and the solvent screening charges as defined within the COSMO solvation model[3] is now included in a new version of the PROMOLDEN code, allowing thus to apply IQA in combination with COSMO-QM methods as well as to partition the electrostatic solvation energy into effective atomic contributions. To test the robustness of this approach, we carry out COSMO-HF/aug-cc-pVTZ calculations in aqueous solution followed by IQA calculations on hundreds of neutral and ionic solutes extracted from the MNSol database. The computational results reveal a detailed atomic mapping of electrostatic solvation energy that is useful to assess to what extent the solvation energy can be decomposed into atomic and group contributions of various parts of a solute molecule, as generally assumed by empirical methodologies that estimate solvation energy and/or log\textit{P} values from multilinear regression models.

\[ \Delta_{\text{tot}}G^{\text{exp}} = -75.9 \text{ kcal/mol}; \Delta_{\text{tot}}G^{\text{IQA}} = -78.5 \text{ kcal/mol}; \Delta_{\text{tot}}G^{\text{IQA/QM}} = -81.8 \text{ kcal/mol}. \]

Atomic labels correspond to the atomic electrostatic solvation energies (in kcal/mol) as determined by the IQA partitioning.

References
20S Proteasome core particle: autolytic activation mechanism

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The great majority of protein degradation in mammalian cells is catalysed by 20S Proteasome [1], mostly being involved in Ubiquitin-26S Proteasome System (UPS). Therefore, proteasome function is directly related with protein homeostasis and influences cell regulation [2]. The proteasome is involved in the turnover of many critical proteins, in the control of cell growth, cell differentiation, or metabolic adaptation. 26S Proteasome consists of 19S regulatory particle and 20S core particle. It is generally accepted that the proteolytic mechanism is carried out in the active sites located inside the core particle. These active sites bear N-terminal Thr residues as central component of the reactivity, thus proteasome is classified as Thr-hydrolase. During 20S core particle biogenesis, catalytic subunits are synthesized as precursors bearing N-terminal propeptides attached to Thr. It is in last stage of core particle maturation when propetides undergo autocatalytic cleavage, leaving Thr catalytic residue exposed [3]. Multiple studies have been published regarding UPS stages towards protein degradation, but few are focused in the proteolytic process occurring in 20S proteasome core particle. Thus, the autolytic and proteolytic mechanisms remain enigmatic.

In this communication we are presenting a theoretical study of the multi-step autocatalytic activation of the active sites of 20S proteasome core particle. The free energy surfaces for each step appearing in different explored mechanisms have been obtained by means of hybrid QM/MM methods, using the semiempirical AM1 Hamiltonian and the M06-2X DFT method to treat the QM sub-set of atoms and the AMBER and TIP3P force fields to describe the protein and solvent water molecules, respectively. The obtained results show the main energetic differences between the proposed mechanisms up to now [4,5] and newly proposed mechanisms. The analysis of these results should provide not only more detailed knowledge about the final maturation step of 20S Proteasome, but also a clear idea of the starting point of the active site for further steps. These and future results of our studies can be paramount, keeping in mind the unsuccessful efforts done to develop the next generation of cancer-fighting proteasome inhibitors. [6,7]

References
Computational study of the alloxydim herbicide degradation

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Pesticides are subjected to degradative processes from the moment they are synthesized. This phenomenon is increased when they are applied in the field or in the place for which is intended to be used. Inorganic end products, such as H₂O, CO₂, and NH₄⁺ would be obtained after their full mineralization. However, the mineralization process is not always performed until completion or it arises slowly in the environment. During this process, diverse intermediates, generally referred as pesticide degradation products, are formed. These new compounds have different physicochemical properties that may greatly affect their environmental behavior. For instance, several studies have documented that some of these DPs persist for longer periods than the parent active compound and show higher mobility values and/or higher toxicity [1].

Density functional theory calculations by using the B3LYP functional allowed us to study alloxydim herbicide and to identify the most stable conformers, the factors that govern their stability. It was possible also, at same level of theory, to highlight the interconversion mechanisms among the most relevant conformers (Figure 1). The degradation chain involves, as a first step, the cleavage of N–O bond, the loss of the oxime ether group and the formation of a stable intermediate difficult to characterize experimentally. The performed study allowed us to identify some properties of this elusive intermediate and to determine that the dominant fragmentation process in the gas phase is the homolytic fragmentation. Stability of alloxydim conformers and its homolytic and heterolytic fragments were also assessed in the water phase by means of the Polar Continuum Model. The bonding characteristics were performed by means of the Quantum Theory of Atoms in Molecules and a Natural Bond Orbital analysis. Computed IR spectra were found consistent with those observed experimentally.

![Figure 1. Most stable alloxydim conformers in both the gas and water phase.](image)

This theoretical study can be employed as a new strategy for initial estimation of the pesticide degradation pathways and by-products formation in order to prioritize experimental investigations for risk assessment [2].

References

Metallophilic Interactions in the Luminescent Cyclic Trinuclear Gold(I) carbeniate clusters, $[\text{Au}_3(\text{RN}=\text{COR'}))]_n$ with $n=1-4$, where $\text{R}=\text{H, Me, and R'}=\text{H/OH}$

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Aurophilic attraction in cyclic trinuclear gold(I) carbeniate clusters, $[\text{Au}_3(\text{RN}=\text{COR'}))]_n$ with $n=1-4$, where $\text{R}=\text{H, Me, and R'}=\text{H/OH}$, are herein investigated. We assess the electrostatic interactions and aurophilic bonding between neighbor trimers using different high correlated calculations. Electronic structure and optical proprieties are analyzed via TD-DFT. The stability of the slipped conformers (e.g., chair oligomer-of-trimers) is found to be due to a balance between less Coulombic repulsion and more aurophilic attraction, whereas non-slipped (e.g., eclipsed/prismatic oligomer-of-trimers) are stabilized by ligand substituent effects. Thus, high-accuracy calculations show that the aromatic ligand induces planarity and prismatic structure of $[\text{Au}_3(\text{PhN}=\text{COMe})]_4$ rather than the chair conformation when $\text{R}=\text{n-pentyl}$. This situation leads to a columnar arrangement whereby weaker repulsion effects take place with a concomitant-twist of stacked metallacycles, which govern the driving forces of this strong aurophilic interaction [1].

Keywords: RIMP2, DFT-D3, Aurophilic interaction, UV-vis spectra, TD-DFT calculations.

References
Fluorine Conformational Effects from the Interacting Quantum Atoms Perspective

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The conformation and binding affinity of fluorine-substituted biomolecules is largely controlled by stereoelectronic and electrostatic effects commonly attributed to the fluorine electronegativity, the high polarization of the C-F bonds and the hyperconjugation between low-energy C-F antibonding orbitals and adjacent bonds or nonbonding electron pairs.[1] Such effects have been exploited to design and synthesize new functional molecules including drugs, biological ligands and peptides. The computational design of fluorine-substituted compounds can further enhance their utility provided that both global and local properties can be predicted reliably in order to address the specific effects induced by the F atoms. In this respect, the interacting quantum atoms approach,[2,3] IQA, provides a robust partition of the energy into intra- and inter-atomic contributions based on the first and second order density matrices. This method, which is normally used within the framework of the quantum theory of atoms in molecules, enables a direct quantification of the relative energy changes experienced by functional groups upon conformational changes. Here, we report the results of ab initio calculations followed by D3-HF IQA analyses on a series of model compounds (CH2F-X with X=CH2F, CONHCH3, CO2CH3, etc.) that allow the estimation of distinct contributions (e.g., classical electrostatic and exchange-correlation) to the gauche conformational preference exhibited by 1,2-difluoro compounds, comparing also with previous theoretical results. In addition, we also study the relative stability and conformational properties of two α,β-difluoro-γ-amino acid derivatives that have been characterized experimentally.[4] The IQA analysis of these larger compounds yields a unique description of the fluorine gauche effects and other factors that determine the conformational preferences of these peptides, showing thus the ability of IQA to ascertain and quantify the impact of fluorine substitution.

References
Periodic Density Functional Theory Approach to the Thermodynamic Properties of Uranyl Containing Materials

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Thermodynamic data are the indispensable basis for a dynamic modelling of the behaviour of nuclear materials [1]. Despite its importance, the experimental measurement of these properties and their temperature dependence for uranyl containing materials has only been carried out for a very small number of uranyl containing materials and within a quite limited range of experimental conditions. The thermodynamic properties of a large series of uranyl containing materials, including uranyl oxides, uranyl oxyhydroxides, uranyl peroxides, uranyl carbonates and uranyl silicates were studied in this work [2-3]. These materials are among the most important secondary phases arising from corrosion of spent nuclear fuel under the final geological disposal conditions [1]. Their crystal structures were determined by means of solid-state theoretical computations based on density functional theory using plane waves and pseudopotentials. By using the optimized structures, their thermodynamic properties were determined, including specific heats, entropies, enthalpies and Gibbs free energies. The computed thermodynamic properties were then used to determine their free energies of formation. The results are shown to be in excellent agreement with experimental data even at high temperatures [1-2]. Finally, the free energies of formation were used to obtain the free energies of many reactions involving these materials and its variation with the temperature. The relative thermodynamic stability of these materials in the presence of intermediate and high hydrogen peroxide concentrations was then evaluated by considering the corresponding reactions (Fig 1).

![Figure 1. Thermodynamic stability order of the considered secondary phases of the spent nuclear fuel in the presence of small and high hydrogen peroxide concentrations.](image)

The results show that at high H₂O₂ concentrations, occurring under very intense radiation fields causing radiolysis of most of the water present, studtite mineral phase is by far the most stable phase within the full range of temperature studied. The application of computational techniques is shown to enhance extraordinarily our knowledge of the physics and chemistry of uranyl containing materials [2-3] and to be an excellent complement for the experimental studies which are very complex due to the radiotoxicity of these substances.

References

The reaction of (R)-Carvone and (R)-pulegone thiosemicarbazones affords two different thiazoles I and II. Their structures have been established by $^1$H, $^{13}$C NMR in solution and X-Ray crystallography supported by density functional theory calculations at the B3LYP/6-311+G(d,p) level. Mass spectrometry and NMR spectroscopy data confirm unambiguously the expected structure of I and show a supplementary rearrangement and oxidation in the case of II. X-Ray and DFT calculations show that the product obtained is certainly the structure (3aR,6R)-3,3,6-trimethyl-2-(4-phenylthiazol-2-yl)-3a,4,5,6,7-hexahydro-2H-indazol-3a-ol. The computational study, reported in this work using B3LYP/6-311+G(d,p) in the case of R and S configurations as well as the dimer and trimer, fully rationalizes the experimental observations at structural and energetic stabilization. Two deferent types of hydrogen bond, OH…O and OH…π have been compared. From the calculated Gibbs energy, these two isomers are almost equally stable in the case of dimer (the difference is only 0.15 kcal/mol). This difference increases dramatically in the case of trimer (16 kcal/mol) and we believe that it can increase even more in the case of the polymer due to the fact that the stacking of the molecules via the OH…π interaction is made in parallel planes, while in the case of OH---O, this stacking is not possible because of the steric hindrance. This result is in full accord with the observed crystal structure.
Oxygen adsorption on graphene/GaN(0001) surface: A first-principles study

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Graphene (Gr) is used in gallium nitride (GaN)-based electronic devices due to its properties. Gr is used as a transparent electrode in GaN-based light-emitting diodes due to its transparency.[1] Also, Gr can be used as a contact in GaN-Schottky diodes to offer stability at high temperatures[2] or as a substrate to growth GaN in LED to decrease the heat generated by its operation due to its high thermal conductivity[3]. However, the theoretical studies regarding the graphene/GaN(0001) interface are limited[4]. In some cases, graphene oxide reduced is used instead of pristine graphene in GaN-based electronic devices due to the similarity in defined properties such as high thermal conductivity [5] or transparency [6]. For this reason is necessary to evaluate the changes generated by the presence of oxygen in the graphene/GaN(0001) interface. In this work, we analyze by first-principle calculations the modifications of the electronic and structural properties of the graphene/GaN(0001) surface produced by the adsorption of oxygen atoms. The results show that depending on where a single oxygen atom is adsorbed onto the graphene/GaN(0001) surface; it can change the character of graphene/GaN(0001) from metallic to semiconductor due to bond formation-modification between the carbon and gallium atoms. The gap generated by the adsorption of oxygen on the graphene/GaN(0001) surface increases suddenly starting at seven oxygen atoms adsorbed. At the same time, the formation energy decreases when the number of oxygen atoms on the surface increases.

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References

Conformational Changes upon Fluorination of the Unguisin-A Peptide

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Unguisin A is a natural macrocyclic heptapeptide derived from a marine fungus. It contains the neurotransmitter γ-aminobutyric acid (GABA) as one of its seven residues (Figure 1a). According to NMR evidences, stereoelectronic fluorination of GABA modifies the geometry, dynamics and binding capabilities of unguisin A.[1] Clearly, a computational characterization of the conformational space of these fluorinated peptides maybe helpful to perform their rational design. However, only low-energy molecular-modeling structures including partially NMR-based hydrogen bond constraints have been reported to date.[2] Macrocycles like unguisin A involves a large number of rotatable bonds and conformational restrictions that compromise structural predictions. In this work, we parametrize the GABA moiety (charges and torsions) and then perform Gaussian-accelerated molecular dynamics (GaMD) simulations to thoroughly sample the conformational space accessible to native unguisin A and the four difluorinated variants. To identify the highly populated conformational states, we use the dual-boost algorithm that introduces a bias on the total and dihedral energy terms and we reconstruct the potential energy surface considering two backbone torsion angles (Figure 1b). Then extensive molecular dynamics (MD) simulations in DMSO solution are performed starting from a low free-energy structure. For each trajectory, structural analysis of polar and hydrophobic contacts and conformational clustering are carried out to provide a detailed description of the fluorine-substitution effects. The resulting computational results compare favorably with experimental NMR data, showing thus that the combination of GaMD and MD simulations can be useful for the de novo prediction of the structure and flexibility of peptide macrocycles.

Figure 1. a) Schematic representation of Unguisin A and b) reconstruction of the potential energy surface obtained from the GaMD of Unguisin A.

References
Taming electronic excited states and deactivation mechanisms of BODIPYs

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The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene dye, more commonly known as BODIPY (Figure 1a) has remarkable optical and photophysical properties, such as very intense absorption at visible wavelengths of about 503 nm and very high fluorescence quantum yields. Interestingly, besides fluorescence, the parent BODIPY also presents 1.1% of intersystem crossing quantum yield [1]. As the dye scaffold allows versatile functionalization, there is a strong drive to introduce chemical modifications to modulate its spectroscopic properties. The meso position, in particular, has been extensively studied. However, predicting the effect substitution has on the photophysics of these dyes is not straightforward and it requires combined experimental and theoretical efforts.

Figure 1. Structures of the BODIPY derivatives discussed: the parent BODIPY (a), a meso-pentafluorophenyl BODIPY (b) and a 6-Br-meso-ethyl BODIPY (c).

In this contribution, we unravel the photophysical properties of a series of BODIPYs and compare them to those of the parent molecule. We show that the introduction of an aromatic group (see compound b) in Figure 1) dramatically quenches the fluorescence, as a result of a very efficient $S_1/S_0$ conical intersection. In contrast, it has been shown [2] that if an ethyl group is attached (Figure 1c), fluorescence is preserved. In that case, intersystem crossing from the first singlet excited state is plausible and can be enhanced by introducing heavy atoms, which increase the spin orbit coupling. Here, the deactivation paths of different BODIPY derivatives are investigated with the objective of increasing the intersystem crossing efficiency and thus boost their application as singlet oxygen photosensitizers. To this aim, the relevant conical intersections and singlet/triplet crossing points have been identified and non-adiabatic molecular dynamics simulations using SHARC [3] have been carried out.

References

Revealing the population mechanisms of singlet oxygen precursors in thionucleobases: On the way to finding novel photoinitiated drugs

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DNA nucleobases’ thioderivatives have attracted the attention of the scientific community in the last few decades for their potential phototherapeutic properties. In contrast to natural DNA nucleobases, the excited-state potential energy surfaces (PESs) of those modified bases lack of efficient deactivation funnels for ground state repopulation. In fact, theoretical and experimental studies have demonstrated that their altered topographical PES features favor the population of triplet manifold with high efficiency[1]. From the triplet states, these chromophores are able to generate in solution DNA-damaging reactive oxygen species and singlet oxygen, which are cytotoxic to cancerous cells[2].

In order to have full understanding of the mechanisms by which the triplet states, responsible for the chemotherapeutic properties of these systems, are populated it is crucial to study in detail their deactivation pathways. In this contribution, our center of focus will be the thiosubstituted derivatives of thymine and uracil nucleobases, paying special attention to the effect that the degree and pattern of substitution have on their photophysics and photochemistry. The decay pathways mapped with state-of-the-art quantum chemical calculations and surface hopping molecular dynamics simulations will be presented for our systems of interest.

Figure 1. Energy transfer scheme leading to singlet oxygen production from the triplet states of thiobases

References
Molecular modeling of the adsorption of 5-aminosalicylic acid on the kaolinite and halloysite nanotube surfaces

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5-aminosalicylic acid (5-ASA) is an anti-inflammatory drug widely used in the treatment of different diseases, as Crohn’s diseases, chronic bowel ulcerative colitis and proctitis. For the treatment of the Crohn’s disease and chronic bowel ulcerative colitis disease is administered orally and the 5-ASA is rapidly absorbed in the stomach and in the small intestine. However, the drug adsorption at the level of the large intestine and the colon is very important for the treatment of these diseases. Therefore, it may be necessary the use of excipients to achieve colon targeted drug delivery systems of the 5-ASA drug. For it, kaolinite and halloysite nanotubes was proposed as a good candidates. Halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \times n\text{H}_2\text{O}$) is a multilayer nanotubular clay mineral resulting from the wrapping of 1:1 layers of kaolinite with 500-1000 nm in length and 15-100 nm in inner diameter. Kaolinite and halloysite nanotubes are common excipients in pharmaceutical products and can modify drug bioavailability, due to their ubiquity, low-cost, high surface with activity and biological safety. In addition, they can retain organic molecules and, after administration, release the retained bioactive compounds under controlled conditions. To date several experimental studies have been carried out to study the interaction between 5-ASA and halloysite nanotubes. After the experimental studies, it was necessary to carry out theoretical studies that explain the interatomic interactions that occur in the processes of 5-ASA adsorption on the kaolinite and inside the halloysite nanotube, when the 5-ASA is adsorbed inside of the halloysite nanotube [1].

Therefore, the aim of this work was to perform molecular modeling studies by methods based on atomistic force fields for molecular modeling and quantum mechanics calculations to predict the interaction between the drug 5-ASA and the kaolinite and halloysite nanotube excipients, being able to explain the use of these excipients as colon targeted drug delivery systems.

![Figure 1. 5-ASA (a), kaolinite (b) and halloysite (c) structures.](image)

References

Collision induced reactions of 5-bromouracyl hydrated clusters

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Previous works have established the importance of the interaction biomolecule –water environment in determining molecular structure and function[1], molecular recognition[2] and the fidelity of DNA replication itself[3]. Already Watson and Crick indicated tautomerization as the main cause of DNA mispairing[4]. The incidence of such mispairing, according to Topal and Fresco, may be enhanced, among other factors, in presence of base analogues, as 5-bromouracyl (5BrU)[5]. Is that true?

Here we present how, by means of experimental and molecular tools, we have tried to answer this question. The experiments, performed at the ARIBE facility[6], involve collisions between neutral clusters of [5BrU]ₙ(H₂O)ₙ and a C⁺²⁺ ion at 36 keV. The computational approach to such a system consisted of both static calculations, aiming to sample the potential energy surface of different possible reactive species at m062x/6-311++g(d,p) level of theory[7], and of Born-Oppenheimer molecular dynamics (BOMD)[8] using the same functional and a SVP basis set, where we have simulated entire sequences of the system after energy has been deposited with an ionizing collision. Figure 1 presents one of the mentioned sequence obtained from the MD. The combination of both results helped us giving an interpretation of the fine chemistry involved in the fragmentation processes occurring in the collision camera, which lead to the formation of unexpected extra-hydrogenated fragments.

References

Ab initio molecular dynamics simulations of catalytic alumina oxide/water interfaces

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The surfaces and interfaces of metal oxides play an important role in many natural and technological processes such as mineral dissolution, adsorption/desorption reactions, pollutant transport in groundwater, corrosion and heterogeneous catalysis [1]. Our interest is mainly in this latest domain, and in order to help industries improve the efficiency of some catalytic processes, one needs a detailed knowledge of the interface at the atomic level in terms of interfacial structure and surface termination.

We present DFT-MD (DFT-based Molecular Dynamics) simulations of the R(1102) α-alumina oxide Al₂O₃/liquid water interface, and unravel the intertwined structural arrangement of surface and liquid water at the interface. Chemical reactivity is highly dependent on surface structure and speciation at the interface with the solvent, therefore the pre-requisite knowledge of the following points: type of surface, surface sites protonation state (O, OH, OH₂), water molecules organization due to the presence of the solid, water and surface site orientations and hydrogen bonding networks. Of particular interest is the comprehension of the H-Bond network formed between the surface aluminols and interfacial water molecules, in terms of which surface chemical types are involved in the network, and in terms of strength of H-Bonds. This will be related to the catalytic activity of the interface. Also of importance is the relationship between interfacial structures and vibrational signatures. These signatures are calculated from the DFT-MD trajectories (IR & SFG in particular) and are compared to experiments.

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Figure 1. Simulation box (left) and schematic representation of the hydrogen bonding at the interface (right).
Densities and Energies: a Perspective from Quantum Chemical Topology

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Density Functional Approximations (DFAs) have progressively become a source of heated debate among scientists. The many advantages of Density Functional Theory (DFT), combined with the ever-increasing number of applications that it powers, have directed significant efforts towards the design and implementation of better DFAs to the exact exchange-correlation functional. While well-known flaws remain an issue, versatile solutions have been devised for many. Yet, in doing so, a certain degree of parametrization has been added to the framework. Most general purpose DFAs are parametrized in different degrees.

It has been recently suggested[1] that the development of DFAs that rely on heavy parametrization compromises the ongoing quest for the exact functional, as the path to the exact functional requires achieving better energies and electron densities simultaneously. However, assessing the quality of the electron density (ρ(𝑟)) and derived scalar fields is non-trivial. Quantum Chemical Topology (QCT) has been developed in order to link the topological features of such fields and chemically meaningful concepts[2]. Therefore, an effort can be made to find connections between chemical notions, densities and energies.

In our work, several simple systems are evaluated using a battery of DFAs in an attempt to correlate energetic and topological discrepancies. The whole scalar field will be investigated to evaluate sources of error, which might come from very different “chemical parts” of the system. Figure 1 exemplifies how HF and PBE errors arise from either lone pairs or bonding regions respectively. Hence, failures can be mapped backwards into chemical concepts to achieve a better understanding. Moreover, since errors seem to be related with chemical regions, additional insight can be derived though more sophisticated scalar fields, such as the Electron Localization Function (ELF) and the Reduced Density Gradient (RDG).

References

Carbon Dioxide and Nitrogen Separation by Multilayer Graphtriyne Membranes: A Molecular Dynamics Study

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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 multilayers, proposing them as membranes featuring pores of subnanometer size suitable for CO\textsubscript{2}/N\textsubscript{2} separation and CO\textsubscript{2} uptake. The potential energy surfaces, representing the intermolecular interactions within the CO\textsubscript{2}/N\textsubscript{2} 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. The new force fields so obtained, tested on accurate ab initio calculations, have been used to perform extensive molecular dynamics simulations of membrane selectivity and adsorption. The accuracy of the potentials granted a quantitative description of the interactions and realistic results for the dynamics under a wide range of conditions of applied interest, indicating that, at low pressure, graphtriyne bilayer membranes exhibit good performances as a molecular sieving candidate for post-combustion CO\textsubscript{2} separation due to a high permeance and a relatively good selectivity. On the other hand, graphtriyne trilayer membranes present a relatively high interlayer adsorption selectivity and high CO\textsubscript{2} uptake. Such properties make these graphyne nanostructures versatile materials competitive with other carbon- based adsorbing membranes suitable to cope with post-combustion CO\textsubscript{2} emissions.

Figure 1. Snapshot of configuration for the CO\textsubscript{2}/N\textsubscript{2} mixture with and trilayer membranes, calculated at 27.548 atm, respectively. In the snapshots, the z-axis is perpendicular to the the horizontal plane where the membranes are laying.

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Study of promiscuous amidase activity of *Candida antartica* Lipase B combining experiment and theory

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Many enzymes in nature are capable to catalyse secondary reactions in addition to their native catalytic activity. This is known as enzyme promiscuity. A well known promiscuous enzyme is *Candida antarctica* lipase B (CALB), a Serine hydrolase capable to catalyze a wide variety of reactions such as hydrolysis of triglycerides and glycolipids, synthesis of esters and epoxidation reactions, etc[1]. For this reason CALB has become an interesting protein to develop new biocatalysts[2] for the production of high value chemical compounds. Among all these reactions, amidase activity has special interest because of its role in many biological and industrial processes. In the present work, we have focused in a theoretical-experimental approach to understand and characterize the catalytic mechanism of hydrolysis of amides displayed by CALB[3] that can be used as starting point to develop more efficient and optimized enzymes.

The theoretical part has been focused in the study of the amidase reaction mechanism in CALB using hybrid quantum mechanics/molecular mechanics (QM/MM) methods, following previous studies on the Diels-Alderase and Hydrolase activity of CALB carried out in our laboratory[4,5]. The evaluation of free energy surfaces of every single step along the explored mechanism, describing the QM subset of atoms at semi-empirical and DFT level of theory, has allowed a detailed description of the reaction mechanism and its kinetics. These theoretical results have been complemented with kinetic experimental studies of the hydrolysis of the amide bond. Recombinant *Pichia pastoris* has been used as expression host to obtain the native free form of CALB, and it was used to test the amidase activity displayed by the enzyme on a short N-acyl-bencyl-amide in an aqueous monophasic system.

These results will serve as starting point to design more efficient biocatalysts via rational mutagenesis to be used in the synthesis of high value organic chemicals.

References


DFT Studies on a Borylative Ring Closing Reaction toward Spiro- and Dispiroheterocycles

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A Cu-catalyzed borylative ring closing C-C coupling of an alkenyl halide towards the synthesis of spiro- and dispiroheterocycles is explored.123 Computational studies reproduce the experimental trends and rationalize the preference of the reactions leading to the strained smaller rings. The identified key step is the concerted halogen abstraction and ring closure through transition state TS2, where the negative charge of the leaving group is stabilized by the nearby presence of the cation, which is also interacting with phenyl rings attached to the phosphines. The formation of the 4-membered ring brings naturally the leaving group in the vicinity of cation. This is not the case for the transition states leading to the 5- and 6-membered rings. The organic chains in these systems have to distort, with the subsequent energy penalty, to keep the attractive interactions. We also identify significant dependence of the key step on the halogen leaving group and the cation of the base employed upon the efficiency.

References
Cow milk - consisting of water, fatty acids, proteins, sugars, minerals and vitamins – is the one of the most consumed food of the world. Milk supplies a healthy dose of essential vitamin A. This vitamin has long been used as a probe in milk: Bindings with fatty acids and β-lactoglobulin protein are related with specific changes in the electronic spectrum and fluorescence of vitamin A [1]. However, it is still an open question what kind of interactions are responsible for these spectroscopic responses [2].

Here a theoretical investigation of vitamin A in its forms: Retinol, Retinal and Retinol-ester is conducted. The geometries of molecules were fully optimized at B3LYP/6-31+G(d,p) level of theory. By means of Time-Dependent DFT, spectroscopic properties were obtained in vacuum (ε=1.0) and some solvents: benzene (ε=2.3), acetonitrile (ε=36.6) and water (ε=78.5), where ε are the respective dielectric constants (Figure 1). The medium effects were included using the polarizable continuum model (PCM) [3].

We reveal which computational tools allow monitoring vitamin A compounds when submitted to solvents with diverse dielectric constants. According our studies the environment has crucial importance in the spectroscopic responses of vitamin A.

References
Study of Fragmentation Mechanism Utility for Drug Metabolites Collision Cross Section Calculation and Reparameterization of N₂ MOBCAL Code

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Ion Mobility Mass Spectrometry (IM/MS) is a technique that allows separation of isomeric species based on differences in their gas-phase collision cross sections (CCSs), thus providing specific information on the potential structure of a compound [1]. Along with Molecular Modelling, it is a potential tool for small molecule identification by measuring their gas-phase CCSs and comparing them to theoretically derived CCS databases. A protocol for theoretical determination of CCS has been introduced in [2] and its improvement is in progress. Our group has developed a script – an extensive automation of the protocol, which allows all the routines and necessary steps of the algorithm to be performed automatically. Furthermore, new atomic parameters employed in the CCS determination software (MOBCAL [3]) have been introduced: the protocol has been modified to be able to distinguish between different atom types and to assign appropriate parameters. Broad tests of the protocol with the featured parameters have been made to assess the performance of the new script. The results have shown that there is a systematic inconsistency with the experimental data that must be studied further.

A possible source for the observed discrepancy may be the fact that experiments were run in the environment filled with Nitrogen gas, whereas theoretical calculations were performed in Helium. Even though a correction factor has been introduced to tackle the issue, a reparameterization of MOBCAL to calculate metabolites’ CCSs assuming atoms interacting with Nitrogen gas has been considered as a better workaround. That required a calculation of new Lennard-Jones parameters for “atom type - N2” pairs and their implementation in the software. Additionally, chemical dynamics simulations for collision-induced dissociation of molecules under study are in course with the aim of getting more information about the fragmentation process. Theoretical identification of fragmentation pathways may contribute to a better understanding of the processes in the MS part [4]. Such simulations are performed with the software packages VENUS [5] coupled to MOPAC [6] for electronic structure calculations.

Thus, further research is aimed at investigating deeper the influence of the introduced changes as well as searching for possible sources responsible for the differences between the theoretical and experimental CCS values taking into account newly obtained results.

References

Computational insight into formation of metathesis active sites from tungsten oxide precursors on silica

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Theoretical chemistry methods are now routinely applied in the field of heterogeneous catalysis. They are helpful in interpretation of experimental results and provide complementary information about active sites and mechanisms of surface reactions, still not fully available from spectroscopic techniques.

WO$_x$/SiO$_2$ system is an industrial catalyst for large-scale metathesis of light alkenes [1]. Tungsten alkylidene sites, required for alkene metathesis, are generated in situ from the surface tungsten oxide species upon contact with alkene [1-4]. The structure and oxidation state of the tungsten oxide precursors, as well as, the mechanism of the transformation of the surface metal oxide species into the active sites are not well recognised, although several routes were proposed [1-4]. In this theoretical study we have made efforts to determine the most feasible initiation mechanisms for olefin metathesis catalysed by WO$_x$/SiO$_2$ system.

Cluster models based on the periodic amorphous structure of dehydrated silica surface [5,6] or β-cristobalite structure were built to represent the WO$_x$/SiO$_2$ catalyst. Geometry optimization of the systems studied was performed using the hybrid PBE0 functional combined with the def2SVP basis set. Harmonic vibrational frequencies were computed to confirm the potential energy minima or saddle points and to evaluate Gibbs energy for each structure. The transition states were additionally verified by the IRC analysis. Single point energies were calculated at the PBE0/def2-TZVPP level and they include the DFT-D3 dispersion corrections. All calculations were done applying the Gaussian 09 software.

On the basis of the reaction pathways calculated, it is concluded that the pseudo-Wittig mechanism involving the formation of oxatungstacyclobutane intermediate is a probable route for the transformation of the surface W(VI) oxide species into metathesis active W(VI) alkylidene centres. The W(V) oxide precursors should be less reactive than the W(VI) species. Regarding the W(IV) oxide precursors, the pseudo-Wittig mechanism, 1,2-hydrogen shift and tungstacyclopentane formation, followed by 1,4-hydrogen shift, might be plausible initiation mechanisms.

References

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Ab-initio calculations of Electronic and Thermoelectric Properties of p-type 
$\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi}$)

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We present systematic study of the effects of substitutional doping on the transport properties and electronic structure of $\text{Cu}_3\text{SbSe}_4$. To this end, the electronic structures and thermoelectric parameters of $\text{Cu}_3\text{SbSe}_4$ and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi}$) have been systematically studied by using Density Functional Theory (DFT) and the Boltzmann semi-classical transport theory. Substitutional doping at Sb site with IIIA ($\text{M} = \text{Al, Ga, In, Tl}$) and IVA ($\text{M} = \text{Si, Ge, Sn, Pb}$) elements significantly increases the hole carrier concentration and the electrical conductivity, while doping with $\text{M} = \text{Bi}$ would be adequate to provide high $S$ values. Changes in calculated thermoelectric parameters are explained based on the effects of the dopant element on the electronic band structure near the Fermi level. Our results allow us to infer significant insights into the search for new materials with improved TE performance by modifying the electronic structure through substitutional doping.
Influence of chromium hyperdoping on the electronic structure of CH$_3$NH$_3$PbI$_3$ perovskite

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Organic-inorganic hybrid halide perovskites compounds are emerging as new materials with great potential for efficient solar cells. This paper explores the possibility of increasing their photovoltaic efficiency through sub-bandgap absorption by way of the in gap band (IGB) concept. Thus, we assess the formation of an in gap band as well as its effect on the absorption features of Organic-inorganic hybrid halide perovskites CH$_3$NH$_3$PbI$_3$ (MAPI). For this task, we use density functional theory (DFT) as well as many-body perturbation methods along to spin-orbit coupling (SOC) to study structural, energetic and electronic properties of partially Cr-substituted MAPI perovskites (CH$_3$NH$_3$Pb$_{1-x}$Cr$_x$I$_3$). Our results reveal that Cr replacement does not lead to an important cell distortion, while the energetic of the substitution process evidences the possibility of obtaining Cr-substituted perovskite. The analysis of the electronic structure shows that Cr 3$d$-orbitals induce new electronic states in the host semiconductor bandgap, which fulfill the requirements to be considered as an IGB. Precise many-body perturbation methods in $G_0W_0$ approach provided an accurate description on the electronic structures as well as the position of the IGB. In short, Pb replacement by Cr could be useful for improved absorption features through new sub-bandgap transitions across the in gap band[1].

References

Excited state deactivation mechanism of pyrimidine free base

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Studying the excited state behavior of nucleobases and their derivatives is crucial to reveal the origin of the photostability of DNA and RNA and the reasons that explain why the five canonical bases were selected in favor of other chromophores during the prebiotic era \cite{1}. In this context, recent works have shown that the photostability of Adenine and Guanine cannot be ascribed to their shared purine core \cite{2}, as its excitation leads to long-lived singlet excited state species that can undergo intersystem crossing to the triplet manifold, that might in turn evolve to photoproducts.

A study of the photophysics of some pyrimidine nucleobase derivatives \cite{3} showed that they (2,4,6-triaminopyrimidine and barbituric acid) are able to dissipate the excess of electronic energy in few picoseconds, although there is no evidence about the mechanisms that would explain their stability. Is the pyrimidine core responsible for the very efficient internal conversion process in these systems or, as it happened with A and G, the substitution pattern of purine is the main responsible for such photostability?

In this communication, we present a theoretical and experimental study of the photophysics of pyrimidine free base. Excitation at 268 nm leads to the direct population of different S\textsubscript{1} (nπ*) minima. Internal conversion funnels leaking population out from these minima to the ground state lie very high in energy or behind non-accessible barriers. On the other hand, intersystem crossing to the T\textsubscript{2} (ππ*) is located very close to those minima, thus allowing the transfer of population to the triplet manifold. Femtosecond broadband transient absorption experimental results are consistent with the topography of the PES, as they show that the population is retained in an excited state in nanosecond timescales.

References

Molecular structure of the intercalation of organo-iron complexes in montmorillonite

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Phyllosilicates are good candidates for nanofunctionalized materials due to their high adsorption properties. The high cation exchange capacity and swelling properties of 2:1 phyllosilicates allow the formation of organoclay where the behavior of water in the nanospace is critical. The Fe complexes with phenanthroline and other diimine derivatives have interesting analytical and catalytic applications. The μ-oxo bridged binuclear Fe complexes show a special interest due to the critical role of μ-oxo bridged binuclear center in the catalytic activity of some iron proteins, such as, hemerythrin and ribonucleotide reductase [1].

In this work, we study the crystal polymorphs of μ-oxo bridged binuclear Fe⁺³ complexes of 1,10-phenanthroline, its intercalation and immobilization in the interlayer of montmorillonite (Figure 1), and its selective adsorption of sulfur compounds. The experimental research has been complemented with computational modeling at quantum mechanical level based on Density Functional Theory and periodical boundary conditions. This complementary has allowed the identification of the geometrical disposition of the complexes, the hydration coordination of the water molecules and the explanation of the physico-chemical properties of these nanofunctionalized materials.

Figure 1. The μ-oxo-di-fac-[triaqua-(1,10-phenanthroline-κ²N,N’)-iron(III)] complex immobilized in montmorillonite.

References
Studying the structural complexity in hydrocarbonaceous nanoparticles using Parallel Tempering Molecular Dynamics

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The study of the spectroscopy of polycyclic aromatic hydrocarbon particles (known as PAHs) in the interstellar medium (ISM) has been a hot topic in astrophysical studies since 1973, when Gillett, Forrest and Merrill discovered a family of mid-infrared emission bands when measuring different regions of stellar objects, planetary nebulae and other extragalactic sources [1-3]. Thanks to posterior observational and experimental evidence [4], and although the exact nature of this mid-infrared carriers is still unknown, these bands are nowadays assigned to a population of PAHs and are referred as AIB’s, aromatic infrared bands [5]. The PACHYNO project (Probing the diversity of Astrophysically relevant Carbon and HYdrogen NanOparticles) relies on the synergy of state-of-the-art computational and experimental techniques to study the isolated carbon/hydrogen-based nanoparticles in the size domain of 20 to 200 atoms as potential AIB carriers.

One of the first steps of this project has consisted on exploring the extensive structural complexity in these hydrocarbonaceous nanoparticles. The chosen approach to this matter has been the analysis of the Potential Energy Surface (PES) of systems of the type CₙHₙ using Parallel Tempering Molecular Dynamics (PTMD) [6]. Due to the complexity of these systems, the use of ab initio wave function approaches or DFT methods to describe the chemical and physical properties is limited to relatively small systems. So, our study has been based on an alternative Tight-Binding approach, the density-functional-based tight-binding method (DFTB) [7]. This method has demonstrated to contribute as a good link between accuracy and computational cost when describing the electronic structure of large systems and in combination with PTMD provides an excellent tool to successfully explore the PES.

In this communication we present the most recent theoretical results of neutral CₙHₙ systems in the gas phase with n = 24 carbons and m = 0, 4, 6, 12 and 18. Coronene-like structures are most probable to find with 0 < m ≤ 12, since the interactions between hydrogen and carbon atoms help with the formation of rings. For values of m > 12 the system dissociates, showing that in atmospheres rich in hydrogen the formation of this kind of structures is impeded.

References
New computational insights on catalytic Wittig reaction

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Computational modeling has been a prominent way of explaining and even predicting experimental results during the last three decades[1]. Redox-driven phosphorus catalysis has been a growing field in the last decade[2]. This paper presents to the audience state-of-the-art approaches in modern computation aiming to understand the synergistic reactivity of phophines, phosphoranes and phosphine oxides in catalytic Wittig reaction[2], Figure 1.

![Transition structures of important steps](image)

**Figure 1.** Schematic representation of CW reaction with transition structures of important steps.

Deterministic integration of simple reaction equations, built on thermodynamic data extrapolated from electronic structures (M06-2X-D3/def2-TZVP/SMD), mimics the complex network of equilibria underlying the reaction. The rate determining steps (Figure 1), the importance of phosphine oxide reduction by \(\text{H}_2\text{SiPh}_2\) and, most of all, the diastereoselective principles are discussed in details. The study proves the influence of ylidic isomers onto the diastereoselective footprint of the catalyst and irrevocably explains why stabilized ylides are inert towards the production of Z-diastereopure olefins.

**References**

Effective potentials to model electron confinement in Quantum Dots

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Quantum Dots (QD) are regions of space where, due to a given potential, particles such as electrons are confined. As these regions shrink, a critical size is reached at which properties from the microscopic world as energy quantization, electronic and magnetic structure formation emerge. This way, these entities gain interesting properties and can be applied to a wide range of technologies, i.e.: quantum bits (QuBits) and photovoltaic panels among others.

From a chemical point of view, a molecule or a nanoparticle that confine their valence electrons can also be taken as quantum dots. Therefore, these systems can be described in two ways: the first one, the most standard one, solving the Schrödinger equation describing all the electrons and nuclei explicitly. The second one is based on using effective Hamiltonians which emulate the effect of the nuclei and the most inner electrons on the valence ones. Thanks to this approach, the dimension of the problem get much smaller and modelling condensed phases (i.e. solids) becomes affordable.

![Gaussian confinement potentials emulate effective wells for electrons in a zero dimensional QD, a dimer and a 3D structure.](image)

**Figure 1**: Gaussian confinement potentials emulate effective wells for electrons in a zero dimensional QD, a dimer and a 3D structure.

**References**

Energy transfer from thermally excited vinyl derivatives to metal surfaces. An Ab Initio Molecular Dynamics study

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Interaction of organic molecules with metallic surfaces has been widely studied in last years, both theoretically[1] and experimentally[2]. These studies usually focus on static properties, such as adsorption geometry, binding energy, electronic structure, charge transfer, etc.

In this communication we present an Ab Initio Molecular Dynamics (AIMD) study of the evolution of vinyl derivatives (acrolein, acrylamide and acrylonitrile) adsorbed on a pristine Cu(111) surface, when they are thermally excited.

The potential is calculated on the fly using Density Functional Theory (DFT), including weak interactions through the use of the methodology proposed by Dion et al[3]. Periodic Boundary Conditions (PBC) are also taken into account, in order to have a correct description of the metallic character of the surface.

Different processes (desorption, bond breaking…) are analysed, as well as the amount of energy transferred from the molecule to the surface and the time that this requires. This information is useful to understand stability upon excitation and heterogeneous catalysis.

\textbf{Figure 1.} Examples of two different processes. Left: molecular desorption and bond breaking; right: molecular desorption without bond breaking.

References

Modelling of DNA intrastrand photolessions induced by natural- by thio-nucleobase substitutions

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For many years, drugs based on thiosubstituted nucleobases have been used as immunosuppressants and anti-inflammatory agents.[1] Interestingly, the dramatic change in the photophysical and photochemical properties of natural nucleobases provoked by sulphur incorporation in the structure of these biomolecules, has awakened a strong interest for the potential use of these prodrugs as photochemotherapeutic agents.

Upon light absorption, these thiobases, either immersed in solution or incorporated in DNA macromolecules, are able to generate long-lived excited states that would interact with environmental molecules, such as molecular oxygen or neighbouring canonical nucleobases,[2] leading to products cytotoxic to cells [3].

In this communication, we present a DFT analysis, including solute-solvent interactions, of the thermodynamics, for a selected group of nucleobase thioderivatives against ground state molecular O₂, of charge (Type I) and energy transfer (Type II) processes responsible for the formation of ¹O₂ and other reactive oxygen species in solution.

Additionally, we propose a reaction mechanism, for the two most important photocrosslinking lessions, cyclobutane pyrimidine dimer and pyrimidine-(6-4)-pyrimidone photoproduct [2], that might result from the exposure of thiosubstituted DNA to UVA light. For this purpose, we have explored the topography of singlet and triplet potential energy surfaces of a dinucleoside monophosphate model, including a thymine and a 4-thiothymine nucleobase, See Figure 1, with DFT and the multiconfigurational methods CASSCF and CASPT2.

Figure 1. Structure of the dinucleoside monophosphate model including stacked thymine-4-thiothymine nucleobases.

A detailed understanding at molecular level of the mechanism leading to DNA damage or to the generation of cytotoxic species is crucial for the improvement or design of new drugs for photochemotherapeutic applications.

References

Hydrotreating process in small heterocyclic rings: DFT study

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Abstract
A theoretical investigation has been realized by use of DFT-B3lyp/cc-pvdz calculation levels to clarify at the atomic scale the hydrotreating process which depends on the remove of sulfur, nitrogen and oxygen atoms from the small heterocyclic rings such as thiirane, aziridine and oxyrane. Activation of C-S, C-N and C-O bonds has been done via a simple and a double protonation followed by a full optimization of geometry. Critical points on the potential energy surface, of the protonated systems, were located by use of the frequency calculation. Our results indicate that the small protonated heterocyclic rings have revealed a carbocationic system as organic reactive intermediates presented by a complex with a weak interaction. In addition, proton affinities and charge delocalizations based on NBO analysis have been taken to check the ability of the lone pair of heteroatoms to participate in the formation of H-S, H-N or H-O bonds.

Keywords: DFT, Hydrotreating processes, Carbocationic system, Small heterocyclic rings, NBO analysis.

References
Theoretical Study of Halosiliconate: Structure and Charge Delocalization

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Structures of pentavalent halo-siliconate R-O-Si(CH₃)₃X⁻ (X = F; Cl; Br) and (R = CH₃; CH₂-CH₃; -CH(CH₃)₂; -C(CH₃)₃; -CH₂CH₂; -C₆H₅) are investigated using density functional theory (DFT) calculations at b3lyp-6-31G(d) level to understand their structure bonding characteristics and delocalization of electronic density. Our results indict that pentavalent fluoro-siliconate R-O-Si(CH₃)₃F⁻ are a stable intermediates for all substitutions with a trigonal bipyramidal geometry, the substituents prefer the axial position and the loss of alkoxy group is observed and detected via electron charge transfer. In the case of X = Cl; Br intermediates adopts a structure in which the alkoxy group is nearly double bonding with silicon atom. The loss of Cl⁻ and Br detected by negative their charge (-0.941) and distance of (3.89). GIAO method permits to calculate ²⁹Si NMR shifts for the R-O-Si(CH₃)₃X⁻ systems as a function of (Si–X) distance and Si-O-C angle.

Keywords: DFT, pentavalent halo-siliconate, charge delocalization, GIAO, NMR shifts.

Figure 1. Structures of chloro and fluoro siliconate in axial position with the alkoxy group.

References

Generation of Stoichiometric Rutile Wulff Shaped IrO$_2$ Nanoparticles


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Many current technological developments in the pharmaceutical, chemical and energetic fields include the use of nanoparticles. [1] In the energetic case, the use of solar energy to split water molecules catalyzed by nanoparticles of metal oxides is one of the most prolific areas of research. Titanium, ruthenium and Iridium oxide nanoparticles are promising materials in this field.

Understanding the mechanism water splitting at the atomistic level facilitates the improvement and development of novel catalysts. Most of the computational mechanistic studies carried out to date have been done using slab surface models, due to their reduced computational cost and the difficult to build realistic nanoparticles. However, these surface models do not include edges, vertices, and intra-surface interactions, which can play a vital role in the nanoparticles chemical properties. [2]

In order to generate realistic nanoparticles models we developed a computational tool to generate Wulff-shaped stoichiometric nanoparticles models systematically, from the bulk structure, Miller indices of the surfaces to be included in the nanoparticle, and their respective surface energies. The generated nanoparticles were classified by a distribution coefficient index that reflects chemical surface uniformity, the smallest value characterize the more homogeneous nanoparticle. Preliminary results on iridium and rutile oxide show that the obtained nanoparticle models are reasonable and stable. Geometry optimization calculations show that the nanoparticle surfaces suffer modifications that cannot be evaluated with more approximated models.

References

Novel $B_{16}X_{16}$ Borane Clusters by the Replacement of H with Different Functional Groups

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As for small boron clusters, $B_{16}$ molecule normally exists in the quasi-planar structure, as proven many times by various experimental and computational studies\cite{1}. On the other hand, cage-like $B_{16}$ cluster can form by H stabilization as in its borane form ($B_{16}H_{16}$)\cite{2, 3}. In this study, we obtained new closo-$B_{16}$ clusters through the stabilization of the molecule with F, Cl and CN groups by means of density functional theory (DFT) calculations. Geometry optimizations and frequency calculations were performed for the neutral clusters and their di-anions with B3LYP hybrid method and 6-311++g(d,p) level of theory in Gaussian package. According to the frequency data, all optimized structures were found to be stable. While the neutral clusters have $T_d$ and $C_{2v}$ ($C_2$ for $B_{16}H_{16}$) symmetry group points for core 1 and core 2 orientations, di-anions have $D_{2d}$ and $D_{4d}$ point groups, respectively. Electronic structures of the clusters were analysed and the band gap data are given in Table 1.

![Figure 1. The boron core of the clusters which are numbered as Core 1 (left) and Core 2 (right).](image)

<table>
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<th>$B_{16}H_{16}$</th>
<th>$B_{16}H_{16}^{2-}$</th>
<th>$B_{16}F_{16}$</th>
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<td>1.19</td>
<td>2.53</td>
<td>4.91</td>
</tr>
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</table>

*1 and 2 correspond to the boron clusters which have Core 1 and Core 2 orientation.

Table 1. Band gaps of the boron clusters.

References

Rationalization of the Electron Transport in polymeric conjugated chains according to its electronic distribution

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The interest in the field of molecular electronics has increased during the last decade. Whereas the experimental works are focused on the determination of the conductance in single-molecules, the theoretical efforts have been oriented to the rationalization of the conductance in terms of chemical properties. The relation between different commonly used chemical concepts such as aromaticity, bond orders, and polarizability, and its electric response, allows predicting the insulator/conductor nature of a molecular-junction by evaluating its fundamental electronic structure.

The conductance of different oligophenyl structures has been theoretically evaluated[1]. Herein, a molecular junction, constituted by benzene units, shows an increase of the electric conductance as the length of the wire increases, this anti-Ohmic behaviour is exceptional and opposed to the one expected for a common conductor. In order to give a chemical explanation to this behavior, the electron deformation orbitals, constructed by combination of occupied and virtual MOs under some symmetry constrains, have been analyzed. The transmission channel formed by the main pair of EDOs (shown in Figure 1 for n=12)[2,3], which in turn are built from a combination of the HOMO and LUMO MOs, reveals the electrons are directly transferred between the chain ends. Calculations of the localization tensor [4], which can be used as a measure of the conducting ability, and the electron delocalization indices confirm this direct electron transfer mechanism.

Figure 1. EDO of the pX2 system with 12 benzene units

References
Iron–sulfur clusters: outstanding challenges for multireference methods

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Iron–Sulfur (Fe–S) clusters are ubiquitous in bioinorganic chemistry, where they serve a number of key roles [1]. Most of their functions are related to redox chemistry: different clusters have reduction potential values ranging from −700 to +500 mV. This behavior is greatly influenced by the complex electronic structure of the clusters, which implies different patterns of spin coupling between the iron centers [2,3].

![Figure 1. Some common Fe–S motifs taken from protein structures.](image1)

In order to study these molecules with accurate multireference methods such as CASPT2 a relatively large active space is required (~26–30 orbitals for the simplest 2Fe2S cluster), and so we must turn to methods capable of treating such a big number of orbitals like the recently developed DMRG approach [4,5].

![Figure 2. A minimal active space for the [Fe$_2$S$_2$Cl]$_2^-$ cluster (16 orbitals).](image2)

Results obtained from multireference ab initio calculations for some Fe–S model systems will be presented and discussed.

References

Overview of the potential energy surfaces of purine and pyrimidine derivatives: Keys to the photostability of DNA

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Photostability or the efficient redirection of the excited population back to the ground state in ultrashort time scales is one of the most prominent spectroscopic characteristics of DNA, for its implications in current terrestrial life\cite{1}.

In fact, the topography of the excited potential energy surfaces (PESs) of the spectroscopic states in DNA nucleobases is such that the Franck Condon region is directly connected to internal conversion funnels involving the ground state, granting this way minimal excited state lifetimes, luminescence and triplet quantum yields\cite{2}.

The aim of this communication is to provide an overview of the main decay routes of a selected group of nucleobase derivatives, including raw purine and pyrimidine cores. To this purpose, we have explored the landscape of the PESs of these species, identifying the most relevant stationary points and interstate surface crossings and mapping minimum energy paths, with high level multiconfigurational methods.

Understanding the existing relation between the functionalization schemes of the purine\cite{3} and pyrimidine cores and their observed photophysics is key to determine the electronic and structural factors that established the superiority of the five DNA and RNA nucleobases against other heterocycles.

References

Complexes between ions of like charges stabilized by halogen bonds

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All the intermolecular interactions are due to forces of diverse nature. Among them, those possessing greater strength of attraction are the ones based on purely electrostatic interactions. Thus, the strongest interaction is established between ions of opposite charge, and the dominant energy contribution comes from the coulombic term. On the contrary, if we put together two ions with charge of identical sign, our intuition will report that such an intermolecular interaction would be the most repulsive we could think of and, therefore, as a result both ions would end up being infinitely separated instead of getting closer until an equilibrium distance is reached. Thus, for a long time it has been assumed that it is not possible to find minima between molecules with the same charge in gas phase. However, several recent articles have reported minima structures in hydrogen bonded systems[1-3]. In fact, it is known that the electrostatically-defying interactions between molecular moieties of charge of identical sign are frequently observed in biological systems; anions are bound to the anionic surfaces of proteins, the synthesis and hydrolysis of RNA and DNA require two or more anion species to be constrained in close proximity within a catalytic domain[4], and protonated arginines form ion pairs within a protein subunit or at protein interfaces[5]. However, almost exclusively, hydrogen bond has been the only explored interaction to study complexes between ions of like charges.

In the present communication, the possibility of finding minima in gas phase for halogen bonded systems has been explored in anion–anion and cation-cation clusters by means of theoretical calculations [6]. In addition, the solvent effect on the stability of the clusters has been considered. Few of the anion-anion and cation-cation complexes subject to study are gathered in Figure 1.

Figure 1. Examples of systems considered to study the formation of anion-anion and cation-cation clusters.

References
DFT study on hydroarylation of alkenes and alkynes mediated by a Rh-NHC catalyst

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Hydroarylation reactions consist of the addition of an aryl group and a hydrogen to an alkene or alkyne. These reactions can produce π-conjugated alkylated arenes, an attractive synthetic target due to their relevant applications in medicinal chemistry and functional materials. The transition metal mediated C-H activation pioneered by Fujiwara and Moritani[1] eliminated the need of preactivated arenes. In the last decades, NHC ligands have made a great impact in the homogeneous catalysis because of the high reactivity and stability they grant to the catalyst. Selectivity issues are still challenging, however the introduction of a directing group can improve greatly the chemoselectivity and regioselectivity.

In this work we present a theoretical study, based on density functional theory (DFT), of the mechanism of hydroarylation using 2-phenylpyridine. We will focus on the origin of its selectivity and different reactivity of the different substrates. The C-H activation of 2-phenylpyridine is followed by the insertion of an alkene/alkyne and the later reductive elimination of the π-conjugated alkylated arene. The high selectivity towards the monoarylated arylpyridines using olefins, allows us to explore a tandem hydroarylation with internal alkynes by the activation of the other free ortho C-H bond on substituted 2,2′-arylpyridines. This combination of two catalytic processes (hydroarylation of olefins followed by hydroarylation of internal alkynes) allowed to the synthesis of a series of new arylpyridines with excellent isolated yields.

References
Understanding ammonia N-H bond activation by Ir(I) complexes

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N–H activation of ammonia by late metal complexes is a topic of current interest in chemistry, especially regarding the context of its catalytic functionalization. This is a challenging task, as ammonia tends to coordinate to metallic centers through the nitrogen lone pair rather than through N–H bond activation, forming stable Werner-type NH$_3$ adducts. Hence, the number of reported processes involving the reaction of ammonia with late metallic precursors leading to the formation of amido late metal reactive species is rather limited.\cite{1}

In this work, an analysis of the electronic rearrangements for the oxidative addition of ammonia to a set of five representative (PXP)Ir pincer complexes (X= B, CH, O, N, SiH) is performed. We aim to understand the factors controlling activation and reaction energies of this process by combining different theoretical strategies based on DFT calculations. Interestingly, complexes featuring higher activation barriers yield more exothermic reactions.\cite{2} The analysis of the reaction path using the bonding evolution theory shows that the main chemical events, N–H bond cleavage and Ir–H bond formation, take place before the transition structure is reached. Metal oxidation implies an electron density transfer from non-shared Ir pairs to Ir–N bond. This decrement in the atomic charge of the metal provokes different effects in the ionic contribution of the Ir–X bonding depending on the nature of the X atom as shown by the Interacting Quantum Atoms methodology.

![Scheme 1. Oxidative addition of ammonia to Ir(I) pincer complexes.](image)

References


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Copper involvement in the electron delocalization of the Cu(x)(CH)n (x= 0, I, II; n= 4, 5, 6, 7) metallacycles

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Metallacycles form key intermediates in important industrial catalytic processes, such as olefin, alkyne metathesis or for the generation of highly substituted and functionalized benzene, pyridine derivatives, or other macrocycles; in fact aromaticity in metal containing compounds constitutes a topic of considerable interest, both fundamental and practical. Indeed, the idea of substituting a C–H unit of an aromatic hydrocarbon by an isolobal transition metal was first put forward by Thorn and Hoffmann in 1979, and has continued to be inspirational for the synthesis of metal containing aromatic compounds.[1-4]

In this work we study the heterocycles Cu(x)(CH)n (x= 0, I, II; n= 4, 5, 6, 7) to determine the copper involvement in the electron delocalization of the metallacycles by controlling the π-electrons from the carbon atoms and computing relevant aromatic indices.

Density functional theory (DFT) has been used to optimize and characterized as stationary points, through the harmonic frequency analysis, the title compounds using the hybrid exchange-correlation functional PBE0 and the def2-TZVP basis set. The electron delocalization indices were obtained with the ESI-3D package,[5] using the quantum theory of atoms in molecules (QTAIM) partition.[6]

References
Structural and optoelectronic properties of lead chalcogenide nanoparticles including spin-orbit coupling and dispersion forces effects

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Lead chalcogenides PbX (X=S, Se, and Te) are versatile semiconductor materials with unique structural and electronic properties, not only in bulk form but also when nanostructured. These properties make them good candidates for a variety of technological applications such as thermoelectrics[1], optoelectronics[2], and thermophotovoltaic energy converters [3].

Here, we present comprehensive a density functional theory study of the structure and optoelectronic properties of bulk and nanostructured lead chalcogenides systems. The influence of London dispersion forces, spin-orbit coupling and the perturbative G₁W₀-BSE approach are considered in all cases.

First, we show that the consideration of a hybrid functional including van der Waals dispersion corrections is compulsory to reproduce the lattice constant and the parameters of the Birch-Murtaghghan equation of state of bulk PbX systems. Given that the most exposed surface on (PbX)ₙ nanocrystals is the (001) we review the properties of this surface with the above presented methodology. In a further step, we study the structures and optoelectronic properties of some (PbS)ₙ nanoparticles including the influence of different capping ligands. We show that the use of capping ligands with different electron-donating/-withdrawing characteristics has significant influence on the optical absorption spectra of these systems. Finally, given its importance on the properties of hybrid colloidal quantum dot (CQD) technologies [4], the interaction with a single layer graphene sheet is examined. We found that there is a significant deformation of the graphene layer as consequence of the interaction with the lead chalcogenide nanoparticle.

Figure 1. (PbSe)₁₆ nanocrystal with methanethiol capping ligands adsorbed on single layer graphene.

References
Development of a universal Electron Force Field

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In many cases, the unavailability of an adequate classical force field is a major barrier for molecular dynamics simulations. In these cases, density functional theory (DFT) provides a universal but expensive option. We aim at an intermediate approach, based in VESPR theory [1], in which the electrons and their interactions are described with a minimum of variables, namely, the positions and widths of 'electron balls' whose superposition approximates the electron density. A similar 'electron force field' (EFF) was developed by Su and Goddard [2] for describing warm matter, in which electrons are highly excited. However, their parametrization of electron interactions is too inaccurate to even predict qualitatively the equilibrium geometry of simple molecules. Recently, new ideas have been proposed to improve these electron interactions [3][4].

By fitting a large number of quantum chemical calculations, our goal is to develop a universal EFF accurate enough for quantitative geometry prediction and for molecular dynamics of general systems.

References

Photophysics of Barbituric Acid: a photostability study of RNA nucleobases analogues

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Conserving molecular integrity upon UV light exposure is considered as one of the most important environmental factors that determined the survival of the components of the genetic code beyond the prebiotic scenario [1]. Canonical nucleobases are considered highly photostable systems for the ease with which they dissipate absorbed energy, via ultrafast internal conversion to the ground state, preventing this way DNA/RNA damage [2]. Investigating the decay mechanism of heterocyclic purine- and pyrimidine-based chromophores can help elucidating the origin of the photostability of life building blocks, and at the same time identifying potential prebiotic genetic ancestors that might have composed the primordial soup.

In this work, we investigate the photophysics of barbituric acid (BA), which has been recently identified as a promising candidate for the ancestor of the RNA nucleobase uracil, see Figure 1 [3]. To this aim we have simulated the absorption spectra and explored the topography of the excited and ground state potential energy surfaces of the most important tautomers that might be present in acidic and neutral aqueous solutions. Additionally, we have computed the absorption spectra at critical points of the excited potential energy surfaces that are expected to be populated for some time, and that will allow for the interpretation of experimental transient absorption spectra.

From the synergic combination of the results from our molecular simulations and the outcome of steady-state and broadband transient absorption spectroscopy experiments [4], we elucidate the decay mechanism of, providing some hints on how the substitution pattern of pyrimidine heterocycle might contribute to the photostability of natural nucleobases.

References

On the aggregation of N-heterotriangulene-based supramolecular polymers

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N-heterotriangulenes (HT) are a family of compounds generally based on a carbonyl-bridged triphenylamine core that gives rise to a planar and aesthetically pleasing π-conjugated scaffold (Figure 1). HTs can be additionally decorated with terminal amide functional groups to foster helical supramolecular self-assembles stabilized by hydrogen bonds and π-π interactions. These HT aggregates have turned to be very promising in the field of organic-electronics; particularly, as potential candidates for an efficient exciton transport.[1]

In this contribution, the supramolecular organization of a series of HT derivatives (Figure 1a) is studied by means of Density Functional Theory (DFT) and Tight-Binding DFT (DFTB) calculations augmented with dispersion-corrected approximations. Calculations show that the HT-based derivatives are able to self-assemble in columnar helical stacks governed by a triple H-bonding array between amide groups and π-π interactions between the HT cores (Figure 1b). Additionally, a nucleation-elongation cooperative mechanism for the supramolecular polymerization is predicted in line with an initial fast increase of the binding energy per monomeric unit with the number of molecular moieties and a subsequent asymptotic limit (Figure 1c).[2]

Figure 1. a) Chemical structure of different HT derivatives studied here. b) Right-handed helical columnar arrangement of a heptamer of a HT system. c) Stabilization energy per monomer unit as the number of monomers (n) increases in the (HT)n aggregate computed at the B3LYP-D3/6-31G** level and fit (red line) to a biexponential decay.

References
Theoretical study of La doped BiFeO$_3$: polarization, magnetic properties and structural effects

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One of the easiest methods to improve the dielectric and magnetic properties of BiFeO$_3$, is through doping with Lanthanum. However, there is still discussion about the mechanisms involved to modify polarization and magnetic properties. In this work, using the density functional theory DFT and Berry phase formalism, we study the effects of doping on the primitive cell of BFO; such effects are evinced through the analysis of symmetry and its variations the amount of dopant is increased. Likewise, the deformations of the octahedra occur with the increase in doping directly affecting the polarization and magnetization of BFO. For this purpose, the anisotropy of the Fe-O$_6$ bonds in the direction [111] of the polarization is included as well as the calculation of ELF, which describes the mostly ionic behavior of BFO.

Acknowledgments

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A comparative study of ten analytical forms to represent potential energy curves of the diatomic systems N$_2$, CO and LiF

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In this work, a review of ten functional forms used to represent potential energy as a function of the interatomic distance for diatomic systems is firstly presented. The starting point is the Morse [1] potential, followed by functions from Rydberg [2], Hulburt-Hirschfelder [3], Linnett [4], Lippincott [5], Simon, Parr and Finlan [6], Murrell and Sorbie [7], Takkar [8], Hua [9] and finalizing with the potential for diatomic systems by Aguado and Paniagua [10]. The mathematical behavior of these functions for the short- and long-range regions are discussed. A comparison highlighting the positive and negative aspects of each representation is also presented. Diatomic systems: N$_2$, CO and LiF are selected as study cases. Ab initio energies were then calculated at multi reference configuration interaction using Dunning basis sets extrapolated to complete basis set limit (MRCI/AVXZ/CBS, X=4,5,6) [11]. For the three studied cases, using such functions, rovibrational levels as well as spectroscopic constants are calculated and compared.

Acknowledgements

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References

Ab Initio Investigation of the Degradation of Hybrid Organic-Inorganic Metal-Halide Perovskites

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Perovskite solar cells have recently attracted much attention as the next-generation photovoltaic systems due to their many advantages including simple fabrication, cheap materials, desirable bandgap and excellent charge-transport behaviour. However, the unusually short lifetime of the perovskite solar cells has greatly limited their potential for practical commercial applications. In particular, it has been found that the photo-active hybrid organic-inorganic perovskite materials degrade rapidly under ambient working conditions. The development of more robust perovskites demands fundamental, microscopic understanding of the degradation processes of this class of materials. In this talk, we will present our recent systematic investigation [1-4] of the degradation of the hybrid perovskites in the presence of oxygen, water vapour and other reactive molecular species generated from photochemical reactions in the air. We will examine the possible degradation mechanisms under different conditions and discuss the key factors affecting the degradation processes. The important roles of the photo-generated charge carriers on the degradation and other properties like hysteresis will also be discussed. Such systematic understanding will provide useful guide for rational design of robust perovskite materials for photovoltaic applications.

References
Kynurenine 3-monooxygenase (KMO) is a flavin adenine dinucleotide (FAD) dependent monooxygenase which converts L-kynurenine (L-Kyn) into 3-hydroxykynurenine (3-HK). This reaction situates in a bifurcating point in kynurenine pathway whose overall function can be summarized as the catabolism of tryptophan giving the product nicotinamide adenine dinucleotide (NAD). Excessive function of KMO leads to the increased levels of neurotoxic substance 3-HK, which is shown to be responsible for diseases like Alzheimer’s and Huntingtin’s [1,2]. However, its inhibition causes excessive production of kynurenic acid (KynA) whose normal levels have a neuroprotective effect but, in increased levels, trigger bipolar disorder and schizophrenia [3].

Herein, the mechanism of the hydroxylation reaction between L-Kyn and FAD-hydroperoxide was investigated in the presence of KMO enzyme by considering various possible pathways that can lead to the product 3-HK. The calculations involving the active site model were based on the KMO of *Pseudomonas fluorescens* bacterial system (pdb code: 5NAK) X-ray structure. The calculations involved a cluster model in which the active site of the enzyme with the substrate L-Kyn was represented with 348 atoms and were carried out with B3LYP functional with 6-31G(d,p) basis set. These calculations allowed us to deduce a mechanistic pathway of KMO catalysed hydroxylation reaction.

![Figure 1. KMO catalysed hydroxylation of L-Kyn.](image-url)

References

Inter and Intramolecular [2+2] Cycloaddition Reactions of Keteniminium Salts - A DFT Study

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Keteniminium salt (KI), nitrogen analog of ketene is widely used intermediate for the synthesis of biologically active substances.1,2 Recently, KI reactions such as electrocyclization reaction,3,4 Michael additions reaction5 and inter and intra-molecular [2+2] cycloadditions6-10 with alkenes/alkynes leading to cycloalkane/cycloalkane have been reported. However, efficient and general method to access substituted cyclobutanones/cyclobutenones are still limited. Therefore, keteniminium chemistry has gained considerable interest. Consequently, a DFT study was performed in order to investigate the experimentally observed reactivity differences in the inter and intramolecular [2+2] cycloaddition reactions (Scheme 1). Additionally, competition reactions between intramolecular [2+2] cycloaddition and 6π-electrocyclization of KI were examined and experimental findings were elucidated by means of DFT study.

Scheme 1. Schematic representation of the [2+2] cycloaddition reactions of KI.

References
Molecular Modeling for the Classifications of Potential Antimalarial Phenazine Compounds

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Abstract

Keywords: Phenazines, cheminformatics, Antimalarials.

BACKGROUND: Malaria is an endemic disease affecting the tropical and subtropical countries with mortality and morbidity expressive, being considered a public health problem. Quinone compounds and their Phenazine derivatives have been implicated in biological activity of the parasite that causes malaria, the Plasmodium vivax, P. ovale, P. malariae, P. falciparum. The Phenazines are tricycle nitrogenous derivatives quinone rings used as antibiotic drugs, besides presenting antitumoral antiparasitic, antimalarial, trypanosomiasis and anti hepatitis C properties [1].

METHODS: Phenazine compounds underwent DFT calculations yielding various various structural descriptors, i.e empirical and non-empirical electronic, topological, geometric stereo and others . Multivariate analysis of the data was performed using chemometric techniques PCA, HCA, KNN, K-means and methods of artificial intelligence-type RNAs [2].

RESULTS: A satisfactory model statistically and mathematically correct was reached after careful consideration of all the circumstances and conformational parameters obtained are relevant to describe the antitumor property of Phenazines. An analysis of the geometry of the molecules and the potential energy maps for regions of interest allowed a viable model to correlate the chemical structure of phenazines with antimalarial properties [2].

References

A quantum dynamics study of collisions between sulphur atom and cation with molecular hydrogen

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The presence of sulphur-bearing molecular species in the interstellar medium (ISM) has attracted the attention of the astrophysics community [1]. Particularly the collision of atomic (neutral and cation) sulfur with molecular hydrogen is believed to play a role in the formation of interstellar ices [2]. Being triatomic species, isolated H₂S and H₂S⁺ can be also considered as benchmark molecular systems already studied by both experimental and theoretical techniques [3-7]. In this work, we present a quantum dynamics study of collisions S⁺ +H₂ (x=0,+1) in the frame of the coupled-channel hyperspherical coordinate method as implemented in the ABC code [8]. Stereodynamics analysis of the studied reactive collisions is carried out. Reaction differential and integral cross section are calculated and compared with available literature. A discussion comparing results obtained with corrected quasi-classical calculations is also presented.

Acknowledgments

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References

Cheminformatics Applied on Psychoactivity in Cannabinoids Compounds

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Keywords: CHEMINFORMATICS; PSYCHOACTIVITY; CANNABINOIDS.

It was recently proven that, Cannabis Δ9-Tetrahydro-Cannabinol (THC, effective substance in Marihuana and Hash) can cause releases of dopamine in the Nucleus accumbens, which are suppressed by the Opioid antagonist. Using DFT was possible to verify that the conformers of AMG3 at the CB1 receptor favor to establish a cis conformation defined between aromatic and dithiolane ring and a trans conformation in the CB2 receptor. Different cannabinoids compounds and his metabolites have been investigated with quantum calculations and Cheminformatics to establish correlations between chemical structure and psychoactivity. Geometric optimizations and several physical-chemical properties were obtained from semi-empirical calculations (AM1, PM3 and PM5) and DFT calculations. Several molecular descriptors were obtained by these properties from multivariate treatment, and some chemometric techniques were applied including PCA, HCA, K-means, KNN and RNAs.

Among all the molecular descriptors calculated, the most relevant ones to discriminate according to their psychoactivity were those related to electronic, lipophilic and stereo-geometric properties (E_{LUMO}, T2 and Log P). Thus, the compounds were classified into psychoactive (A1), moderately psychoactive (A2) and psychoinactive (B) groups. The models obtained were used to study additional 22 cannabinoids compounds, and our predictions related to the psychoactivity were in good agreement with the experimental evidences1.

A satisfactory model statistically and mathematically correct was reached after careful considerations of all the circumstance and conformational parameters obtained are relevant to describe the property cannabinoids.

References

Conformational Effects of the Novel Eight-Membered Heterocyclic Structure on Asymmetric Aldol Reaction

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Homoboroproline catalyzed asymmetric intermolecular aldol reaction between \(p\)-nitrobenzaldehyde and acetone was reported by Georgiou et al [1]. The mechanism of this reaction was computationally investigated by our group which revealed that the formation of the eight-membered heterocyclic ring was the crucial step [2]. Rate-determining step of the aldol reaction was found to be proton transfer step while in some cases it was the water addition step. In trans-eight membered ring water approaches from the top of the ring while in cis-eight membered ring it approaches below the ring (Figure 1).

Conformational analysis of cis- and trans-cyclooctene ring was investigated and well documented in the literature; however, our novel pirolodine fused eight membered ring structure has not been studied yet [3,4]. In order to explore the effect of the structure and conformations of this novel eight-membered heterocyclic molecule in the transition states, quantum chemical calculations were performed employing Gaussian 09 [5] at M06-2X[6]/6-31+G(d,p) level of theory with a PCM [7] solvation model in acetone. The outcome of the conformational and structural analysis will provide valuable insights on the factors influencing the stability of the eight-membered ring transition states. The results obtained from the calculations can be also used to deeper understanding of the mechanism of the aldol reaction.

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References

Conceptual Quantum Chemical Analysis on the Nature of the Chalcogen Bond

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In the last decades, the importance of noncovalent interactions has been recognized in various subfields of chemistry, particularly in supramolecular chemistry, materials chemistry and the chemistry of living matter.[1] Besides its well-known noncovalent sisters, the hydrogen bond and the halogen bond, more and more attention is paid to the chalcogen bond, describing the interaction between group VI elements acting as electron-deficient chalcogen donor (Ch) and a Lewis base as chalcogen acceptor.

In our study, we have explored the main features of chalcogen bonding through an in-depth computational study on a series of donors (with Ch=Te/Se/S) and acceptors (halides and neutral Lewis bases) spanning a wide range in strength and character[2] of this type of bond. A preliminary analysis based on Pearson’s Hard and Soft Acids and Bases principle,[3] in which the Molecular Electrostatic Potential (MEP) quantifies the hard nature and the Fukui function the soft nature of the interaction (see Figure 1), showed a more pronounced σ-hole when going down in the periodic table (Te > Se > S) and n®σ* electron donation of the Lewis base to the chalcogen centre.

Subsequently, additional conceptual quantum chemical techniques have been applied to further scrutinize the characteristics of the chalcogen bond. A Ziegler-Rauk energy decomposition analysis revealed that electrostatic interactions dominate orbital interactions more distinctly for neutral Lewis bases than for the halides. A Natural Orbital for Chemical Valence (NOCV) analysis, used to visualize and quantify the charge transfer upon formation of the chalcogen bond, confirmed the n®σ* electron donation as described above. Furthermore, the Quantum Theory of Atoms in Molecules (QTAIM) study at the bond critical point and the Noncovalent Interaction (NCI) analysis classifies the chalcogen bond as a strong, noncovalent interaction, in the same range as typical strong hydrogen bonds.[4]

References
Reductive Amination Reaction by Control of Solvent and a Co-Catalyst

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Green chemistry approaches and utilization of natural products from sustainable sources are becoming relevant for industrial applications. The investigation of a facile and more efficient route for a novel hydroaminomethylation process is of great interest to the chemical and pharmaceutical industry. Reductive amination reactions are an efficient route to synthesize long chain amines by using a broad range of aldehydes and ketones, and a variety of amines (Figure 1). The exact mechanism, is dependent on the role of a coordinating solvent from the condensation step and the pH of the reaction medium and thus the protonation states of the intermediates. These parameters which affect the reaction yield and the selectivity are still not fully understood.

Here, we present a computational work on the mechanism of reductive amination including neutral and co-catalyst assisted (as explicit water and acid) reaction conditions. The reaction mechanism and the energy profile were characterized by MP2 calculations and an implicit SMD approach to account for polarization by the solvent. With explicit water assistance, the first addition step proceeded in a stepwise fashion rather than concerted and the activation barrier was lowered. In the co-catalyst assisted system, the nucleophile addition is kinetically disfavored compared to the neutral one. On the other hand, the elimination reaction is thermodynamically driven in the presence of an acid as a co-catalyst. Consequently, altering the reaction parameters does not only influence the reaction kinetics, but also the detailed thermodynamic profile of the pathways in all cases. Further understanding of the microkinetics of each step is essential to develop a kinetic network model of the reaction, to control and steer the process in order to rationally design routes to specific products.
Enzymatic Kinetic Isotope Effects in Human Purine Nucleoside Phosphorylase

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In the present study we report the effect of heavy isotope labeling on the reaction catalyzed by human purine nucleoside phosphorylase (hPNP) to elucidate the origin of its catalytic effect and of the enzymatic kinetic isotope effect (EKIE)[1]. This enzyme catalyzes the reversible phosphorolysis of 6-oxypurine nucleosides and deoxynucleosides to generate α-D-(deoxy)ribose 1-phosphate and the corresponding purine base (see Scheme 1).

Using quantum mechanical and molecular mechanical (QM/MM) molecular dynamics (MD) simulations, we study the mechanism of the hPNP enzyme and the dynamic effects by means of the calculation of the recrossing transmission coefficient. A free energy surface (FES), as a function of both a chemical and an environmental coordinate, is obtained to show the role of the environment on the chemical reaction. Analysis of reactive and nonreactive trajectories allows us to study the geometric, dynamic, and electronic changes of the chemical system. Special attention is paid to the electrostatic potential created by the environment on those atoms involved in the chemical reaction. The EKIE for hPNP has been obtained within the variational transition state theory (VTST) framework[2-4] in very good agreement with the experimental value.

PNP is used as target for transition state analog inhibitor design because is a promising target for the treatment of leukemia, gout and autoimmune disorders. Thus, detailed analysis of transition state structure and a better understanding of enzyme dynamics will allow us to perform a rational approach to the computational design of novel and potent drugs.

References
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XCHEM Approach to the Ionization of Pyrazine

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In order to describe the photoionization of pyrazine, a good description of the electron continuum is required. However, as opposed to bound state calculations, there are not similar and standardized tools and methods. Our group has developed a new approach to account for the electronic continuum1. This new method has been applied successfully to atomic systems like hydrogen and neon2, and diatomic molecules like nitrogen3. In this work we apply the XCHEM method to a molecule as complex as pyrazine.

The XCHEM method uses what is called a GABS basis interfaced with standard QCPs (MOLCAS, MOLPRO) and close-coupling scattering methods for multichannel ionization calculations. By merging both methodologies, we can use multideterminant ab initio techniques to obtain accurate photoionization cross sections.

In this contribution we have studied the photoionization of pyrazine using the XCHEM method and compare it with a well-establish DFT approach4. In this case, single channel-single reference calculations were performed for several angular momenta of the ejected electron with both techniques. Finally, multichannel scattering cross sections were calculated with single reference and multireference methods. These simulations, which describe the effect of the electron correlation in the configurational interaction picture, were used to understand the photoionization cross sections of pyrazine. With the results of single reference and multireference calculations, we can estimate the importance of electron correlation in the description of the bound states and when single channel calculation and multichannel calculations are compared, we can observe the effect of coupling several electronic continua.

References

Computational studies on the interaction of
\([\text{Mo} (\mu-C_3H_5) \text{Br} (\text{CO})_2 (\text{phen})]\) with G-quadruplexes

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It has been shown that G-quadruplex structures have a key role in the transcription process regulation \([1]\) and the interaction between G-quadruplex and planar ligands in metallic complexes have proven to have good anti-tumoral activity, which can be used in chemotherapy \([2]\). Different studies have shown that phen and derivatives interact directly with G-quadruplex guanine bases and stabilize the structure \([3,4]\). Stabilization of the G-quadruplex structures inhibits telomerase activity \([5]\), which is involved in most of cancer cell lines, and stops the cancer cell growth. Because the \([\text{Mo} (\mu-C_3H_5) \text{Br} (\text{CO})_2 (\text{phen})]\) was observed to be cytotoxic to several cancer cell lines in previous experimental studies \([6]\), we studied its interaction with G-quadruplexes by means of computational techniques, such as semiempirical, QM/MM and DFT-D. One of the most stable structures contains the \([\text{Mo} (\mu-C_3H_5) \text{Br} (\text{CO})_2 (\text{phen})]\) totally inside the G-quadruplex.

References

XUV-pump/XUV-probe spectroscopy of N₂

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The theoretical description of observables in XUV-pump/XUV-probe experiments requires a good representation of the system’s ionization continuum. For polyelectronic molecules, however, this is still a challenge due to the complicated short-range structure of correlated electronic wave functions. Whereas Quantum Chemistry Packages (QCP), implementing sophisticated methods to compute bound electronic molecular states, are nowadays standard in most laboratories, comparable tools for the continuum are not yet widely available.

To tackle this problem a new approach developed in our group that uses a hybrid Guassian-B-spline (GABS) basis [1] (see Fig. 1), interfaced with existing QCPs via close-coupling scattering methods [2], has been used for the study of the multichannel ionization of molecular nitrogen.

Nitrogen ionization has been described in our group before [3,4], but this study goes one step further and includes a proper nuclear dynamics propagation and at the same time a good description of the continuum with the methodology described above, allowing us to study the photoionization process with ultrashort XUV laser pulses from a time-dependent perspective. Therefore, different kinds of XUV-pump/XUV-probe experiments can be reproduced theoretically.

References

Figure 1. Schematic representation of the GABs basis.
RuO$_2$ – Water Interface Analyzed by Means of Ab-Initio Molecular Dynamics Simulations: Effect of Surface Morphology and Water Coverage

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The formation of molecular oxygen from the oxidation of water is the most challenging step in the water splitting process. To overcome this critical semi-reaction, heterogeneous catalyst or nanoparticles based on metal oxides have been used. In particular, ruthenium oxide based materials have been shown to be good candidates, due to its unique redox surface chemistry and conductivity.[1]

In this contribution, DFT calculations with periodic boundary conditions [2] have been carried out to analyse water adsorption on different RuO$_2$ based materials. In particular, we have analysed the water adsorption energy onto the most stable RuO$_2$ surfaces paying special attention in to the effect of water coverage. In addition, Ab-initio Molecular Dynamics (AIMD) of the whole surface-water interface have also been performed to study the effect of additional non-directly adsorbed water as well as the thermal effects. On the other hand, Wulff construction [3] approach has been used to build RuO$_2$ nanoparticle and analyse how water adsorption is influenced by the nanoparticle shape and size. Results show that water coverage, surface morphology and temperature play an important role in the degree of water dissociation on the surface, which is characterized by the formation of [H$_3$O$_2$]$^-$ units. [4] Moreover, comparison between surface and nanoparticle models reveals an important influence of the size of the material.

![Figure 1. Artistic representation of the nanoparticle model.](image-url)

References

Benzothiadiazole-Based Hole-Transporting Materials for Perovskite Solar Cells: A Theoretical Insight

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In the search for low-cost alternatives to power sources based on fossil fuels, perovskite solar cells (PSCs) have emerged as a potentially disruptive technology. PSCs are generally sandwiched between layers of electron-transporting materials (ETMs) and hole-transporting materials (HTMs) to optimize the extraction of holes and electrons toward the corresponding electrodes and, thus, for the improvement of the device performance. In the last years, a great effort has been made to synthesize novel and efficient HTMs for their use in PSCs [1]. However, a deep understanding about what structural and electronic features are essential to make an HTM optimal for efficient PSCs is scarce [2,3].

In this contribution, we present a quantum-chemical characterization of the structural, electronic and optical properties of two different families of HTMs with implications for PSCs by means of density functional theory (DFT) and time-dependent DFT (TDDFT) calculations. The first family of HTMs (Figure 1a) is based on a benzothiadiazole (BT) core substituted with different electron-rich groups, whereas the second family is based on isomeric forms of the BT core substituted with peripheral $p$-methoxytriphenylamine groups (Figure 1b). Our main goal is to establish precise structure–property relationships that can help for the design of novel and enhanced HTMs for PSCs.

![Figure 1. Chemical structure of the two families of BT-based HTMs with different terminal electron-rich groups (a) and a different core pattern (b).](image)

References

Triplet population mechanism of 4-thiouracil:
A CASSCF/CASPT2 quantum-chemistry study

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In this work the photochemistry of 4-thiouracil is studied to verify its usefulness as a photosensitizer in photodynamic therapy. This study is carried out by exploring its most favourable deactivation paths after the light absorption process and determining the possible triplet electronic state population paths. To carry it out, high precision computational techniques based on the determination of minimum energy paths and the location of conical intersections and singlet-triplet crossings, which are responsible of the internal conversion and intersystem crossing processes, respectively, were used. In order to describe correctly the electronic excited states, the CASSCF/CASPT2 methodology was employed. The calculations indicate that the molecule irradiated with UV light mainly populates the $S_2$ state. Then the 4-thiouracil relaxes vibrationally to the minimum of this electronic state. From here, there are two accessible triplet state population routes: $S_2 - S_1 - T_1$ and $S_2 - T_2 - T_1$. The first path can be considered more favourable since the spin-orbit coupling between $S_1$ and $T_1$ is greater than that between $S_2$ and $T_2$. Once in the $T_1$ state, the molecule relaxes to the minimum of this state and, from here, it is capable of transferring energy to molecular oxygen ($^3O_2$) forming then singlet oxygen ($^1O_2$), which can destroy tumour cells.

Figure 1. Illustrative scheme of the main photophysical and photochemical processes in 4-thiouracil.
Effects of complexation with a metal ion on the intramolecular hydrogen bonds in acylphloroglucinols

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Acylphloroglucinols are a large class of compounds structurally derivative from 1,3,5-trihydroxybenzene and characterised by the presence of a COR group. Many of them are of natural origin and possess a variety of biological activities. Nearly all of them are characterised by the presence of an intramolecular hydrogen bond (IHB) between the sp$^2$ O of COR and a neighbouring phenol OH [1]. Several of them contain substituents with groups that can form additional O–H•••O IHBs [2] or O–H•••π IHBs [3].

Complexes with a Cu$^{2+}$ ion have been calculated for selected acylphloroglucinols having antioxidant activity, and also for some other structurally-related molecules, to evaluate their ability to coordinate and reduce the Cu$^{2+}$ ion [4, 5]. All the sites to which the ion can bind were considered in each case. The complexation causes changes in the parameters of the IHBs (above all the bond length) and in their red shifts, and, for O–H•••O IHBs, may also cause the transfer of the proton to the other O atom. The changes depend on the site/s to which the Cu$^{2+}$ ion binds.

The presentation offers an overview of the effects of complexation on the IHBs present in these molecules, highlighting similarities and differences in relation to the characteristics of each molecule, to the type of IHB (O–H•••O, O–H•••π) and to the binding site of the ion.

Figure 1. The best-energy complex of arzanol with a Cu$^{2+}$ ion.

References
Drastic effect of the peptide sequence on the copper-binding properties of tripeptides and the electrochemical behaviour of their copper(II) complexes


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The amino terminal copper(II)- and nickel(II)-binding (ATCUN) motif (Figure 1) is a peptidic sequence of type Xaa–Xaa–His (Xaa = any amino acid), involved in several biological processes such as metal transport, DNA and protein cleavage or protein cross-linking. As a result, ATCUN-based compounds have been developed as potential metallodrugs. In this study we investigate the effect of the inclusion of a second histidine in the peptidic triad on the binding and physical properties of the ATCUN motif. Hence, the behaviour of five different tripeptides, namely HAH, HWH, Ac-HWH, HHW, and WHH interacting with copper has been examined in great detail, both experimentally by means of cyclic voltammetry measurements and theoretically with DFT calculations.[1] The thorough computational and experimental study clearly reveals that the addition of a histidine residue within the ATCUN motif considerably alters its metal-binding properties and, consequently, the redox behaviour of the resulting copper complexes. The differences observed are directly related to the metal coordination environment, as clearly demonstrated by comparing experimental electrochemical results with those computed using DFT methods for different structures. For CuII–HAH and CuII–HWH, no cathodic processes are observed up to −1.2 V; i.e., the complexes exhibit very high stability towards copper reduction. This behaviour is associated with the formation of a very stable square-planar (5,5,6)-membered chelate rings (ATCUN motif), which encloses two deprotonated amides. In contrast, for non-ATCUN CuII–Ac-HWH, CuII–HHW complexes, simulations seem to indicate that only one deprotonated amide is enclosed in the coordination sphere. In these cases, the main electrochemical feature is a reductive irreversible one electron-transfer process from Cu(II) to Cu(I), accompanied with structural changes of the metal coordination sphere and reprotonation of the amide. Finally, for CuII–WHH, two major species have been detected: one at low pH (< 5), with no deprotonated amides, and another one at high pH (> 10) with an ATCUN motif, both species coexisting at intermediate pH.

Figure 1. Schematic representation of the ATCUN binding site.

References
While coupled cluster methods, especially if the effect of linked triples excitations is taken into account in a perturbational manner, are considered the reference theoretical methods, their high scaling with system size makes them hard to use for calculations that intrinsically require large computational costs. This is the case of the theoretical determination of $C_6$ and $C_8$ coefficients using the Casimir-Polder formulation. Therefore, density functional theory, with a very much smaller computational cost, can become a fundamental tool. However, the intrinsic arbitrariness in the election of the parameterization of the correlation-exchange (XC) functional introduces an extra complication, which can be solved only by carrying out reference calculations. Here we use CC3 [1] (a generalization of CCSD(T) that allows for the definition of a wave function and so the determination of the corresponding response function) to benchmark a large number of XC functionals with different atomic basis sets.

Linear response functions were computed analytically using Dalton [2], except those for DFT quadrupole polarizabilities, which were numerically determined with Camcasp [3]. Furthermore, polarizabilities at the coupled cluster level were calculated from Cauchy coefficients [4] by means of Padé approximants $[n, n-1]$. The integration was done through 6-points Gauss-Legendre quadrature. Finally, the difference between reference CC3 and DFT results has been measured in terms of a distance defined from a generalized form of the Minkowski metric [5].

Calculations show that simple augmentation in correlations consistent basis is enough for stabilizing dipole polarizabilities, but at least double augmentation is required for quadrupole ones. Similarly, while $C_6$ coefficients can be calculated with triple zeta basis, $C_8$ requires quadruple zeta basis. Also, it was determined that a reasonable accuracy is obtained with $n = 4$ in Padé approximants. A theoretical study on light hydrocarbons with results analogous to those shown in Table 1 suggests that the BHPW91 parameterization is the one to choose, while in the case of noble gases also the KMLYP parametrization could be suitable.

<table>
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<tr>
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<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
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Table 1. C$_6$ coefficients (a.u.) calculated with aug-cc-pVTZ atomic basis set.
Excited states for orbital-optimized second-order perturbation theory

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Unrestricted Hartree-Fock (UHF) wave functions with spin contamination are usually poor zero-order approximations for second-order Møller-Plesset perturbation theory (MP2). Orbital-optimized second-order perturbation theory\textsuperscript{[1,2]} (OOMP2) tackle this problem by using approximate Brueckner orbitals. In OOMP2 the orbitals are optimized in the presence of the mean-field energy plus the second-order many-body correlation energy. Since in OOMP2 the energy is fully minimized with respect to orbital rotations, a Hellman-Feynman condition is fulfilled and first-order properties do not present discontinuities. This method improves the description of geometries, vibrational frequencies, and relative energies. Additionally, in OOMP2 the response function does not show spurious second order poles, making it suitable for linear-response excited state properties. In this contribution, we present an extension of the OOMP2 method to excited states\textsuperscript{[3]} and we report test calculations for closed-shell systems and doublet radicals. The performance of method is compared with other second-order methods for excitation energies such as the approximate coupled-cluster singles and doubles model (CC2), configuration interaction with doubles corrections (CIS(D)), and the algebraic diagrammatic construction through second order (ADC(2)).

References

Theoretical insight into the high-spin to low-spin relaxation in Fe(II) spin crossover complexes

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Spin-crossover is a phenomena produced in transition metal complexes wherein two electronic states with different spin moment can be populated through an external perturbation such as a variation of pressure or temperature, the influence of an external magnetic field or light irradiation. They have been widely studied in the last years due to their potential applications as switches, in data storage or optical displays.

Iron(II) tris-(2,2’-bipyridine), [Fe(bipy)3]2+, has been largely studied and is considered as a model system.[1,2] After green light irradiation, the stable 1A1 is excited to a metal to ligand charge transfer state (1MLCT) and then the system relaxes through two intersystem crossings to arrive to the metastable high-spin state, 5T2. The whole process is called light induced excited spin state trapping (LIESST).

In the current work, we study the mechanisms for going from the 5T2 back to the 1A1 again. Two different processes are studied, the first one involves light, and is known as reverse-LIESST and the second mechanism is the straightforward thermal relaxation. In the reverse-LIESST process, we study the deactivation path to the low spin state after the initial excitation to the 1E state. In the thermal process, the direct deactivation from the 5T2 to the 1A1 at geometries where both states are closely degenerate is studied. For this purpose, complete active space self-consistent field and complete active space second order perturbation theory (CASSCF/CASPT2) method including effective spin-orbit coupling (SOC) is required. Both mechanisms only involve metal centered states, because the MLCT states are high in energy for larger Fe-ligand distances. Hence, ligand-π* orbitals are not necessary to be included in the active space and CAS(10,12) is enough. Previous studies demonstrated that geometry distortions due to thermal disorder has large effects on the SOC [3] and therefore we run molecular dynamics to sample the conformational space in the region where reverse-LIESST is taking place and where the singlet and quintet state are close in energy.

References

Aromaticity as a guiding concept for spectroscopic features and nonlinear optical properties of porphyrinoids

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Porphyrinoids are macrocyclic compounds consisting of five-membered rings, linked directly or through atom bridges [1]. With their versatile molecular topology and aromaticity, porphyrinoid systems combine remarkable chemistry with interesting photophysical properties and nonlinear optical properties. Hence, the field of application of porphyrinoids is very broad range from near-infrared dyes to opto-electronic materials [2]. Despite the existence of relationships between aromaticity, photophysical properties and two-photon absorption cross sections, the fingerprints of aromaticity on the absorption spectra and optical properties are not fully unravelled. To assess such structure-property relationships, we performed a computational study in a set of Hückel porphyrinoids with varying number of π-electrons to: i) evaluate their (anti)aromaticity using an extensive set of aromaticity descriptors based on different criteria [3]; ii) determine the dependence of the UV/vis spectra on the aromaticity and iii) assess the role of aromaticity on nonlinear optical properties (NLO) properties. Using an extensive set of aromaticity descriptors based on magnetic, structural, reactivity and electronic criteria [3,4], the aromaticity of [4n+2] π-electron porphyrinoids was evinced as was the antiaromaticity for [4n] π-electrons. In agreement with previous studies, aromaticity dictates the photophysical properties leading to more intense absorption bands in the UV/vis spectra of aromatic systems than in antiaromatic homologues. The nature of these absorption bands was analysed in detail in term of polarization, intensity, splitting and composition. Finally, the relationship between aromaticity and NLO properties such as first and second hyperpolarizability is far more complex because planarity, macrocycle size and molecular symmetry also play a non-negligible role in determining the magnitude of polarizability, first and second hyperpolarizability. Summarizing, aromaticity plays a key role for photophysical properties whereas it is not the only factor determining the magnitude of NLO properties [5].

References
Multi-states global fitting of Singlets and Triplets of $\text{H}_3^+$: analytical description of potential surfaces and non-adiabatic couplings

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The high interest that $\text{H}_3^+$ produces, due to his presence in the interstellar medium$^1$, is evident from the large number of studies on its spectroscopy and formation by different methods (collisions, etc...). Theoretical studies require as a first step the calculation of the potential energy surfaces. In the literature there are several global potential energy surfaces for the ground and some of the singlets$^2$-5 and triplets$^5,6$ excited states of $\text{H}_3^+$. However the accuracy of these surfaces is high, the intermediate and long range description is not as high as certain calculations may require. In addition, the nonadiabatic processes for the singlet states are of great importance due to the crossings between the ground and the first electronic states. The potential energy surfaces normally used for the nonadiabatic processes are based on the diatomics-in-molecules (DIM)$^8$, approximation that we use as the basis of the full procedure for the singlet and triplet states. The full description of the potential surfaces for the three first singlets and three first triplets and their couplings is the goal of this study.

In this work I present the full process followed to obtain the analytical description of the potential surfaces and non-adiabatic couplings of the three first singlets and three first triplets of the $\text{H}_3^+$, with special attention to the description of the non-adiabatic couplings. The multi-states global fitting considers the right permutation symmetry of nuclei for the individual terms in the DIM matrix, being of symmetry $S_2$, and the full system, of symmetry $S_3$. We have added new terms to the long range interaction, including the exchange splitting of the interaction energy between H and H$^+$, and for the ground state a multipole expansion, accounting for the long range interaction between an ion ($\text{H}^+$) and a homonuclear neutral molecule ($\text{H}_2$). The new long range terms allow the description of the intermediate and long distances of the dissociation channels with accuracies lower than 10 cm$^{-1}$. The rms of the global fit, up to total dissociation energies, are lower than 50 cm$^{-1}$ for all the fitted states.

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**References**

Direct chemical dynamics simulations to study gas-phase fragmentation of Pro-Phe dipeptide

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The main aim of this study is to define the mechanism that steers the dissociation of Pro-Phe*OMe dipeptide ester anion (Fig.1) into two fragments: methanol and a $b_2^-$ fragment. Gas phase unimolecular dissociation is studied by means of chemical dynamics simulations [1]. Experimentally the fragmentation is induced by slowly heating the molecule via several low energy collisions between the ion and an inert gas. In order to mimic experimental conditions we activate the molecule by giving a fixed amount of energy that will be uniformly distributed among the normal vibrational modes. Venus code[2] is used for propagating trajectories on the potential energy surface computed on-the-fly at RM1 level [3] with Mopac 2012 code [4]. In particular cases we computed the PES using B3LYP/6-311++G(d,p) and RM1.

Trajectory analysis shows twenty remarkable fragments. We studied the internal energy dependency of this fragmentation pathways. In the next figure, we can see that there can be different fragments, including the ones we are interested in.

Figure 1. ProPhe*OMe and possible fragments.

References

De novo Designed Enzymes: A Computational Study

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Nowadays there are two major complementary strands for the development of new enzyme-based catalysts: directed evolution and rational design. The first one is based on performing random mutations and recombination, followed by screening processes. One of the advantages of this technique is that prior structural knowledge is not necessary, but a threshold of activity with respect to the reaction that is intended to catalyse in order to initiate the process is essential. On the other hand, rational design allows to introduce directed mutations and analyse their impact on the overall process, although it is crucial to have the structural information of the protein (usually the X-ray structure). Over the time, three strategies or starting points have been adopted for conducting the rational design: i) use of immuno-globulins (catalytic antibodies), ii) promotion of the enzymatic promiscuity (boosting of secondary reactions) and iii) de novo design (or theozymes).

In the present work, we have carried out a computational study of a set of theozymes designed to catalyse the retro-aldolic reaction[1], and other for the Kemp elimination[2], both having in common the fact that there are no natural enzymes known which catalyse them at a good efficiency. The first reaction consists of a multi-stage process leading to a C-C bond breaking, meanwhile in the second one gives rise to the conversion of benzisoxazoles into salicylonitriles. We intend to shed light on both reaction mechanisms and improve the catalytic efficiency of the processes.

References

Trans-Urocanic acid (UA) is a natural sunscreen which can suffer an isomeric reaction triggered by solar radiation. In counterpart E isomer has been recognised as a human immune suppressor related with skin cancer[1]. The establishment of an intermolecular hydrogen bond in cis-UA makes feasible a charge transference. The excited state profile of the hydrogen migration have already been analysed in gas phase pointing out the presence of a conical intersection between the fundamental and the first excited state ($n\pi^*$)[2]. Nevertheless, the energy and the order of the states can be twisted due to the influence of the aqueous medium. In this work, it have been studied this influence in the energy profile of the fundamental and two first excited states of the hydrogen migration by two different procedures. Firstly, by microsolvation up to five water molecules using CASPT2 calculations and secondly by performing a statistical simulation with a combination of a Monte Carlo and QM/MM method denoted as QMSTAT[3] where the solvent is represented by approximately 200 explicit water molecules surrounded by a continuum. The results show that the gap between the excited states decreases due to the solvent effects.

References

Computational approaches for describing clathrate hydrates interactions

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Accurate energy benchmarks, from wave-function quantum mechanical calculations are presented for sI, sII and sH type clathrate cavities in order to provide an independent mean of assessing DFT approaches as well as semiempirical model potentials. Such analysis contributes to extract valuable information of the underlying interactions and to improve existing approaches or develop new ones for describing condensed-phase systems. Our results show that binding/cohesive energies of such clathrate cavities suffer from huge BSSE, and thus extrapolation schemes were used to obtain more reliable results. Further, dispersion interactions are important on the stabilization energies of such clathrate cages, and the encapsulation of molecules such as CO₂ into guest-free clathrate cages is always energetically favorable. Despite the difficulties faced by current water models and DFT functionals to accurately describe the interactions in such water systems, we found some general trends that could serve to extend their applicability to larger systems.

![Figure 1](image1.png)

Figure 1. Cage structures of the sI, sII, and sH clathrate hydrates (left panel). Cohesive energies obtained from the best-performed DFT functionals and ab initio water models with respect to the reference DF-MP2/CBS1 values (right panel)

References
We investigate the charge migration process initiated by an attosecond XUV pulse in amino acids. Regardless the molecule under study, Quantum Mechanics states that the expectation value of a time independent Hermitian operator will exhibit a temporal dependence as long as the system is described by a non-stationary state of that operator, i.e., any superposition of eigenstates of a given system leads to a time-varying observable such as the probability density. This lies at the core of the so-called ultrafast charge migration, concept introduced by Cederbaum and Zobeley in the nineties to describe the charge fluctuations occurring in the attosecond time scale upon sudden ionization of a molecule [1]. These investigations were indeed inspired by the pioneering work of Weinkauf and coworkers on peptides chains [2], where charge-directed reactivity induced by nanosecond UV radiation sources was concluded to occur due to purely electronic effects. However, the first experimental observation of this phenomenon obtained with attosecond resolution has only been achieved in 2014 for the amino acid phenylalanine [3]. New theoretical approaches are being developed to provide a solid knowledge of these ultrafast light-induced processes.

Most of existing methods describe the process by assuming ionization as a sudden transition from the ground state, avoiding the evaluation of ionization amplitudes [4,5]. And, even in those works where the ionization step is more accurately represented [3,6] the nuclei remain frozen, which is expected to be a reasonable approximation in the first tens of femtoseconds [7,8]. We will present our progresses to achieve a complete theoretical description of the ultrafast charge migration process triggered in glycine molecule, and more recently in a larger amino acid – tryptophan-, which include both an accurate evaluation of the ionization step and the nuclear degrees of freedom in the time propagation. We employ a Static-exchange DFT-based approach [9,10] to extract reliable ionization amplitudes, while the correlated electron-nuclear dynamics of the ionic subsystem is obtained from a TDDFT-Ehrenfest simulation in our very first approach. We also show how the choice of the ionizing laser pulse modifies the ensuing charge dynamics, thus opening the door to the control of charge-directed reactivity in biologically relevant molecules.

References

Triplet electronic states are characterized by an open-shell or diradical nature which makes them highly reactive as compared to singlet close-shell ground states. Moreover, triplet species have much longer lifetimes than singlet excited states and therefore they can diffuse and more frequently promote inter-molecular processes giving rise to induced reactivity in surrounding molecules. This sensitization process take place in biological structures such as the DNA chromophores with relevant implications in Molecular Medicine. In the last years, we have determined the molecular basis of distinct chemical mechanisms involving triplet species which give rise to the production of lesions in the DNA. Benzophenone has been selected as model of photosensitizer, whereas melanin monomers have been used as chemisensitizers. Triplet-triplet energy transfer, hydrogen abstraction, and photo-oxidation reactions are available photochemical processes in the former [1]. Meanwhile, melanin dioxetanes have been suggested in recent experiments as responsible of the production of melanoma in dark conditions [2]. In this contribution, we shall discuss on such sensitization phenomena focusing on the comparison between distinct available mechanisms and providing hints on the most favourable ones.

References
Theoretical study of photovoltaic processes in organic solar cells

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Organic photovoltaic (OPV) solar cells represent a highly attractive choice in terms of low cost and flexibility for harnessing green energy. However, the low efficiencies achieved so far limit their massively production. It is believed that if the photovoltaic processes in semi-conductor materials are understood, such low efficiencies would be overcome. That has led to an active research both experimental and theoretical on materials and architecture design. It is worth mentioning the collaborative work between the theoretical chemistry group of the University of Groningen and the excited state quantum chemistry group of the University of Valencia [1]. There, the excited state properties of OPV materials and π-conjugated systems of general relevance in optoelectronics (see Figure 1) are studied by using the time dependent density functional theory (TDDFT) and multiconfigurational methods. In the TDDFT framework, donor:acceptor blends are studied for which the discrete reaction field (DRF) method is also used in order to model large systems. Through multiconfigurational methods, such as the complete active space self-consistent field method (CASSCF) in combination with the complete active space second order perturbation theory (CASPT2), nonradiative deactivation paths that lead to losses, are studied. The analysis of such channels is performed over distyrylbenzene cyano functionalized type molecules, namely DSC molecules for which a large amount of experimental data is available [2] and a systematic analysis of intrinsic features which gives rise to efficiency losses is feasible. It is proven that the performance of OPV solar cells (and optoelectronic devices in general) may be controlled when properly selecting materials with appealing excited state properties.

![Figure 1. Chemical structure of molecules under study. From left to right, and from top to bottom, PTB7, PTB7-Th, PCBM, DSB and α or β DMDCS molecules.](image)

References

How could a free electron be stabilized in water?
A first approach to its solvation

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The free aqueous electron and its analogues, the anionic water clusters, have drawn attention for several decades, not only from a theoretical point of view, but also experimentally. Nevertheless, a system that seems simple at first, ends up being quite controversial [1]; without having been able to reach yet a final conclusion about how the electron is distributed among the water molecules. Thus, it could be stabilized within a cavity among the water molecules [2] or placed at the surface where the electron could be delocalized. In our work, we analyze this system by performing computational calculations in anionic water clusters up to twenty molecules (Fig. 1) at different computational levels, i.e. B3LYP/6-31 ++ G (d), M06-2X/6-31 ++ G (d) and MP2/6-31 ++ G (d); allowing us to make a comparison between the obtained results and the experimental values. Also, the nature of the intermolecular forces between the electron and the water molecules is analysed using a QM/MM method based on a perturbational model. DFT results show the electron delocalized among the water molecules and partially embedded in the structure in clusters big enough for this to happen. MP2 results locates the electron on top of the atoms. The calculated spectra and excitation energies show similarities with the experimental results. However, higher level of calculations and larger systems will be needed in order to throw light on the elusive structure of this system.

Figure 1. Structure of one of the water clusters employed in the simulations, composed by 20 water molecules.

References

Structural, spectroscopical and transport properties in aqueous systems

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Nowadays the most important nature substance (water) is still a mystery and our molecular understanding of aqueous systems at various environments, or around solutes is still very poor. Aiming to provide further insights on this subject, a discussion will be presented regarding the representation of molecular interactions and their effect on different static and response properties of the pure liquid, as well as in ion-water systems. In the present work, molecular dynamic simulations have been carried for different purposes. As a first step, an efficient computational methodology capable of providing statistically accurate estimates for collectives transport properties in the liquid will be shown for shear and bulk viscosities at different thermodynamic conditions. By a detailed analysis of existing interaction potentials and thorough comparisons with experiments and previous studies [1-4], a discussion on the influence of each term will be presented with guidelines for further refinements and new developments [5-7]. Concerning ions in aqueous environments, recent structural, as well as spectroscopical properties of such molecular systems will be presented from a bottom-up approach [8]. The results are based on new polarizable interaction potentials [9], compatible with available water models and parametrized against highly accurate ab initio data. After comparison with reference electronic structure calculations as well as experimental studies [10], this systematic route offers an efficient alternative to DFT+D calculations and enable dynamic simulations from finite-size cluster systems to condensed phase environments.

References

Reaction mechanism for obtaining NO from NONOates derivatives

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Nitric oxide (NO) is a small biological molecule, acting as interneuronal messenger, involved in a great number of physiological functions. NO carries out its biological functions through chemical reactions with a limited number of biomolecules, therefore it is important to study in detail the molecular liberation mechanisms of NO from donor compounds. The biological and pharmaceutical roles of diazeniumdiolates molecular donors have been widely studied as useful pharmaceutical tools due to their wide experimental half-lives [1]. These compounds have a general structure $X$–[$N\left(O\right)$NO]–, with amino moieties like $X$=$R_1R_2N$− (called NONOates) are extensively studied because of their ability for liberating NO in neutral media [2].

In this work, we present the reaction mechanism for the liberation of NO from NONOate: $\text{NNH}_2\text{NH}_3^+\text{−}\text{[N(O)NO]}^−$ (1). Calculations were carried out using DFT with the functional M06L [3] and 6–311++G(d,p) basis set. Mechanism is proposed by protonation of 1 and then several protonated tautomers (mainly H1 and H5) are involved for obtaining the intermediaries and transitions states, see Figure 1. Tautomer H5 is found to be 16 kcal mol$^{-1}$ respects to the lowest energy tautomer H1. Finally, as products a secondary amine and two molecules of NO are obtained. Geometry optimization of reactants, intermediaries, transition states and products were carried in aqueous solution using Polarizable Continuum Model (PCM) [4]. Harmonic vibrational frequency calculations were computed using the same level of theory for all the stationary points to ensure their assignation of local minima and TS. All electronic structure calculations were carried out with the Gaussian16 program [5].

Figure 1. Molecular structures for optimized structures of 1 and its protonated tautomers H1 and H5.

References
Reaction mechanisms and catalysts for the formation of methanimine and methanol in the ISM: Study from the Reaction Force perspective

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Theoretical studies in conditions of the interstellar medium (ISM) are being carried for two relevant reactions. The analysis of the Reaction Force ($F(\xi)$), along the reaction coordinate ($\xi$)[1,2], is used as a method to provide insight into the reactions mechanisms and the role of other species as possible catalysts.

The first reaction is the formation of methanimine, as an important precursor in the formation of amino acids [3], from ammonia and formaldehyde, under possible catalysis of hydrogen cyanide. Calculations at B3LYP/6-311+G(2d,p) level of theory have shown 61% reduction of the activation energy in the limiting step versus non-catalysed reaction.

For the other reaction, CO hydrogenations to form methanol on the surface of dust grains[4], the interest is mainly to study the role of organic molecules as possible catalyst and compare them with water clusters. The energies related to the adsorption and desorption processes of the formed species are also relevant to understand the observed abundancies in gas phase. Taking advantage of the small size of the system, in this case CCSD/cc-pVTZ level of theory is being used.

References

Vanadium complexes against breast cancer. A combined DFT and molecular docking theoretical study

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Breast cancer is the leading cancer detected among women worldwide, for this reason there are new therapeutic alternatives against cancer such photodynamic, that mainly needs of two basic elements for acting in the best way possible: a photosensitizer and an appropriate wavelength [1]. In the searching of new photosensitizer and anticancer agents, the vanadium complexes are highlighted. In this research project had been studied three oxo-vanadium (V) complexes [2] with the aim of elucidate their activity as photosensitizer and their anticancer activity by inhibiting PTP1B protein, which is involved in the malignancy of breast cancer [3].

The optimization of the geometries, UV-Vis spectra and population analysis were carried on with DFT functionals such as B97D and M06-2X using 6-311++g(d,p) basis set for all atoms except vanadium, which uses LANL2DZ basis set for describing the core electrons by a Pseudopotencial. All calculations where done in gas and solution phase (water, ethanol and dimethylsulfoxide) using Gaussian 16 package [4]. The molecular docking was carried out by Autodock 4.2 software [5]. M06-2X was the functional that better described the complexes geometries and the UV-Vis spectra. The absorption bands of the complexes were observed between 430-460 nm, being proposed as photosensitizer.

The interaction energies between protein PTP1B and the three complexes were close to -6.20 kcal/mol and the interactions observed are mainly hydrophobic interactions between Cys215, Asp181 and Asp48 amino acids, which are related with the cancerogenic activity of the PTP1B protein.

References

Counterions for controlled dissolution, aggregation and cluster growth of metal-oxo clusters

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The behaviour of transition metal oxides in an aqueous solution or interface is dictated by numerous complex and interrelated phenomena. Even for simple salt solutions, the scientific community is still developing an explanation of hydration of ions and formation of ion-pairs.\(^1\)

Group V/VI Polioxometalates (POMs) offers an opportunity to investigate these multiple roles of counterions, Group V clusters have higher charge density compared to group VI, both subclasses lead to opposite solubility trends: Group VI solubility trends Cs>Na>K>Rb>Cs (normal solubility) and Group V does it Li >Na>K>Rb>Cs.

Through ongoing experiments and dynamical and statical calculations, we have quantified the critical features of POMs that drive the turning point between anomalous and normal solubility. From Molecular dynamic simulations we observed that low charge density POMs are more soluble than high charge density POMs in alkaline water: low charge density POMs cannot break through its counter-ion’s hydration shell, on the contrary high charge density POMs will be able to attract/remove water from solvation alkali shell (disrupting it) and form a contact ion-pair, which leads to the formation of aggregates (see Figure 1). In order to understand alkali-driven aggregation of POMs, the special case of decaniobate, which has never been synthetized as any other salt than TMA, is studied in detail across alkali series, because it offers clues about the role of counteraction in aggregation. We show that Nb10 dissociates to Nb7, is controlled by addition of alkalis within the formation of \{Nb7\}-based high nuclearity clusters. The dissociation and speciation depends on the size of alkali.

![Figure 1](image)

Figure 1. Illustration of ions interaction in strong cases of high charge density and low charge density of POMs.

With this work we are one step closer to understand the interactions between ionic metal-oxo clusters and their counterions in water and its role in controlling solubility, aggregation and formation of pre-nucleation clusters.

References

Mechanisms in V(V)- and Mo(VI)-catalyzed oxygen transfer reactions to valorize biomass subproducts

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Oxygen atom transfer (OAT) reactions are key in transforming oxygen-rich by-products obtained in biomass processing into useful feedstocks for the chemical industry. Such valorization of biomass by-products would help reduce our dependence on conventional fossil oil derivatives both as raw materials and as energy sources, it would also make more viable the production of biodiesel.

Transition metals in high oxidation states (mainly vanadium, molybdenum and rhenium) have been found to efficiently catalyze different kinds of OAT reactions from and to a variety of substrates. The most widely used reactions in this context are those involving the deoxydehydration of diols and the deoxygenation of an array of functional groups. In most of these OATs an external reductant (phosphine, for example) is used, but the fact that this external reductant can be an alcohol itself, makes these reactions very versatile, as sometimes a single substrate can be oxidized and reduced in the process.

In our group we have used DFT to study in detail the mechanism of several V(V)/V(III), Mo(VI)/Mo(IV) and Re(VII)/Re(V) catalytic cycles leading to the deoxydehydration of glycols, the reductive cyclization of nitrostirenes to indoles, the deoxygenation of epoxides and the transfer of an oxygen atom between sulfoxides and phosphines.[1] We have found that these mechanisms proceed through more complex paths that those traditionally proposed, in which spin-crossing events are common, diradical structures play a central role and the metal can act as a purely red/ox catalyst or as a Lewis acid at different stages of the mechanism. Interestingly, a common triad of interconnected intermediates can be found in most of these mechanisms, allowing for parallel comparisons and systematic catalytic enhancements. We have analyzed the effect of the metallic center, its coordination number and the type of ligands around it on the preference for one or other pattern of reactivity, and propose ways of exploiting this knowledge for the design of improved catalysts.

Figure 1. Homogeneous metal-catalyzed oxygen transfer reactions in biomass valorization.

References

Self-assembly stability and halogen bonding

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Understanding the stability of self-assembled halogenated aromatic hydrocarbons on liquid-graphitic interfaces is relevant in areas such as environmental research, nanodevice design and two-dimensional crystal engineering. However, calculating free energies of formation of organic self-assembled adlayers at the liquid-solid interface is challenging, due to the many factors involved (i.e. solvation, weak intermolecular interactions, large system sizes, ...).

In this joint experimental and computational study we have investigated the free energies of formation from solvation of self-assembled layers of 1,3,5-trichlorobenzene (TCB) and hexachlorobenzene (HCB) on graphene. Accurate periodic, dispersion-corrected DFT calculations including entropic effects predict the instability of the former and the spontaneity of the latter. In both cases, the free-energy landscape is enthalpy dominated, with molecule-surface interactions playing the main role in stabilizing the molecular adlayer. Nonetheless, halogen bonding dictates the intermolecular binding motifs. In HCB, cyclic X3 synthons with elongated Cl-Cl distances evidence the need for non-geometrical criteria in order to assess the presence of halogen bonding. In TCB, cooperativity between halogen and hydrogen bonding

Scanning Tunneling Microscopy and Raman experiments are in excellent agreement with the computational predictions regarding adlayer geometry and free energy of formation of TCB and HCB self-assembled layers.

\textbf{Figure 1.} Molecule-surface interactions and intermolecular halogen bonding drive the self-assembly of HCB (bottom) on graphite from solution, but are not enough for TCB (top). Molecular electrostatic potentials (left), molecular models (center) and experimental STM image of HCB on graphite (bottom right).

References

Interactions of dimethyltin(IV) with uracil as studied in the gas phase

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The gas-phase interactions of uracil with dimethyltin(IV) dichloride have been studied by a combined experimental and theoretical approach. Positive-ion electrospray spectra show that the interaction of dimethyltin(IV) dichloride with uracil (Ura) results in the formation of the [(CH$_3$)$_2$Sn(Ura-H)]$^+$ ion. The MS/MS spectrum of this complex is characterized by numerous fragmentation processes, notably associated with elimination of H,N,C,O and C$_3$H$_3$N,O moieties, as well as the unusual loss of C$_2$H$_6$ leading to the [Sn(Ura-H)]$^+$ complex. In turn, the [Sn(Ura-H)]$^+$ complex fragments according to pathways already observed for the [Pb(Ura-H)]$^+$ analog. Sequential losses of CH$_3$ radicals are also observed from the [(CH$_3$)$_2$Sn(N,C,O)]$^+$ species (m/z 192).

Comparison between DFT-computed vibrational spectra and the IRMPD spectrum recorded between 1000 and 1900 cm$^{-1}$, shows a good agreement as far as the global minimum is concerned. This comparison points to a bidentate interaction with a deprotonated canonical diketo form of uracil, involving both the N3 and O4 electronegative centers. This binding scheme has been already reported for the Pb/uracil system. The bidentate form characterized by the interaction between dimethyltin with N3 and O2 centers is slightly less stable. Interconversion between the two structures is associated with a small activation barrier (56 kJ/mol). The potential energy surfaces were explored to account for the main fragmentations observed upon collision induced dissociation.
Photofragmentation of bare and nanosolvated [leucine-enkephaline-H]+ studied by means of dynamics simulations

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We report a comparative theoretical and experimental study on the photo-induced fragmentation of bare and nanosolvated (three water molecules) protonated leucine-enkephalin (Leu-Enk: YGGFL). Tandem mass (MS²) spectrum of nanosolvated [Leu-Enk-H]+ obtained after peptide ion exposition to vacuum UV light (VUV), shows an incredible influence of the water molecules into the backbone fragmentation pattern, while no significant changes are observed in the peptide structure by addition of the water molecules (being the three waters attached to the protonated N-terminal side of [Leu-Enk-H]+ forming a cluster (Fig.1)). This suggests that new fragmentation pathways are open up (for the same photon energy) by the presence of the water.

Figure 1. Solvated [Leu-Enk-H-3H₂O]+ optimized at B3LYP/6-31G(d,p) level.

With the aim of investigating the fragmentation dynamics of both systems, we have carried out two kind of dynamical simulations. As a first approach to the problem, we have used direct dynamics simulations[1] on which [Leu-Enk-H]+ ion is activated by uniformly distributing a fixed amount of energy through its vibrational modes and eventually dissociates. These simulations have allowed establishing the fragmentation pattern for statistical dissociation and how this pattern varies as a function of the ion’s internal energy. The main fragment ions observed in the MS² spectrum are found with the dynamics simulations and thus the origin and fragmentation mechanisms of these fragments have been rationalized at a molecular level.

Since the experiments consists on activation of the ion by irradiation with VUV light, we also performed nonadiabatic molecular dynamics simulations starting from the excited state in order to study ion’s relaxation from the excited state. The comparison of the output of these two kinds of simulations has allowed deciphering how the fragmentation pattern changes from vibrational excitation to electronic excitation and the fragmentation mechanisms.

References

Donor - Acceptor Interactions: Transition metal carbonyl group ligand $[\text{Me(CO)}_6]^q$ complexes. A case study at correlated level from the topological density point of view

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The analysis of metal-ligand interactions between one metallic atom and several carbonyl group ligands ionic d$^6$ complexes $[\text{Me(CO)}_6]^q$ ($q$ net ionic charge) for the transition metal isoelectronic series, $\text{Me}=\text{Ti, V, Cr, Mn, Fe}$ is presented from an electron density point of view. An emphasis on the relationship between the molecular orbital $\sigma$-, $\pi$-donation for the description of the rearrangement and the existence of complex binding interactions of the type of two electron over three or four centers ($2e-3c$, $2e-4c$), is the driving idea of this analysis. The detailed description is made within the framework of the local and non-local topological analysis of the electron density field coming from its decomposition into characterized pairing and unpairing nature contributions. [1, 2] This reveals the nature of metal-ligand interactions.

![Figure 1. Geometrical structure of $[X(CO)_6]^q$ ($X = \text{Fe; Mn; Cr; V; Ti}$) complexes. Oxygen, carbon and metal atoms are indicated by red, grey and light blue balls, respectively.](image)

References

TCCM WORKSHOP
Biochemistry in silico: Enzymatic Reaction Pathways and Transition States

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One of the challenges in theoretical characterization of biochemical processes is the huge number of configurations that might be visited by the enzyme-substrate complex during the reaction. A common approach to tackle this problem is to determine an adequate reaction coordinate that brings the system from reactants to products through a well-defined transition state, thus allowing to distribute the computational load evenly along the path.

We present recent efforts to find good enzymatic reaction coordinates and the implications of these findings in the interpretation of enzymatic efficiency. In particular, we present strategies based on the use of minimum free energy paths and direct localization of the dividing surface on multidimensional free energy surfaces. Finally, we discuss the applicability of the transition state theory to enzymatic catalysis by explicitly calculating the errors associated to the choice of the reaction coordinate and the intrinsic error of the theory. Our findings can be extrapolated to other chemical processes in condensed phases.

References
Rationalization of the Electron Transport in polymeric conjugated chains according to its electronic distribution.

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In the last decade, the area of molecular electronics has gained much interest due to significant progress in both the theoretical and experimental fields, being theoretical efforts oriented to the rationalization of the conductance in terms of chemical properties, and experimental works focused just on the fabrication of new highly conducting molecular junctions. Thus, it has been demonstrated that chemical concepts such as aromaticity, bond order, and polarizability, are intrinsically related to the insulator/conductor nature of molecular systems.

Recently, different oligophenyl molecular wires were theoretically investigated [1]. Surprisingly, an exceptional anti-Ohmic behaviour, reflected in the increase of the electric conductance with the length of the wire, was found for structures terminated by methylene linkers (pX2). In order to shed light on this behaviour, the electron deformation orbitals (EDOs), constructed by combination of occupied and virtual MOs under the action of a static electric field, have been evaluated. The main pair of EDOs (shown in Figure 1 for a oligophenyl chain of twelve units) [2,3], is the responsible of the principal transmission channel of the system, which in turn is built from a combination of the HOMO and LUMO unperturbed MOs. This representation evidences a direct electron transfer mechanism between the chain ends. Using the localization tensor [4], which is a measure of the conducting ability, and its relation with the electron delocalization between different molecular regions, we have been able to confirm this mechanism.

Figure 1. EDO of the pX2 system with 12 phenyl units.

References
A novel caspase-1 reaction mechanism. A theoretical study based in QM/MM potentials and the string method

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Caspase-1 is an enzyme that catalyzes the hydrolysis of the proinflammatory cytokine Interleukin 1-beta into its active form and is involved in inflammatory and apoptotic processes. For this reason, a detailed molecular description of the caspase-1 mechanism has a great pharmacological interest. In spite of this, there are no clear experimental evidences that can support the mechanism proposed so far for the acylation step[1,2] based in a mechanism previously reported for the papain family, another class of cysteine proteases[3].

We have performed a study using a Constant pH Molecular Dynamic Simulation (CpHMDS)[4] in order to determine the most probable protonation state of Cys285 and His237 in the active site of the enzyme. We found that in the Michaelis complex these residues should be found in its neutral state. The mechanism accepted for the acylation step involves deprotonation of the nucleophilic cysteine by the δ-nitrogen of a close histidine. However, these residues are separated by more than 5 Å in the 29 available crystals in the Protein Data Bank for the caspase-1 enzyme, preventing the direct proton transfer between them. In contrast, using QM/MM hybrid potentials in combination with the string method[5] to explore free energy surfaces, we found that Cys285 can be deprotonated by the oxygen in the carbonyl backbone of the aspartate of the peptide substrate, facilitating the formation of the carbon sulfur bond in the acylation process (see Figure 1).

References
Hydrogen bonding (HB) is probably the most important intermolecular interaction, responsible for the conformation, aggregation and hence, the properties and activity of many biochemical systems, among others. One of the best known examples of HB is found in water, where the main features exhibited either as a solvent or as a pure substance are ultimately determined by this kind of bonding.\cite{1}

Water clusters are prototypical systems where HB takes place, and where the effect that the addition of new molecules to the previous clusters has on H-bond strength can be better rationalised. More specifically, water clusters show HB cooperative effects, thus revealing the non-additive character of these interactions.

With the aim of shedding light on the understanding of cooperative effects in these systems, previous studies based on a robust real-space methodology were carried out.\cite{1,2} Within the Quantum Theory of Atoms In Molecules (QTAIM), the Interacting Quantum Atoms (IQA)\cite{3,4} approach has emerged as a useful tool to address the energetic effects that certain atoms have on others, as well as to understand the changes experienced by their bonds upon environmental perturbations. IQA offers a robust energy decomposition based on the first- and second-order density matrices, providing a partition of a given system’s global energy into intra- and inter-atomic contributions. Nonetheless, IQA entails some drawbacks: far from an ideal linear scaling, it is limited to small systems, as its cost grows dramatically with the size of the basis set. Also, the need of a second-order reduced density matrix has constrained its applicability to wave function methods, leaving perturbation approaches or DFT out of its strict scope. However, in the last few years, these main limitations have begun to be overcome.\cite{5}

Given that Density Functional Theory (DFT) is still one of the most widespread theories in computational chemistry, we benchmark herein sixteen different functionals and compare the IQA DFT implementation to \textit{ab initio} reference methods such as HF or MP2. We report IQA-based descriptors of HB in water clusters. Our results show a remarkably good description of both the main features of HB and those related to its non-additive character by most of the DFT functionals employed, thus paving the way for future work with larger and more complex systems.

References


In order to describe the photoionization of pyrazine, a good description of the electron continuum is required. However, as opposed to bound state calculations, there are not similar and standardized tools and methods. Our group has developed a new approach to account for the electronic continuum. This new method has been applied successfully to atomic systems like hydrogen and neon, and diatomic molecules like nitrogen. In this work we apply the XCHEM method to a molecule as complex as pyrazine.

The XCHEM method uses what is called a GABS basis interfaced with standard QCPs (MOLCAS, MOLPRO) and close-coupling scattering methods for multichannel ionization calculations. By merging both methodologies, we can use multideterminant ab initio techniques to obtain accurate photoionization cross sections.

In this contribution we have studied the photoionization of pyrazine using the XCHEM method and compare it with a well-establish DFT approach. In this case, single channel-single reference calculations were performed for several angular momenta of the ejected electron with both techniques. Finally, multichannel scattering cross sections were calculated with single reference and multireference methods. These simulations, which describe the effect of the electron correlation in the configurational interaction picture, were used to understand the photoionization cross sections of pyrazine. With the results of single reference and multireference calculations, we can estimate the importance of electron correlation in the description of the bound states and when single channel calculation and multichannel calculations are compared, we can observe the effect of coupling several electronic continua.

References
Theoretical insights on the reactivity of rhenium carbonyl complexes towards activated alkynes

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The reactivity of rhenium(I) complexes of type [ReX(CO)\(_3\)](bipy)] (X = NH\(_p\)Tol (para-tolylamido), OH (hydroxo), OMe (methoxo), PPh\(_2\) (diphenylphosphanido); bipy = 2,2’-bipyridine) towards activated alkynes has been studied experimentally[1] and, in some cases, theoretically[2]. Although all reactions start with an initial attack of the nucleophilic ligand X to the least substituted acetylenic carbon of the alkyne, they may evolve to different products (Figure 1): the alkyne bonds to one ortho carbon of the bipy ligand (ccb route), to the CO ligand in cis disposition (cco route), or to the metal centre (ins route), with the consequent breaking of the Re-X bond.

Our theoretical analysis of the reactions with all the nucleophilic ligands experimentally used may help to elucidate the factors that determine the preferred product. The influence of the bidentate ligand on the reaction routes has already been checked[2], but there are other factors such as the nucleophilicity of the ligand X, the orbitals involved in the reaction steps, the distance of the Re-X bond, and the charges of the atoms, among others. All of them have been considered in this computational work through a variety of analysis tools including the Atoms in Molecules (AIM) method, Natural Bonding Orbitals (NBO), Fukui indexes, etc.

![Figure 1. Stepwise reaction mechanisms and products depending on the nucleophilic ligand.](image_url)

References


Short-range effects on the excitonic coupling of N-heterotriangulenes

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N-heterotriangulenes (HT) are a family of compounds generally based on a carbonyl-bridged triphenylamine core that gives rise to a planar and aesthetically pleasing π-conjugated scaffold (Figure 1a). HTs can be additionally decorated with terminal amide functional groups to foster helical supramolecular self-assembles stabilized by hydrogen bonds and π-π interactions. These HT aggregates have turned to be very promising in the field of organic-electronics; particularly, as potential candidates for an efficient exciton transport.[1]

In this contribution, we evaluate the excitonic coupling and its fluctuation in a helical columnar HT aggregate (Figure 1b). Total excitonic couplings (short- and long-range effects) are computed by employing a diabatization scheme in molecular dimers, previously reported by Aragó and Troisi,[2] and electronic structure calculations within the time-dependent density functional theory (TDDFT) framework. The Coulombic excitonic coupling is, however, assessed by using atomic transition charges at the atom positions and the transition density cube (TDC) method (Figure 1c).[3] The significant difference between the total excitonic coupling and the Coulombic contribution highlights that short-range effects are expected to play an important role for the exciton transport properties in N-heterotriangulene derivatives.

![Figure 1. a) Chemical structure of the HT derivative studied here. b) Minimum energy structure of an N-heterotriangulene decamer computed at the DFTB-D3 level within periodic boundary conditions. c) Plot of the transition density of the first bright excited state of an N-heterotriangulene derivative.](image)

References

Arbitrary order calculus is a natural generalisation of usual calculus in which the order of differentiation and integration operators is not restricted to integer numbers. In engineering fractional order derivatives are used for describing the behaviour of materials with memory (i.e., viscoelastic materials) due to the fact that these materials lay somewhere in between Hookean springs and Newtonian fluids [1,2]; there are also many dynamical systems which can be better described when arbitrary order derivatives are included [3].

Lanskin [4] formulated the first Fractional Schrödinger Equation (FSE) along with the Fractional Continuation Equation in 2002; however, we are still far from fully understanding the effect of the FSE on physical properties such as: Tunnelling [5], Diffraction [6] and Scattering [7]. Due to the properties of fractional derivatives, many jobs have been done in which relativistic properties and effects of extrinsic magnetic fields are obtained by incorporating an arbitrary order to the kinetic energy in the Hamiltonian [8,9].

Further studies of the FSE applied on astrophysically interesting systems such as $H_2^+$ [10] and even hydrogen atom [11] seem to be promising. We shall take the FSE for a particle in a ring (1) as a first step into this world for which the eigenvalues are (2) and the eigenfunctions (3).

\[
\left[ -\frac{i\hbar}{(2m)^{1/\alpha}} \frac{d}{d\theta} \right]^\alpha \Psi_\alpha(\theta; r) = \lambda_\alpha \Psi_\alpha(\theta; r) \tag{1}
\]

\[
\lambda_\alpha = \frac{1}{2m} \left( \frac{\hbar e^{in_\perp}}{r} \right)^\alpha \mid m_\perp = 0, \pm 1, \pm 2, \ldots \tag{2}
\]

\[
\Psi_\alpha(\theta; r) = \frac{1}{2\pi} 1^{1/2} e^{-i(2m\lambda_\alpha)^2/\alpha r} \tag{3}
\]

References
Molecular Dynamics of Aqueous $[\text{UO}_2]^2+$ Diffusion in Clays

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Knowledge of actinide aqueous solution confined in smectite clay interlayers are crucial when designing permanent geological high level radioactive waste facilities. The actinide ions are sealed using montmorillonite containing clays to prevent radionuclide escape$^1$. A computational study of $[\text{UO}_2]^2+$ (aq) hydration structure and diffusion inside montmorillonite clay was accomplished. The first actinide-clay ab initio interaction potential has been created based on the Hydrated Ion concept$^2,3$. Additionally it is the first application of the hydrated ion model to a confined medium chemical problem. The developed potential was used to carry out NPT classical molecular dynamics simulations for Montmorillonite clay containing $[\text{UO}_2]^2+$ with two possible interlayer water contents. The z-density profiles reflect the formation of stable pentaaquo uranyl outer-shell complexes in agreement with EXAFS studies$^3$ without any external imposed constraint. The complex interacts with the clay by the formation of 1.4 hydrogen bonds between its first hydration shell and the surface. Groups of three Mg substitutions were identified as strong interaction sites of the pentahydrate. The constrictivity factor, $\delta_{\text{int}}$, calculated from the self-diffusion coefficients agrees semiquantitatively with experiment. Diffusion is enhanced by an increase of concentration of uranyl in the clay interlayer.

References

Computational studies on the interaction of [Mo(μ-C₃H₅)Br(CO)₂(phen)] with G-quadruplexes

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It has been shown that G-quadruplex structures have a key role in the transcription process regulation [1] and the interaction between G-quadruplex and planar ligands in metallic complexes have proven to have good anti-tumoral activity, which can be used in chemotherapy [2]. Different studies have shown that phen and derivatives interact directly with G-quadruplex guanine bases and stabilize the structure [3,4]. Stabilization of the G-quadruplex structures inhibits telomerase activity [5], which is involved in most of cancer cell lines, and stops the cancer cell growth. Because the [Mo(μ-C₃H₅)Br(CO)₂(phen)] was observed to be cytotoxic to several cancer cell lines in previous experimental studies [6], we studied its interaction with G-quadruplexes by means of computational techniques, such as semiempirical, QM/MM and DFT-D. One of the most stable structures contains the [Mo(μ-C₃H₅)Br(CO)₂(phen)] totally inside the G-quadruplex.

References

Theoretical Study of inhibition of 20S Proteasome core particle

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The great majority of protein degradation in mammalian cells is catalysed by 20S Proteasome [1], mostly being involved in Ubiquitin-26S Proteasome System (UPS). Therefore, proteasome function is directly related with protein homeostasis and influences cell regulation [2]. The proteasome is involved in the turnover of many critical proteins, in the control of cell growth, cell differentiation, or metabolic adaptation. 26S Proteasome consists of 19S regulatory particle and 20S core particle. It is generally accepted that the proteolytic mechanism is carried out in the active sites located inside the core particle. These active sites bear N-terminal Thr residues as central component of the reactivity, thus proteasome is classified as Thr-hydrolase. During 20S core particle biogenesis, catalytic subunits are synthesized as precursors bearing N-terminal propeptides attached to Thr. It is in last stage of core particle maturation when propetides undergo autocatalytic cleavage, leaving Thr catalytic residue exposed [3]. Multiple studies have been published regarding UPS stages towards protein degradation, but few are focused in the proteolytic process occurring in 20S proteasome core particle. Thus, the autolytic and proteolytic mechanisms remain enigmatic.

In this communication we are presenting a theoretical study of the inhibition processes occurring on the active sites of 20S proteasome core particle. The free energy surfaces for each step appearing in different explored mechanisms have been obtained by means of hybrid QM/MM methods, using the semiempirical AM1 Hamiltonian and the M06-2X DFT method to treat the QM sub-set of atoms and the AMBER and TIP3P force fields to describe the protein and solvent water molecules, respectively. The obtained results show which steps of the proposed mechanisms are crucial for the reactivity and how the active site is involved, considering the different processes that can undergo. These and future results of our studies can be paramount, keeping in mind the unsuccessful efforts done to develop the next generation of cancer-fighting proteasome inhibitors. [4,5]

References
Non-radiative decay paths in organic $\pi$-conjugated compounds of interest in optoelectronics

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In the framework of organic optoelectronics (and photovoltaics), the luminescence properties of distyrylbenzene cyano functionalized type molecules, namely DSC molecules, are studied (see Figure 1). The nonradiative deactivation paths of DCS molecules are explored by using the time dependent density functional theory (TDDFT) and multiconfigurational methods. A preliminary study of the absorption and emission channels is performed at TDDFT/CAM-B3LYP level. Further, a deeper analysis of such channels is carried out with the complete active space self-consistent field method (CASSCF) in combination with the complete active space second order perturbation theory (CASPT2). For comparison, the absorption, emission and conical intersections (CIs) of simpler but chemically similar molecules such as ethene, styrene and bistyrene, are also studied, together with the related spectroscopic features in other molecules of interest in solar cells and optoelectronics (indoline [1] and fluoren-9-ylidene malononitrile [2]). Both TDDFT and CASSCF/CASPT2 methodologies lead to absorption and emission properties in line with experiments. A rough TDDFT exploration of the CI region in and cyano functionalized DCS molecules as reported by Shi et al [3] gives the hint for the main geometrical parameter that might be involved to reach such CI regions (twisting of the non-cyclic double bond). However, to more accurately discriminate between or cyano functionalized DCS molecules, in terms of their luminescence, a CASSCF/CASPT2 determination of the energy profiles along distortions of the vinyl double bond is desirable. This one is in progress, and might elucidate the actual influence of cyano groups in the accessibility of the CI region.

![chemical structure]

Figure 1. Chemical structure of molecules under study. From left to right, ethene, styrene, bi-styrene, DSB $\alpha$ or $\beta$ DMDCS molecules.

References

Study and application of polypyridyl iron(II) complexes: in search of a sustainable photoredox catalysis

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Photoredox catalysis has emerged as a very powerful tool in synthetic organic chemistry, giving access to a unique reactivity impossible to achieve in the ground state. As a matter of fact, Ir and Ru complexes have proved their worth as photoredox catalysts by activating otherwise inert substrates like aryl halides and N-protected amino acids [1].

However, the toxicity of classical organometallic catalysts has triggered the search of alternative “green catalysts”, capable of performing same transformations while being eco-friendly. In this context, Fe and Ni complexes have been succesfully tested as Pd replacements for cross-coupling reactions; moreover, Ni has been recently applied in combination with Ir in a photoredox/cross-coupling dual catalysis procedure [2]. Nevertheless, the search for a green photoredox catalyst is still on an early stage.

In this work, we present the theoretical calculation of excited state redox potentials for Fe(II) polypyridyl complexes, following the methodology described in ref. [3] in the framework of DFT and TD-DFT. Functional screening shows that a modified version of B3LYP [4] provides the best fit for both vertical excitations and oxidation potentials compared to experimental data.

Moreover, we also present the application of [Fe(bipy)3](PF6)2 as an efficient photoredox catalyst in the reductive cyclization of haloalkenes under UV irradiation. Such transformations were previously achieved with Ru complexes [5], giving a crucial proof for the plausible replacement of Ir / Ru for Fe in other kinds of reactions.

References

Iron–sulfur (Fe–S) clusters are ubiquitous in bioinorganic chemistry, where they serve a number of key roles [1]. Most of their functions are related to redox chemistry: different clusters have reduction potential values ranging from −700 to +500 mV. This behavior is greatly influenced by the complex electronic structure of the clusters, which implies different patterns of spin coupling between the iron centers [2,3].

In order to study these molecules with accurate multireference methods such as CASPT2 a relatively large active space is required (~26–30 orbitals for the simplest 2Fe2S cluster), and so we must turn to methods capable of treating such a big number of orbitals like the recently developed DMRG approach [4,5].

Results obtained from multireference ab initio calculations for some Fe–S model systems will be presented and discussed.

References

The effect of UVA light in thionucleobases: 
the origin of crosslinking lesions

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The simple substitution of an oxygen of a carbonyl group by a sulphur atom in nucleobases can dramatically alter their photophysical and photochemical properties as compared to natural nucleobases. For this reason, drugs based on thionucleobases have been used for years, as immunosuppressants and anti-inflammatory agents.[1] An unavoidable consequence of the treatment with this kind of drugs, is their accumulation in DNA. Although, these compounds are not considered intrinsically dangerous for DNA, their combination with non-lethal doses of ultraviolet radiation produces long-lived excited states, which could interact with environmental molecules, such as molecular oxygen or adjacent canonical nucleobases, leading to other species that may pose a threat to DNA and other biomolecules. [2] In this way, several studies have concluded that there exists an indisputable relationship between thiobases prescription and the development of certain types of cancer, especially skin cancer. [3]

The aim of this communication is to offer a general overview on the mechanism behind dimerization processes in thiosubstituted DNA upon UVA light absorption, being the two main photoproducts cyclobutane pyrimidine dimer and pyrimidine-(6,4)-pyrimidone. [2] For the modelling of these photoproducts, a dinucleoside monophosphate including a thymine and 4-thiothymine has been used, as depicted in Figure 1.

Figure 1. Structure of the dinucleoside monophosphate model including stacked thymine and 4-thiothymine nucleobases.

With the purpose of clarifying the mechanism for the dimerization reactions and determining the potential implication of the excited states, not only singlet but also triplet multiplicity pathway have been described with DFT and the multiconfigurational methods, CASSCF and CASPT2.

A picture at molecular level of the mechanisms, which lead to the formation of these DNA damaging species, is expected to contribute to the development of novel prospective of these drugs for photochemotherapeutic applications.

References
Assessment of sulphur-gold bonding in the adsorption of monosubstituted thiourea derivatives on Au(111) surface

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Capped nanoparticles are hybrid inorganic-organic systems formed by a metal nanoparticle protected with an organic molecule. Recent studies have demonstrated the potential applications of these capped nanoparticles in fields like sensing, drug delivery and antibacterial control[1]. Gold nanoparticles and organosulphur compounds have been widely employed in the formation of capped nanoparticles due to the strong chemical affinity between sulphur and gold[2]. In addition, gold nanoparticles exhibit a high level of biocompatibility which highlights its stability on biological systems[3]. Thiourea derivatives are organosulphur compounds with a special attractive as capped agents owing to its catalytic, ionophore, luminescent and biological properties. In the present computational study we assessed the strength and stability of sulphur-gold bonding during the adsorption of different monosubstituted thiourea derivatives on Au(111) surface (see Figure 1).

The adsorption of monosubstituted thiourea derivatives isomers on the Au(111) surface was modelled in the framework of DFT employing the PBE functional implemented in the VASP code[4]. The density dependent dispersive correction was included to take into account van der Waals interactions[5]. According to our calculations the strength of electron donating/withdrawing groups affected the final arrangement of thiourea derivatives. In addition, we obtained significant differences in the deposition of the thiourea derivatives isomers on Au(111) which was attributed to interactions of different nature between the molecule and the metal surface. The strengthening or weakening of sulphur-gold bonding was also a consequence of the electron donating/withdrawing groups within the thiourea derivatives. Using atomic polarizabilities we were able to address the changes occurred in the thiourea derivatives-Au(111) interface during adsorption. These results allowed us to establish, under a simple approach, rules for the prediction of adsorption geometry in functionalized thioureas.

References
Designing an enzyme from scratch is the most rigorous way of testing our understanding of how natural enzymes function and, at the same time, a challenge to prepare environmentally friendly catalysts. Over the course of history, the study of the enzyme catalytic efficiency never has stopped to surprise. The enormous diversity of the biocatalysts that we know today is the product of evolution from ancestral enzymes, the mechanisms of which are now being elucidated in unprecedented detail. [1] It is crucial to stress the importance of their well-known ability to work under mild conditions of temperature and pressure, and their advantages with respect to non-natural catalysts that make them better candidates to catalyse many reactions employed in the chemical and biochemical industry[2] Therefore, the use of enzymes in synthetic reactions is decisively more advantageous than resorting to metallic or organic catalysts. On the other hand, in order to extend their applicability in wide array, they must be modified by means of protein engineering techniques.

We know that class I aldolases is a wide family of enzymes that form product containing both an aldehyde and an alcohol functional groups.[3][4]–[6] The mechanism through which they operate is a multistep pathway involving an amine and an enzyme - bound Schiff base intermediates. Analogous to the strategy used by type I aldolases,[3] new enzymes that are, mechanistically, the most complex designed to date, have been de novo designed with certain activity for the retro-aldol reaction. They promote the cleavage of a carbon-carbon bond of the 4-hydroxy-4(6-methoxy-2-naphthyl)-2-butanone to obtain 6-methoxy-2-naphthaldehyde (a nonnatural substrate).[4] In order to enhance their catalytic power, these artificial enzymes differ each other in the protein scaffold and in the active side residues. [6] Successful designs have used a catalytic motif comprising a hydrophobic pocket for substrate binding and a reactive lysine residue. The goal of this work is to study the reaction mechanism of the best variant of retro-aldolase de novo designs, the RA95.5-8F (whose experimentally measured \( k_{cat} / k_{uncat} \) value was \( 1.7 \cdot 10^9 \)),[5] and to understand the origin of catalysis of this new design.

Our theoretical studies have been based on the analysis of free energy surfaces employing hybrid QM/MM molecular dynamics simulations, with the QM subset of atoms described by semiempirical (AM1) and DFT (M06-2X) methods. QM/MM Molecular dynamics simulations have been employed later to generate the free energy surfaces for each step of the mechanism in terms of the potential of mean force (PMF), obtained through the combination of WHAM+US techniques [7]–[9] using the tDYNAMO library.[10]

References:
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 the triplet state. 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 dimers [3] and in the crystal [4].

In the present work we aim to unravel the properties of the lowest triplet state ($T_1$) in molecular and crystal PDI thought electronic structure calculations. For that, a preliminary analysis has been done in order to stablish a robust computational protocol to accurately account for the details regarding the ground and low-lying electronic states of the PDI molecule and also its aggregates. In particular we have investigated the impact of the chosen exchange-correlation functional and basis set in the computation of relative energies and electronic character of the states.

References

Theoretical study of promiscuous amidase activity of *Candida antarctica* Lipase B

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*Candida antarctica* lipase B (CALB) is a well known Serine hydrolase capable to catalyze a wide variety of reactions such as hydrolysis of triglycerides and glycolipids, synthesis of esters and epoxidation reactions¹. This promiscuous activity has converted CALB in an interesting protein to develop new biocatalysts² for the production of high value chemical compounds. Among all these reactions amidase activity has special interest because of its role in many biological and industrial processes. Consequently, the understanding of such catalytic activity has a huge interest for the design of new biocatalysts for the production of high value chemicals. In the present work, we have focused in a theoretical approach to understand and characterize the catalytic mechanism of CALB amidase reaction³ that can be used as starting point to develop more efficient and optimized enzymes.

Here we have focused in the study of the amidase reaction mechanism in CALB using hybrid quantum mechanics/molecular mechanics (QM/MM) methods, following previous studies on the Diels-Alderase and Hydrolase activity of CALB carried out in our laboratory⁴,⁵. The evaluation of free energy surfaces of every single step along the explored mechanism, describing the QM sub-set of atoms at semi-empirical and DFT level of theory, has allowed a detailed description of the reaction mechanism and its kinetics.

These results will serve as starting point to design more efficient biocatalysts via rational mutagenesis to be used in the synthesis of organic chemicals.

References

Frustrated Lewis pairs as dynamic cross-links for self-healing materials

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The combination of Lewis acids and bases, defined as electron pair donors or acceptors, usually results in the formation of strong Lewis acid-base adducts. Nevertheless, when bulky acids and bases are combined, their steric demands may preclude these classical donor-acceptor interactions, giving rise to the so-called frustrated Lewis pairs (FLP)[1], which lead to unique and unprecedent reactivity[2]. In particular, these species can activate various small molecules or bonds[3].

The activation of diethyl azodicarboxylate (DEAD) by a FLP has been recently exploited for the production of a dynamic cross-link[4]. Thus, the addition of DEAD to a FLP-functionalized polystyrene promotes network formation, cross-linking the reactive polymer chains, and produces a dynamic, self-healing and heat-responsive gel.

The aim of this work is to explore computationally this process to get a deeper understanding of the nature and reversibility of the interaction between the FLP and DEAD. According to do that, TPSSTPSS method combined with 6-31+G(d) base had been used. Besides, an analysis of the interaction had been done using three different methods, where we would be able to see the strength of the interaction between the FLP and DEAD. The knowledge achieved will allow us to pursuit new FLPs combined with small molecules that may be useful for the experimental community as a first step towards new self-healing materials.

References
Gas adsorption on graphene: Introducing flexibility in the graphene sheet

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Graphene and derived products have shown great promise in the context of gas adsorption, possible applications range from environmental protection over gas sensing to energy storage. An important issue in the understanding of the involved principles, will be the movement of graphene itself. We have performed molecular dynamics calculations on the adsorption of different gases like methane, hydrogen, nitrogen, water and carbon monoxide including an intramolecular force field for graphene [1]. More specifically we have used and compared three different force fields found in the literature [2][3][4], one of which was originally developed for carbon nanotubes, while the other two were constructed specifically for graphene. Two of the force fields include stretch, bending and torsional terms, while the third one only uses stretch and bending terms. We have thus compared the behavior of a flexible graphene sheet to a more conventionally used rigid graphene sheet within the context of gas adsorption.

Figure 1. Adsorption of methane on a rigid (left) and flexible (right) graphene sheet.

References

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Noncovalent Interactions as a tool for understanding Structure of Bimetallic Fluorinated Hybrid Crystals

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Metal–organofluorine interactions play a key role in catalysis, biochemistry, and self-assembly of functional materials, as they directly affect the structure and reactivity of hybrid fluorinated materials. Hence, an in-depth understanding and modulation of these interactions would enable the rational design of functional materials from fundamental chemical principles. However, at present, the toolbox to achieve synthetic control over these kind of interactions is limited to empirical crystallographic rules; this limitation preventing its potential applications.

Within this context, we propose a computational approach that enables a comprehensive characterization of noncovalent interactions in hybrid fluorinated crystals. Our approach couples dispersion-corrected density-functional theory (DFT) to Noncovalent Interactions (NCI) analysis [1]. The versatility of this approach to probe a wide range of noncovalent interactions is demonstrated for a series of four bimetallic fluorinated crystals incorporating alkali–manganese(II) pairs and trifluoroacetato ligands[2]. Noncovalent interactions in these hybrid crystals include metal–oxygen, metal–fluorine, hydrogen bonds, and van der Waals. The computational approach presented herein have general applicability to the quantitative study of noncovalent interactions in metal–organic materials and its role within crystal structure.

Figure 1. Three-dimensional NCI plot for a) hydrogen bonds; b) alkali–oxygen and alkali–fluorine interactions in K₂Mn₂(tfa)₆(tfaH)₂·H₂O.

Images are colored in the [-0.04, 0.04] a.u. range of \(\text{sign}(\lambda_1)\cdot\rho\) (isosurface \(s = 0.5\) a.u.).

References

Second-principles study of topological properties of ferroelectric nanodomains

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Nowadays, the study of magnetic structures with nontrivial topological properties is very important as they may open the door to novel nanotechnologies with huge potential impact. The interest of the scientific community in such structures has been growing in the last few years, with many studies reporting skyrmions in magnetic systems [1]. In this context, some authors have discussed electric skyrmions, whereby an exotic arrangement of electric dipoles would yield skyrmion-like structures in ferroelectric materials. Indeed, the recent experimental discovery of a dipole vortexes in PbTiO3/ SrTiO3 superlattices [2] has added to earlier theoretical predictions of skyrmions in ferroelectric nanocomposites [3] and Bloch-like structures in ferroelectric domain walls [4], and the possibility of stabilizing and manipulating electric skyrmions currently attracting a lot of attention.

Following these ideas, we have used a novel first-principles-based (second-principles) force field developed for PbTiO3 [5,6] to investigate the behavior of ferroelectric nanodomains immersed in a big domain of opposite polarization. Our simulations yield the first prediction of an electric skyrmion in a single-phase material. We have also found that these dipole structures can be controlled applying an epitaxial strain or external electric fields, which may open the door to interesting applications.

References
Topology-based simple model for prediction of fullerenes selectivity:
Diels-Alder reaction

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Exohedral functionalization of fullerenes has enabled the preparation of many derivatives of empty
and endohedral fullerenes with applications in material and biological sciences [1,2]. In particular,
Diels–Alder (DA) cycloadditions are a powerful tool for the introduction of a six-membered ring to
a fullerene cage.

Since there exist different types of C–C bonds on a fullerene cage, regioselectivity is com-monly
exhibited. Taking $C_{60}$ as an example, the DA addition prefers to take place on the [6,6] bonds over the
[5,6] ones, as revealed by experiments and computations. For larger and less symmetrical cages, a
great number of possible regioadducts may be formed. Due to the existence of many isomers, it is not
straightforward to predict structures that are found in experiments. Thus, it is necessary to establish
simple models and rules that allow making reliable predictions [3].

Our Hückel-based simple model, that incorporates the effects of $\pi$ delocalization energy, $\sigma$ strain
and steric repulsion, has been used to predict the most stable fullerene structures for charged [4] and
neutral exohedral fullerenes [5]. In this work [6], it has been used to predict the preferential addition
site of DA reactions to empty fullerenes. We found that activation barriers and reaction energies
obtained from DFT calculations correlate well with each other and the latter can be well reproduced
by our simple model. We further show that DA cycloadditions to empty fullerenes occur preferentially
at a few simple bond patterns, which can be used as a visual guide for approximate prediction of the
DA reactive sites. Moreover, we suggest two quantitative descriptors that have a direct chemical
interpretation in terms of bond forming and breaking ability and in terms of local aromaticity.

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Computational approaches for describing clathrate hydrates interactions

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Accurate energy benchmarks, from wave-function quantum mechanical calculations are presented for sI, sII and sH type clathrate cavities in order to provide an independent mean of assessing DFT approaches as well as semiempirical model potentials. Such analysis contributes to extract valuable information of the underlying interactions and to improve existing approaches or develop new ones for describing condensed-phase systems. Our results show that binding/cohesive energies of such clathrate cavities suffer from huge BSSE, and thus extrapolation schemes were used to obtain more reliable results. Further, dispersion interactions are important on the stabilization energies of such clathrate cages, and the encapsulation of molecules such as CO₂ into guest-free clathrate cages is always energetically favorable. Despite the difficulties faced by current water models and DFT functionals to accurately describe the interactions in such water systems, we found some general trends that could serve to extend their applicability to larger systems.

![Figure 1. Cage structures of the sI, sII, and sH clathrate hydrates (left panel). Cohesive energies obtained from the best-performed DFT functionals and ab initio water models with respect to the reference DF-MP2/CBS1 values (right panel).](image-url)

References
New diagnostic tool for the analysis of the nonlinear optical properties

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While most of the theoretical works in the field of nonlinear optical properties (NLOPs) have been devoted to the search of the most effective quantum chemical methodology for the electronic contribution to NLOPs, the number of tools to analyze their nature is still limited. For example, in the experimentally oriented studies, atomic-type partitionings of NLOPs based on the Mulliken-type \cite{1} and the real-space electron density \cite{2} analyses are usually adapted, though hitherto they have showed limited utility in NLOP benchmarking of quantum chemical methods. In the pioneer work of Chopra \textit{et al.} \cite{3}, the possibility of an orbital partitioning of the polarizability was proposed and years later was expanded in the analyses of Nakano \cite{4} and Ye and Autschbach \cite{5}.

In this work, we present a new Partitioning of NLOPs into (natural) Orbital Contributions (PNOC). The response of natural orbitals is properly captured via changes in the one-particle reduced density matrix, overcoming the approximations of the commonly used uncoupled sum-over-states partition of the NLOPs. The implementation of this decomposition is straightforward and can be implemented for all computational methods available. Furthermore, such obtained overall NO contributions to the NLOPs can be used directly in the local description of these properties (i.e. as functions of the position in a real-space). Besides demonstrating the main features of the PNOC scheme, the important question about the importance of different type of electron correlation, namely static and dynamic correlation, in the computations of the NLOPs will be discussed. With the aid of our analysis, we obtain more insight on that using two different chemical model systems, chain-like conjugated and radical systems (both possess high values of NLOPs). Due to both the simplicity and the orbital consistency of the PNOC scheme, PNOC is an excellent tool for benchmarking the performance of quantum chemical methods in the NLOPs computations and for designing new molecular systems with enhanced NLOPs.

References

Study of the Structure and Degradation Products of Alloxydim Herbicide Using Quantum Chemistry

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Different degradation products (DPs) are formed during mineralization processes of pesticides, once applied on the field. However, there is very limited information on DPs of some pesticides. These new by-products have different physicochemical properties that may greatly affect for example to their environmental behaviour. In this sense, the legislative requirements for the registration of this kind of agrochemicals are becoming stricter, in order to minimize consumer and environmental risk [1].

The present study provides an exploration of the degradative process of alloxydim herbicide by means of density functional theory calculations using the B3LYP functional. The main aim is to identify not only the structure and properties of the parent compounds but also the most relevant by-products, i.e., those formed after the breaking of the most labile N−O bond and the loss of the oxime ether group. In this sense, the formation of stable intermediates difficult to be characterized experimentally are also studied, allowing us to identify some properties of this elusive compound and to determine that the dominant fragmentation process in the gas phase is the homolytic fragmentation. Stability of alloxydim conformers and its homolytic and heterolytic fragments are also assessed in the water phase by means of the Polar Continuum Model. The bonding characteristics are studied by means of the Quantum Theory of Atoms in Molecules and a Natural Bond Orbital (NBO) analysis (Figure 1). Computed IR spectra are found to be consistent with those observed experimentally.

![Figure 1. NBO molecular orbital interactions between occupied and empty orbitals in the most important conformer in the gas phase. Energy values are in kJ mol⁻¹.](image)

This study could be used as innovative strategy for initial estimation of the pesticide degradation pathways and DPs formation, in order to prioritize experimental investigations for risk assessment [2, 3].

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