VIRTUAL SYMPOSIUM ON CHEMICAL THEORY AND COMPUTATION (VS-CTC)

ORGANIZZATO DALLA DIVISIONE DI CHIMICA TEORICA E COMPUTAZIONALE (DCTC) DELLA SOCIETÀ CHIMICA ITALIANA (SCI)

MONDAY DECEMBER 21 | 2.30 PM CET | ON ZOOM

SCIENTIFIC COMMITTEE:

Prof. Maria Cristina Menziani

Prof. Vincenzo Barone

Prof. Isabella Daidone

Prof. Giovanna Fronzoni

Prof. Claudio Greco

Dott. Gloria Mazzone

Prof. Michele Pavone

Prof. Mirco Zerbetto

ORGANIZING COMMITTEE:

Prof. Isabella Daidone

Dott. Gloria Mazzone

Prof. Michele Pavone

Virtual Symposium on Chemical Theory and Computation (VS-CTC)

PROGRAM

2:15 - 3:00 PM: _Invited talks of the winners "Best Paper in Computational Chemistry 2020"_
Chair: Prof. Maria Cristina Menziani

- **Fortuna Ponte**
  Insights from Computations on the Mechanism of Reduction by Ascorbic Acid of Pt^{IV} Prodrugs with Asplatin and Its Chlorido and Bromido Analogues as Model Systems.

- **Jacopo Fregoni**
  Strong Coupling with Light Enhances the Photoisomerization Quantum Yield of Azobenzene.

- **Silvia Alessandrini**
  Extension of the "Cheap" Composite Approach to Noncovalent Interactions: The jun-ChS Scheme.

- **Francesco Di Maiolo**
  Dynamical Disorder and Resonance Energy Transfer: a Novel Quantum-Classical Approach.

3:00 - 4:00 PM: _1st Flash Talk Session_ - Chair: Prof. Mirco Zerbetto

- **Federica Lodesani** - _Study of lithium disilicate crystallization from melt using well- tempered metadynamics._
- **Andrea Phan** - _Modelling TADF emitters: a joint theoretical and experimental study._
- **Francesca Fasulo** - _Ab initio study of singlet Oxygen formation at Li-air battery cathode_.
- **Stefano Pantaleone** - _Schreibersite: a meteor which brings life._
- **Martina Nucci** - _Mechanochemical improvement of norbornadiene-based molecular solar-thermal systems performance._
- **Yasi Dai** - _Exploring the low-lying double-exciton state of conjugated diradicals with cost-effective single-reference and multi-reference approaches_.
- **Angela Parise** - _Inhibition of main protease of SARS-CoV-2 by different candidate drugs from a computational point of view._
- **Giulio Poli** - _Discovery of monoacylglycerol lipase (MAGL) inhibitors based on a pharmacophore-guided virtual screening study_.
- **Alessandra Gilda Ritacca** - _Reactivity of Cu(II)-TSC (thiosemicarbazone) complexes with glutathione in cytosolic environment. Theoretical study and disentanglement of Cu(II)-reduction mechanism._

4.00 - 4.20 pm: _Virtual Coffee Break and Poster Session_

- **Marco Bertani** - _Inclusion of three-body interactions as a way to improve empirical forcefields for the molecular dynamics simulation of oxide glasses_
- **Matteo Capone** - _Multi-scale QM/MM investigation on the mechanistic features of the water oxidation reaction center_
- **Michele Nottoli** - _General formulation of polarizable embedding models and of their coupling_
- **Giulia Dall'Osto** - _Investigating ultrafast two-pulse experiments on single DNQDI fluorophore: a stochastic quantum approach_

- **Lorenzo Tinacci** - *Ammonia binding energies distribution strategy on amorphous models of water ice by ONIOM ab-initio calculations*
- **Alejandro Jodra** - *Mechanochemical treatment of TADF molecules*
- **Germain Aurèle Roger** - *Modeling interstellar amorphous solid water grains by tight-binding based methods*
- **Stefano Scoditti** - *Computational investigation of anticancer activity, DNA-binding and photodynamic properties of a N^C^N-coordinated Pt(II) complex*
- **Valerio Mazzilli** - *Preliminary computational studies of membranes probed by ^{129}Xe NMR*
- **Fulvio Perrella** - *A new approach to increase the accuracy of ADMP extended Lagrangian Molecular Dynamics*

4:20 - 5:20 PM: *2nd Flash Talk Session* - Chair: Prof. Carlo Adamo

- **Jonathan Campeggio** - *Multiscale modeling of reaction rates: application to archetypal SN$_2$ nucleophilic substitutions.*
- **Mariagrazia Fortino** - *Hamiltonian excited state Replica Exchange for photoisomerization processes in conjugated polymers.*
- **Tommaso Nottoli** - *CASSCF second-order algorithm with Cholesky Decomposition of the two-electron integrals matrix.*
- **Anna Perfetto** - *Towards new theoretical approaches for the description of excited state properties and reactivity: A Density Based Approach.*
- **Mirko Vanzan** - *On mechanism of hot-electron injection.*
- **Alessandro Rognoni** - *How many water molecules are needed to solvate one?*
- **Sandra Monica Vieira Pinto** - *A computational insight into the relationship between side chains IR lineshapes and local environment in fibril-like structures.*
- **Marco Mendolicchio** - *A unified GVPT2 treatment of abelian and non-abelian symmetries for the energies and intensities of vibrational spectra.*
- **Anna Rovaletti** - *Hydrogen activation by the aerobic MoCu-dependent CO-dehydrogenase*
- **Diego Sorbelli** - *Unravelling the electronic structure of heavy-element-containing molecules with relativistic approaches: the case of gold dihydride.*

5:20 - 5:40 PM: *CTC Video Contest* & Videos Poll

5:40 - 6.10 PM: *Keynote Lecture* - Chair: Prof. Isabella Daidone

- **Rommie E. Amaro** - *Computational Microscopy of SARS-CoV-2*

6:10 PM: *Conclusions & Greetings*

BOOK OF ABSTRACTS

KEYNOTE LECTURE

Computational Microscopy of SARS-CoV-2

Rommie E. Amaro

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ABSTRACT

I will discuss our lab's efforts, together with collaborators, to understand the SARS-CoV-2 virus in atomic detail, with the goals to better understand molecular recognition of the virus and host cell receptors, antibody binding and design, and the search for novel therapeutics. I will focus on our studies of the spike protein, its glycan shield, and our efforts to model the SARS-CoV-2 virion with atomic detail.

Short CV

Rommie E. Amaro holds the Distinguished Professorship in Theoretical and Computational Chemistry at the Department of Chemistry and Biochemistry at the University of California, San Diego. She received her B.S. in Chemical Engineering (1999) and her Ph.D. in Chemistry (2005) from the University of Illinois at Urbana-Champaign. Rommie was a NIH postdoctoral fellow with Prof. J. Andrew McCammon at UC San Diego from 2005-2009, and started her independent lab in 2009. She is the recipient of an NIH New Innovator Award, the Presidential Early Career Award for Scientists and Engineers, the ACS COMP OpenEye Outstanding Junior Faculty Award, the ACS Kavli Foundation Emerging Leader in Chemistry, and the Corwin Hansch Award. Rommie's scientific interests lie at the intersection of computer-aided drug discovery and biophysical simulation. Her scientific vision revolves around expanding the range and complexity of molecular constituents represented in such simulations, the development of novel multiscale methods for elucidating their time dependent dynamics, and the discovery of novel chemical matter controlling biological function.

INVITED TALKS

PT(IV) PRODRUGS: COMPUTATIONAL INVESTIGATION OF THE MECHANISM OF REDUCTION BY ASCORBIC ACID OF ASPLATIN AND ITS CHLORIDO AND BROMIDO ANALOGUES

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ABSTRACT

In the development of new platinum-based anticancer drugs is of great interest the emerging class of "dual action" Pt(IV) prodrugs that, undergoing a reductive elimination process, the key step for their activation, are able to release the active Pt(II) complexes and bioactive axial ligands that together lead to cell death.

A detailed understanding of the activation mechanism of these prodrugs and the influence of the ligands in axial and equatorial position, will allow to obtain useful guidelines for the subsequent design of new molecules with improved anticancer properties.

Here, aiming at contributing to the elucidation of the mechanism of the key reduction step of Pt(IV) prodrugs, the activation by reduction of the recently synthesized Asplatin Pt(IV) complex, c,c,t-[PtCl$_2$(NH$_3$)$_2$(OH)(aspirin)] [1], in presence of L-ascorbic acid as reducing agent was carried out by means of density functional theory (DFT). The study was also extended to similar complexes, obtained by replacing the OH$^-$ ligand with Cl$^-$ and Br$^-$.

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Strong Coupling with Light Enhances the Photoisomerization Quantum Yield of Azobenzene

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ABSTRACT

Strong coupling between molecules and light can be achieved in resonant cavities[1], giving rise to hybrid light-molecule states (polaritons). In these systems, light does not act only as an external driving to trigger photochemical processes, but it is actively involved in modifying photochemical properties[2]. As such, polaritonic chemistry[3] is emerging as a compelling and non-conventional approach to manipulate photochemical reactions, toward increasing reaction specificity or enhancing yields down to the single molecule level[4]. By relying on accurate quantum chemistry multiscale simulations, we find that strong coupling can lead to enhanced photoisomerization yields for azobenzene in a realistic nanoplasmonic setup[5]. To characterise the mechanism leading to such enhanced yields, we recognise that the strong coupling regime acts as a quencher of non-reactive pathways, typically responsible for the low *trans-cis* photoisomerization quantum yield of azobenzene[6]. Our results show the potential of polaritonic chemistry to control single-molecule photochemical reactions at the nanoscale.

[1] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, J. J. Baumberg, *Nature* (2016) **535**, 127-130

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The junChS composite scheme: an affordable model chemistry for noncovalent interactions

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ABSTRACT

Non-covalent interactions are fundamental in several field of chemistry, playing a major role in catalysis and regulating, for example, the supramolecular structure of biological molecules like proteins or DNA. Therefore, the description of such interactions is of paramount interest in computational chemistry and molecular modelling. However, these types of bond are ruled by contributions of different nature, like electrostatic and dispersion terms, which in turn results in a wide range of interaction energies (from ~1 to ~30 kJ/mol). Thus, a univocal computational model for the description of these weakly-bounded systems is not straightforward. In view of this, I will discuss the derivation of a new composite scheme for the computation of accurate interaction energies (IEs) of intermolecular complexes. Such approach is based on the coupled cluster singles and doubles method augmented by a perturbative treatment of triple excitations, namely CCSD(T), and on second-order Møller-Plesset perturbation theory (MP2). The latter is employed to correct the CCSD(T) interaction energy by means of two terms: (i) the contribution due to the extrapolation to the complete basis set limit (performed with the n^{-3} formula by Helgaker et al.[1]) and (ii) the effect of core-valence correlation. The resulting composite scheme, denoted as "cheap scheme" (shortly indicated as ChS), has been tested against the accurate IEs reported in ref. 2, the results being collected in ref. 3. Since intermolecular systems are particularly sensible to the presence of "long tail" functions, different families of basis sets including diffuse functions have been considered in the evaluation of the IEs. The benchmark study[3] shows that the ChS model computed with the cc-pVnZ family of basis set (with n=T and Q) has a relative mean error of ~3\%, while the use of fully augmented basis sets leads to an error of 1.5%. However, the employment of fully augmented basis sets does not represent the most convenient way to improve the accuracy at a fair computational cost, thus the partially augmented basis sets developed by Papajak et al.[4] have also been considered. The ChS employing the jun-cc-pVnZ basis sets (thus leading to the scheme shortly denoted as junChS) well suits the standards of accuracy, with a mean error of 1.2% and maximum deviations with respect to the reference values within 0.1 kJ·mol^{-1}, and leads also to a slightly lower computational cost. To underline the performance of the latter approach, a test case will be presented and the strategies, currently under development to further improve the junChS approach will be discussed.

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DYNAMICAL DISORDER AND RESONANCE ENERGY TRANSFER: A NOVEL QUANTUM-CLASSICAL APPROACH

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ABSTRACT

The description of quantum molecular dynamics as influenced by a polarizable and dynamically evolving environment is critical to understand the nature of various physical processes, from solvation phenomena in the liquid state to photobiological processes in protein environments, and transport of charge carriers and excitons in nanostructures. Indeed, experimental molecular systems, S, are not closed systems due to the interaction with the surrounding environment, generically denoted the bath, B. Large effects on S dynamics can be expected depending on the nature of the environment as well as on the SB interaction strength. The typically used dielectric continuum picture for B – relying on the well-established polarizable continuum model (PCM) [1] or the conductor-like screening model (COSMO) [2] – is likely to fail when dealing with nonequilibrium solvation effects, notably the time-dependent Stokes shift. Also, linear response approximations typically fail in such situations. [3] On the other hand, fully atomistic first principles quantum calculations are hardly feasible due to the large number of environmental degrees of freedom.

To tackle the above problems, a number of mixed quantum-classical approaches were developed over the past few years. Among them, the Quantum Mechanics/Molecular Mechanics (QM/MM) technique [4] coupled to approximate trajectory-based quantum dynamics of Surface Hopping type [5] is among the most popular approaches. However, to properly describe the correlation between quantum and classical parts, improved quantum-classical approaches are required.

Against this background, I will present a novel quantum-classical approach where, starting from a Quantum- Classical Liouville Equation, [6] we combine for the first time a non-secular Redfield bath with a multistate Smoluchowski equation. The resulting multistate Redfield-Smoluchowski theory naturally lends itself to describe polar solvation effects on photoexcited molecular systems in a fully dynamical way. Accordingly, after benchmarking the new approach against the optical properties of a single chromophore in solution, we use it to investigate the effects of a dynamical polar environment on the Resonance Energy Transfer (RET) process between two different dyes. In particular, we show how the dynamical disorder as induced by a liquid polar solvent can boost RET efficiency. [7]

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FLASH TALKS

STUDY OF LITHIUM DISILICATE CRYSTALLIZATION FROM MELT USING WELL-TEMPERED METADYNAMICS

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ABSTRACT

Understanding crystallization in silicate glasses and melts is of fundamental importance to both produce glass-ceramic materials with tailored properties, and to avoid devitrification during glass manufacturing. Researchers [1] have tried for years to explain with different theories the crystallization, however, with specific regard to nucleation, primary formation of crystalline embryos, many aspects still remain uncertain. Metadynamics has proven to be an efficient tool to study the crystallization process for different systems [2], giving the possibility to drive homogeneous nucleation and crystallization even in very viscous materials, as silicate melts are, overcoming time-scale limits of classical Molecular Dynamics simulations. We have applied well-tempered metadynamics to study nucleation and crystallization of lithium disilicate glass, one of the most studied systems [3] in this field. In this communication, I will show which are the most effective collective variables to bias crystallization and to analyze its evolution in order to gain physical insights on its mechanism at the atomic level. In particular, free energy surface reconstruction [4] has allowed us to identify a two-step mechanism where a critical nucleus with stoichiometry and topology similar to the crystalline phase but disordered is formed and which subsequently rearrange into the stable structure.

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Modelling TADF emitters: a joint theoretical and experimental study

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ABSTRACT

Thermally activated delayed fluorescence (TADF) is arguably the most promising triplet harvesting strategy to improve the efficiency of organic light-emitting devices. The efficiency of TADF emitters is affected by (a) nature of excited states, (b) spin-orbit coupling, (c) conformational degrees of freedom, (d) environmental effects, etc. A proper understanding of these interrelated factors is very much necessary to improve the design of TADF materials.

To tackle the topic, a representative TADF dye, DMAC-TRZ, was selected as a target for this work.[1] An essential state model (ESM) for DMAC-TRZ is defined that accounts for a reduced number of states, but can easily be extended to account for conformational and vibrational degrees of freedom, spin-orbit coupling and solvation effects in terms of electronic and orientational solvent degrees of freedom. Specifically, we exploit a novel antiadiabatic approach to describe the coupling between DMAC-TRZ and the electronic degrees of freedom of the environment.[2] Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations are used to parametrize the ESM. The ESM is then validated against experimental spectra in solution and frozen solvent.

The model reveals the interplay between solvent degrees of freedom and molecular properties relevant to the reverse intersystem crossing process. Moreover it offers a solid foundation for dynamical simulations of TADF using an approach based of the Redfield master equation.

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Ab initio study of singlet Oxygen formation at Li-air battery cathode

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ABSTRACT

During discharge in Li-air batteries, lithium oxidation and oxygen reduction lead to lithium peroxide (Li_2O_2) [1]. The reaction is reversible, but secondary reactions severely limit the cycle life of the batteries, yielding undesired products and decomposition of the electrolyte and the cathode [2]. In particular, several recent experiments have shown that singlet oxygen is formed ($^1O_2$) [3,4]. Such highly reactive specie leads to degradations of the electrolyte, undermining the performance and the long-term stability of the battery. Nevertheless, how singlet oxygen is formed it is still not fully clear, and studying this elusive mechanism represents a challenging task for both experiments and theory.

Here, we address the formation of $^1O_2$ from a computational perspective, comparing the results of periodic DFT with an embedded cluster approach at the CASPT2 level of theory. Our work addresses the Li_2O_2 surface, and namely the (110) facet, which is among the most exposed ones in the lithium peroxide nanoparticles. We characterize the release of triplet- and singlet-oxygen species from this surface by considering different oxygen-surface distances and different oxygen bond lengths.

A first important result of our study is that the starting oxygen bond length is a key descriptor to predict the formation of the singlet specie over the triplet. Further analysis of our results highlights that the charging mechanism with release of oxygen occurs via the formation of superoxide species, as also suggested by recent experiments [5]. In particular, this mechanism is well characterized by the CASPT2 method that is able to predict also an energy barrier, which is absent in DFT.

Beside the interesting computational comparison between two different ab initio approach for studying localized processes in extended chemical environment, our results offer interesting insights for the optimization and further development of nanostructured cathodes for the very promising Li-air battery technology.

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Schreibersite: a meteor which brings life

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ABSTRACT

How life began on earth is a mystery. Despite during the last decades more and more discoveries threw light on many aspects of this phenomenon, there are still many missing pieces in this big puzzle. One of the big unanswered questions concerns the presence of phosphorous on the earth, in particular in its biological form of phosphates and derivatives which are a fundamental requirement for life (ATP, ADP, nucleic acids, etc.).[1] The hypothesis is that phosphorous is available as phosphide in meteors and comets, and schreibersite ($(Fe,Ni)_3P$) is particular interesting for two reasons: i) it is present in meteorites and ii) its interaction with water molecules produces oxidized-phosphorous compounds. In this work we present results based on first- principle simulations on the interaction of water with schreibersite. In the specific we will present results obtained from the VASP periodic code,[4,5] on the bare material (bulk and surfaces), which has never been studied theoretically, and the water adsorption on its most stable surface. The final aim is to study the reaction route (see Figure 1) towards the formation of phosphoric acid (H_3PO_4).
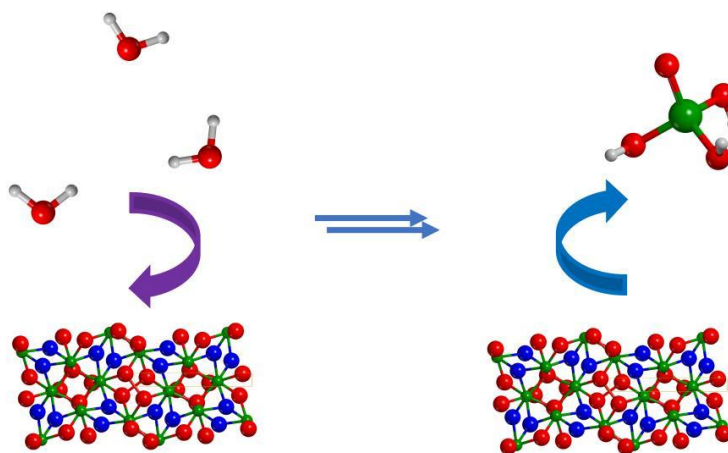
Figure 1: Schematic reaction: H_2O + Schreibersite → H_3PO_4 + Schreibersite.

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MECHANOCHEMICAL IMPROVEMENT OF NORBORNADIENE-BASED MOLECULAR SOLAR-THERMAL SYSTEMS PERFORMANCE

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ABSTRACT

The development of large-scale renewable energy technologies is the main goal for the sustainability of the world society. The direct conversion from solar energy to stored chemical energy has the advantage that both harvesting and stored functions are combined in a single process. Molecular solar-thermal systems (MOST) offer a promising alternative to store and release solar energy, compared to more conventional solar cells.[1] Especially, the norbornadiene-based system was found to be, until now, the most efficient organic-based MOST offering, when opportunely substituted, several promising candidates that could lead to a commercial use. Nevertheless, all carried out experimental attempts largely lack a proper design, hence finding difficulties in improving selected MOST properties. In this work, a novel theoretical approach is described and applied to the norbornadiene-quadricyclane system, with the goal to study the effect of applied mechanical external forces, see the figure, that can be traduced into a steric substitution effect. Moreover, we show that optimal complex forces, resulting from a combination of different contributions, could be suitably converted into substitution patterns and allow further improvements of the MOST properties.[2]
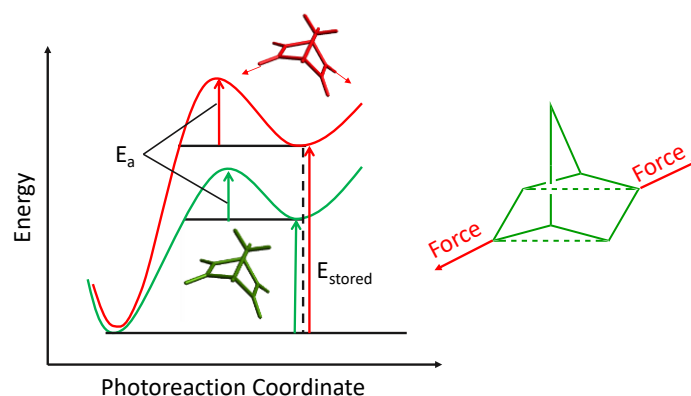
Figure. Schematic PES profile for (green) the photoisomerization reaction without applied external forces and (red) when the reaction is altered by an external costant force, and the corresponding variation of activation (E_a) and stored (E_{stored}) energies.[1]

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EXPLORING THE LOW-LYING DOUBLE-EXCITON STATE OF CONJUGATED DIRADICALS WITH COST-EFFECTIVE SINGLE-REFERENCE AND MULTI-REFERENCE APPROACHES

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ABSTRACT

Diradicals are generally known as molecules with two unpaired electrons. Recently, they have attracted considerable attention due to their potential applications in optoelectronic devices [1]. One feature of such molecules is to exhibit a low-lying double-exciton (DE) state dominated by the doubly excited H,H→L,L configuration. The DE state is generally symmetry-forbidden or weakly allowed in organic diradicals and it can influence the photophysical properties of such molecules (e.g., two-photon absorption, possible quenching of the fluorescence…). Thus, individuating its relative position (for instance, with respect to the bright H→L state) is important. However, a reliable prediction of its excitation energy is challenging because of correlation effects and generally, expensive methods such as MCSCF + CASPT2 or similarly correlated methods are required. In this regard, cost-effective computational approaches able to capture correctly the position of the DE state are needed. To this contribution, we have investigated a series of conjugated diradicals [2] (Figure 1) employing two variants of the time-dependent density functional theory (TDDFT): TD-Unrestricted DFT (TDUDFT, based on the unrestricted spin antiparallel reference configuration) and spin-flip TDDFT [3] (SF-TDDFT, based on the unrestricted spin parallel reference configuration). Both two methods are able to predict the DE state in good agreement with the experimental data. Nevertheless, limitations of these methods are also pointed out. In addition, the newly developed DFTMRCI [4], a multi-reference configuration interaction method based on DFT molecular orbitals, has been employed and its general quality is discussed.

Figure 1: chemical structures of the investigated diradical systems with varying diradical character
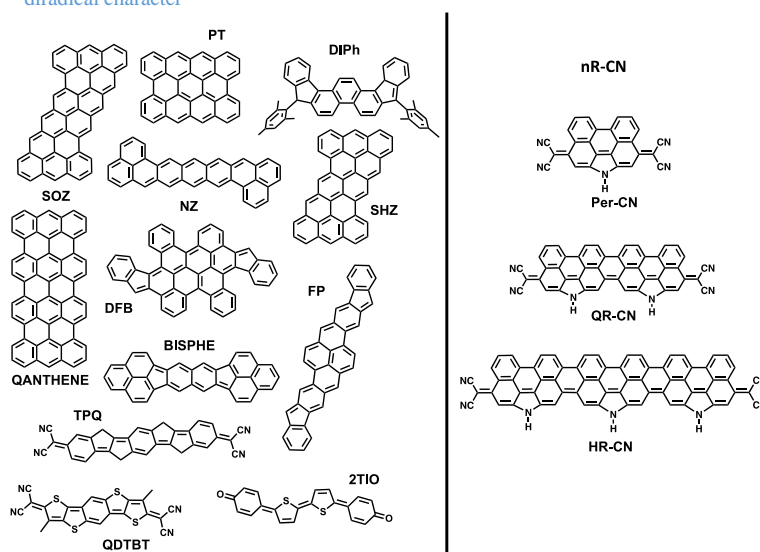
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Inhibition of main protease of SARS-CoV-2 by different candidate drugs from a computational point of view.

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ABSTRACT

Antiviral drugs for the management of human coronavirus infections represent a serious challenge in current global efforts to counter the serious consequences of the spread of COVID-19 syndrome. Coronavirus genome encodes several structural proteins including the glycosylated spike S-protein that acts as a major inducer of host immune responses. The viral genome also encodes several nonstructural proteins including RNA-dependent RNA polymerase (RdRp), coronavirus main-protease (Mpro) and papain-like protease (PLpro).[1] Considering that Mpro is only found in the virus rather than in the host cell, this protein represents an interesting target for the development of new promising anti-coronavirus therapeutic agents.

Jang at al [2] applying a screening strategy on the over 10000 compounds as inhibitors of the SARS-CoV-2 virus main protease indicated some compounds as particularly effective in inhibiting Mpro through in vitro experiments reported in terms of IC50 and spectrometric characterization. Starting from a really recently deposited structure of the COVID-19 Mpro bound to potent broad-spectrum non-covalent inhibitor (PDB codes: 6W63) [DOI:10.2210/pdb6W63/pdb] a series of reversible and irreversible protease inhibitors was considered for a comparative computational study based on the classical molecular dynamics and molecular recognition simulations with the aim to analyze their behavior. Furthermore, in order to obtain a deeper insight on the irreversible inhibition mechanism of Mpro useful to design more selective and more potent inhibitors, theoretical investigation based on QM-cluster model has been performed.
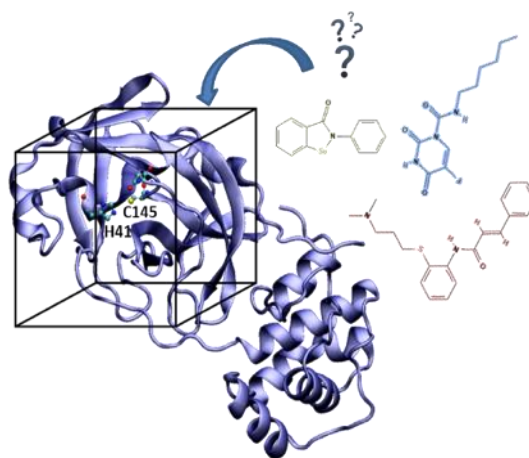

Figure. Ribbons representation of Mpro and some of it's covalent/non-covalent inhibitory candidates.

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DISCOVERY OF MONOACYLGLYCEROL LIPASE (MAGL) INHIBITORS BASED ON A PHARMACOPHORE-GUIDED VIRTUAL SCREENING STUDY

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ABSTRACT

Monoacylglycerol lipase (MAGL) is an important enzyme of the endocannabinoid system that catalyzes the degradation of the major endocannabinoid 2-arachidonoylglycerol (2-AG). Since a product of MAGL-catalyzed 2-AG hydrolysis is arachidonic acid, which is the precursor of eicosanoids that promote neuroinflammation, MAGL is associated with pathological conditions such as pain, inflammation and neurodegenerative diseases like Parkinson's and Alzheimer's disease. [1] Furthermore, MAGL plays a key role in the development and spread of cancer, and elevated levels of MAGL have been found in aggressive breast, ovarian and melanoma cancer cells. [2] Due to its different potential therapeutic implications, MAGL is considered as a promising target for drug design. The discovery of novel small-molecule MAGL inhibitors, especially non-covalent reversible inhibitors lacking the side effects associated to irreversible ligands, is of great interest in the medicinal chemistry field. [3,4] In this context, we developed a pharmacophore-based virtual screening (VS) protocol for the identification of new non-covalent MAGL inhibitors. A pharmacophore screening based on the ligand-protein interactions observed in the latest MAGL-ligand X-ray complex was combined with a consensus docking strategy and molecular dynamics simulations. The application of the whole *in-silico* protocol showed a final hit rate of almost 60%, thus validating the reliability of the VS workflow, and led to the identification of two promising and structurally different MAGL inhibitors, VS1 and VS2. These ligands, for which a reversible character of inhibition was experimentally confirmed, represent a valuable starting point for structure-based hit-optimizations studies aimed at identifying new potent MAGL inhibitors.

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Reactivity of Cu(II)-TSC (thiosemicarbazone) complexes with glutathione in cytosolic environment. Theoretical study and disentanglement of Cu(II)-reduction mechanism.

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ABSTRACT
Copper compounds are cancer chemotherapeutics used alone or in combination with other drugs [1]. They represent also a good alternative to conventional chemotherapeutic agents like cisplatin, and are less toxic than Pt(II)-complexes since the copper is an essential metal ion already present in human body. Currently, pharmacological research is focusing on the therapeutic actions of a new class of metal ionic ligands, thiosemicarbazones (TSCs), that possess antitumor, antibacterial, antifungal and antiviral properties. Nowadays, the main known effects related to their anti-cancer activity are ribonucleotide reductase (RR) inhibition, reactive oxygen species (ROS) production, topoisomerase II inhibition, mitochondria disruption, and, more recently, a multidrug resistance protein (MDR1) inhibition [2]. The exact mechanism of action and biological targets of Cu(II)-complexes are still unclear. At first glance, the relative stability of such metal-compounds in cytosol and nucleus can be investigated against metallothionein (MT) and glutathione (GSH), strong cysteine-containing metal ligands, that have the potential to reduce Cu(II) and to deactivate their pharmacological action. Based on experimental evidence [3] that showed the ability of MT/GSH to modulate metallo-drugs activity in the cell, especially the metal-dependent ROS production, two Cu(II)-TSC complexes, Cu(II)-3AP and Cu(II)-Dp44mT (Scheme 1), have been studied by using a quantum-chemical approach. These complexes react rapidly due to the reduction of Cu(II) to Cu(I), which is then transferred to MT. This suggests that Cu(II)–TSCs are fast dissociated in a cytosolic-type environment and the catalytic generation of ROS by Cu(II)–TSCs is stopped. The aim of the work is to characterize and evaluate the properties of Cu(II)-TSC complexes and to establish the most reliable mechanism of Cu(II) reduction in presence of GSH. Moreover, since TSCs have, in Cu(II)-3AP and Cu(II)-Dp44mT, different structures, have also different kinetics of reaction. DFT computational exploration, together with the experimental counterpart [3], helps to study how those structural differences can influence the stability of synthetized compounds in presence of typical cytosolic concentrations of GSH and to obtain information about the unknown chemistry toward thiol rich molecules. The results could be, in the future, an important explanation for other Cu-complexes that act as drugs in cancer treatment and other applications.
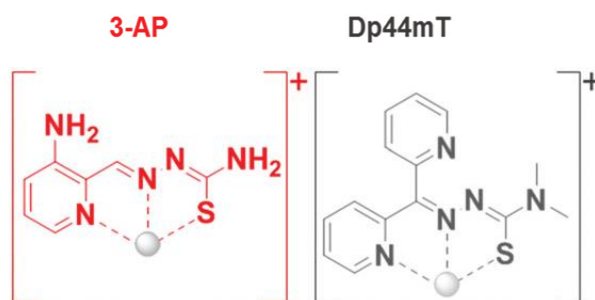
Scheme 1. Cu(II)-TSC complexes: Cu(II)-3AP in red and Cu(II)-Dp44mT in black.

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Multiscale modeling of reaction rates: application to archetypal S_N2 nucleophilic substitutions

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We present a multiscale approach for the evaluation of the kinetic rates of elementary reactions. [1] It is based on Kramers' theory, which accounts for barrier recrossing.

The reaction coordinate is defined as a linear combination of natural, pseudo Z-matrix, internal coordinates of the system, following the work of Mendels *et al.* [2] The usage of internal coordinates represents a more natural way of thinking for chemists, especially in dealing with chemical reactions. The friction along the reaction coordinate is evaluated according to a hydrodynamic approach, which is implemented in the software package DiTe2 recently developed in our laboratory. [3]

To test the capabilities and the flaws of the approach we use as case studies two archetypal S_N2 reactions. Firstly, we consider the substitution of chloride ion to bromomethane, a classic reaction from organic textbooks. The rate constant at 295.15 K is evaluated to $k/c^{\o} = 2.7 \cdot 10^{-6}$ s^{-1} (with $c^{\o} = 1$ M), which compares well to the experimental value of $3.3 \cdot 10^{-6}$ s^{-1}. [4] Secondly, the method is applied to the S_N2 reaction of methylthiolate to dimethyl disulfide in water. In biology, such an interconversion of thiols and disulfides is an important metabolic process not completely rationalized. The predicted rate constant is $k/c^{\o} = 7.7 \cdot 10^{3}$ s^{-1}. A quantitative comparison is not possible since no experimental data is available for this reaction. However, the order of magnitude agrees with the observation that alkyl thiolates to dialkyl disulfides substitutions in water have been found to be fast reactions. [5]

The source code is written in Python employing a modular approach typical of object-oriented programming. A future perspective is to introduce a stochastic treatment of reaction kinetics based on the subset of relevant internal coordinates rather than working with the ill-defined concept of reaction coordinate. Machine learning techniques may be exploited to select such relevant degrees of freedom. The objective is to provide a computational tool tailored to the interpretation of the mechanism of the reactions occurring in large biomolecular systems, accessing also their kinetic rates.

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Hamiltonian excited state Replica Exchange for photoisomerization processes in conjugated polymers

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ABSTRACT

In recent years, conjugated polymers are attracting considerable interest in view of their light-dependent torsional reorganization around the π-conjugated backbone, affording peculiar light-emitting properties [1-3]. Owing to the interest in devising conjugated polymers with tunable photoisomerization pathways [4], we devised a computational framework based on the combination of Hamiltonian Replica Exchange, free-energy perturbation theory and parallel bias metadynamics [5] in order to estimate ground to excited-state free-energy pathways with enhancing sampling of the polymer conformations, with an increase of the parallel efficiency. Specifically, we applied the method on a 5-mer of poly(9,9-dioctylfluoren-2,7-diyl) where each replica shares and exchanges its electronic state torsional potential, derived through TD-DFT simulations at the B3LYP/6-31G* level of theory.

The accuracy of the method was evaluated through a comparison with the emission energies experimentally recorded [6], showing an excellent agreement with the one predicted within this simulation framework.

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CASSCF second-order algorithm with Cholesky Decomposition of the two-electron integrals matrix

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ABSTRACT

A large manifold of chemical systems like transition metal complexes, intermediates in chemical reactions, photoisomerizable chromophores and so on, often require the treatment of static correlation to get a qualitatively correct picture of their behavior. A good starting point is here represented by the Complete Active Space Self-Consistent Field (CASSCF) method. However, the steep computational cost it presents limits its application to small/medium molecules. Specifically, for small active spaces, the bottleneck of the method resides in the manipulation of the two-electron integral (ERI) matrix and its transformation from the atomic orbitals basis to the molecular orbitals one.

We exploited the Cholesky Decomposition (CD) of the ERI matrix [1] for the purpose of reducing computational cost and allowing the application of CASSCF to larger systems.

As a first step, a direct formulation that exploit the CD has been implemented into an existing second order CASSCF optimization algorithm [2] within the CFOUR suite of programs.

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Towards new theoretical approaches for the description of excited state properties and reactivity: a Density Based Approach

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ABSTRACT

Light-matter interaction is the driving force behind many phenomena and technologies ranging from artificial photosynthesis to molecular electronics. Upon light absorption, matter can emit radiation as a cause of a series of phenomena, affecting the electronic and structural properties of the irradiated object. Understanding these processes at the molecular level requires the characterization of excited states, thus allowing the prediction of the photophysical behavior of new molecular systems. Indeed, the purpose of my theoretical work is to develop and apply theoretical tools for the detailed description of the potential energy surfaces of excited states not exclusively in the Frank-Condon area. To this end, quantum methods based on time-dependent density functional theory (TD-DFT), in combination with descriptors based on the electronic density are used. The ultimate goal is the interpretation of the photophysical behavior of systems and the rationalization of the structural and electronic characteristics of excited states giving rise to radiative and non- radiative decay pathways. This allows the *in silico* design of new compounds to solve important problems, including the use of sustainable materials and the global energy crisis.

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On mechanism of hot-electron injection

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ABSTRACT

The recent improvement of the experimental techniques, together with the massive development of theoretical and computational tools, allow nowadays to precisely explore and characterize the physical properties of the matter at the nanoscale. In this sense, the study metallic nanoparticles (NP) gained a lot of interest since their peculiar opto-electronic features, related to the presence of Surface Plasmon Resonance (SPR) makes them suitable for a broad variety of applications in biomedicine, catalysis, electronics, optics and more. [1,2] In recent years, many efforts are being made to investigate the photocatalytic features of metallic NP. As the SPR start to dephases, there is the generation of the so called hot-carriers (HC) which are out of equilibrium electrons (and holes) with higher (or lower) energy compared to the unperturbed system. Once formed, these carriers can migrate to the NP edges and their energy can be transferred to a molecule adsorbed on the surface, activating chemical reactions such as water splitting [3] and CO_2 reduction [4]. Although many theoretical advances have been made to determine the physics below this phenomenon [5,6], there still are an open debate on the precise interaction mechanism with the adsorbate. It is indeed not yet understood how the HC energy can be transferred to the intramolecular motions. [7] Our work aim to investigate one of the possible HC injection routes which implies the transient tunneling to the adsorbate and further energy release the molecular vibrational states. To do that, we explored the interaction among an hot-electron (HE) and a small molecule at the Time Dependent Density Functional Theory (TDDFT) level. In order to simplify the system, we represented the NP structure as a linear metal (Ag or Au) chain and the adsorbate as a small molecule (CO or H_2O) adsorbed on the edge. By simulating the real-time dynamics of a set of single HE on the metal chain, we observed that they can interact with the adsorbate by releasing part of their kinetic energy on some specific molecular normal modes, which are the ones involved in bonds dissociation. The magnitude of such interaction strongly depends on the HE energies and thus on the SPR frequency. Even if a single HE can release a small amount of kinetic energy this effect would become significant when the collective contribution of all produced HE is taken into account. Globally our work suggests that, regardless their energy, all generated HE can compete to the activation of the motion involved in the photocatalyzed reaction, in contrast with the dominant idea of direct electron transfer. [7] However, the more energetic is the HE, the higher would be the transferred energy rate. In this sense, the NP nature and morphology would play a prominent role in the HE injection process efficiency.

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How many water molecules are needed to solvate one?

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ABSTRACT

The comprehension at the molecular scale of the processes involved during solvation still remains a challenge in chemistry. Remarkably, the question concerning how many solvent molecules are necessary to solvate a solute one is still open. By exploring several water clusters of increasing size, we employ semiclassical spectroscopy [1-5] to determine on quantum dynamical grounds the minimal number of surrounding water molecules to make the central one display the same vibrational features of liquid water. We find out that double-acceptor double-donor tetrahedral coordination constituting the standard picture is necessary but not sufficient for solvation, and that particular care must be reserved to the quantum description of the combination band due to the coupling of the central monomer bending mode with network low-frequency modes. The minimal structure eventually responsible of proper solvation is made of a total of 21 water molecules and includes two complete solvation shells, of which the whole first one is tetrahedrally coordinated to the central molecule [6].

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A computational insight into the relationship between side chains IR lineshapes and local environment in fibril-like structures

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ABSTRACT

Infrared spectroscopy is a widely used technique to characterize protein structure and protein mediated processes. While amide I band provides information on proteins secondary structure, amino acid side chains are used as infrared probes for the investigation of protein reactions and local properties. In this work we utilize a computationally cost effective, yet accurate, approach based on the perturbed matrix method [1, 2] to compute the infrared band due to the C=O stretching mode of amide-containing side chains. We calculate at first the infrared band of zwitterionic glutamine in water obtaining results in a good agreement with the experimental data and, thus providing validation of the methodology. [3] Then, we compute the signal arising from glutamine side chains in a microcrystal of the yeast prion Sup35-derived peptide, GNNQQNY, with a fibrillar structure (see Figure). The infrared bands obtained by selective isotopic labelling of the two glutamine residues, Q4 and Q5, of each peptide were experimentally used to investigate the local hydration in the fibrillar microcrystal. [4] The experimental spectra of the two glutamine residues, which experience different hydration environments, feature different spectral signals that are well reproduced by the corresponding calculated spectra. In addition, the analysis of the calculated spectra clarifies the molecular origin of the experimentally observed spectroscopic differences, that arise from the different local electric field experienced by the two glutamine residues, which is in turn determined by a different hydrogen bonding pattern.
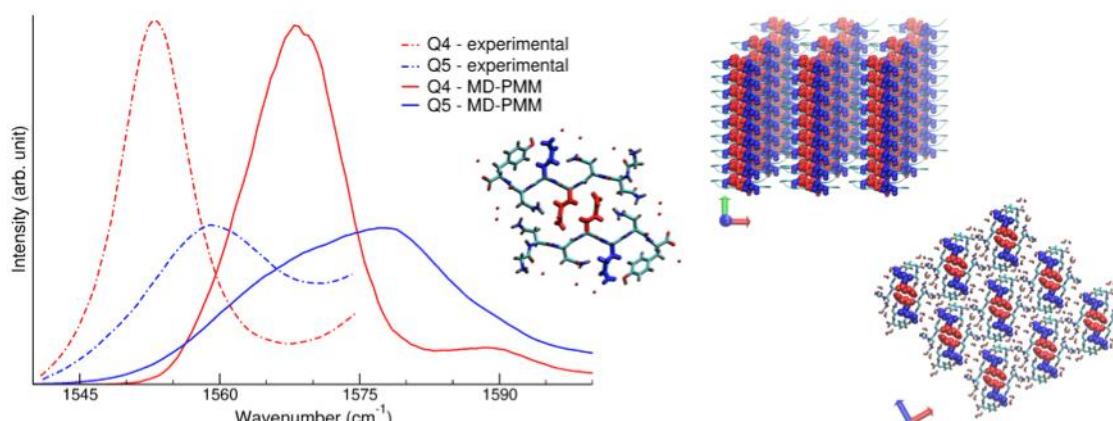
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A UNIFIED GVPT2 TREATMENT OF ABELIAN AND NON-ABELIAN SYMMETRIES FOR THE ENERGIES AND INTENSITIES OF VIBRATIONAL SPECTRA

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ABSTRACT

Spectroscopies, such as infrared and Raman, are powerful tools for the investigation of the physical- chemical properties of molecular systems, providing detailed information related to the structure and dynamics. However, experimental spectra are characterized by several intertwined effects which can make their interpretation challenging without the support of computational models, required to obtain accurate predictions of the transition energies and intensities leading to line-shapes directly comparable to experiment [1]. As a matter of fact, ongoing developments of hardware and algorithms, including the underlying physical-mathematical models, have been essential to the improvement of the quality of the simulations, which can then provide data to analyze the underlying stereo-electronic, dynamic, and environmental effects. Despite the unquestionable success of static structure-property relationships and of the basic rigid rotor harmonic oscillator model to introduce dynamic effects, accurate results, directly comparable with experiment, can be obtained only employing more refined models, and, in particular, including anharmonicity effects. Among the possible methods employable for the inclusion of anharmonic effects in the simulation of vibrational spectra, the second-order vibrational perturbation theory (VPT2) [2] has shown to offer a good balance between accuracy and computational cost, giving the possibility to target even medium-to-large systems. Historically, different formulations of VPT2 have been proposed based on the type of molecules (linear, symmetric, spherical, or asymmetric rotors) [3 5]. With the aim of building a versatile computational platform able to support other types of coordinates (e.g. internal) and to combine perturbational and variational calculations, a unified theory is of primary importance.

In this paper we show that the standard VPT2 approach for Abelian groups can be used also for non-Abelian groups without employing specific equations for two- or three-fold degenerate vibrations, but rather handling in the proper way all the degeneracy issues and deriving the customary spectroscopic signatures of non-Abelian groups (e.g., l-type doubling) by *a posteriori* transformations of the eigenfunctions. In particular, the results for frequencies are exactly the same as those delivered by previous conventional implementations (including accidental resonance contributions), but we are now able to compute also intensities for both IR and Raman spectra without any need of using complex algebra. The whole procedure has been implemented in our general engine for vibro-rotational computations beyond the rigid rotor / harmonic oscillator model and has been validated for a number of test cases employing different levels of electronic structure computations.

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Hydrogen activation by the aerobic MoCu-dependent CO-dehydrogenase

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MoCu-dependent CO dehydrogenase (MoCu-CODH) is a molybdoenzyme, belonging to the xanthine oxidase family, characterized by a $MCD–Mo^{VI}(=O)_2–S–Cu^I–S-Cys$ active site, (MCD = molybdopterin cytosine din ucleotide) [1]. MoCu-CODH derives from the aerobic soil bacterium *Oligotropha carboxidovorans* that is able to exploit the highly toxic carbon monoxide molecule as its sole source of carbon and energy to grow, thanks to the oxidation of the latter to CO_2. Moreover, this enzyme also shows the ability to oxidize H_2 to protons [2]. Substrate binding and its oxidation are believed to occur at the Cu^I center [3], thanks to the high degree of delocalization within the $Mo(\mu$-S)Cu unit, which allows facile electron transfers toward the redox-active Mo ion during catalysis [4].

Even if its hydrogenase activity has been known for decades, a debate is ongoing on the most plausible mode for the binding of H_2 to the enzyme active site and the hydrogen oxidation mechanism. We performed theoretical investigations of the hydrogenase activity of the enzyme using the hybrid quantum mechanics/molecular mechanics (QM/MM) approach. Only one previous computational study on this topic had been published before where a small QM- cluster model was employed. In such publication, it was evidenced that changes in the MoCu-CODH active site were necessary for the binding of H_2 to Cu [5], differently from what was previously hypothesised by the experimental group of Wilcoxen and Hille [6].

By means of QM/MM, we were able to suggest a new plausible mechanism for the hydrogen molecule splitting that involves a frustrated Lewis acid/base pair (FLP), where the frustration is enforced by the protein secondary structure preventing acid/base quenching [7]. In this scenario, the protein active site should be viewed as a $Mo^{VI}=O/Cu^I$ FLP, where the Cu^I acts as a Lewis acid and the equatorial oxo ligand of Mo acts as a Lewis base toward the oxidation of H_2. Our results indicate that the $Mo=O_{eq}$ represents the strongest base of the active site and therefore it proved to be the most favourable site for the first deprotonation event of H_2 oxidation. This reaction would lead to the formation of a Mo OH–Cu(I) H hydride with a correspond ing intramolecular hydrogen bond that would stabilize the copper hydride, otherwise known to be very unstable. Interestingly, in a recent work on a synthetic model of the MoCu-CODH active site, the authors considered the possibility that an FLP-based mechanism may also characterize the enzymatic oxidation of CO to CO_2 [8].

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Unraveling the electronic structure of heavy-element-containing molecules with relativistic approaches: the case of gold dihydride

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ABSTRACT

Photoelectron spectroscopy (PES) is a well-known technique which provides unique information about the electronic structure of simple molecules containing heavy elements. However, the interpretation of the experimental spectra can often be very complex and for this reason coupling experiments with relativistic quantum chemical approaches that accurately account for scalar relativistic (SR) effects and spin-orbit coupling (SOC) is mandatory. Concerning gold dihydride, PES experiments on anionic AuH_2^-, which upon photodetachment lead to the six lowest-lying electronic states of neutral AuH_2, reveal that these species, despite being among gold's simplest $ML_2^{-/0}$ compounds, has a far from obvious electronic structure, with the ground state that undergoes bending upon photodetachment [1]. From the experiment, Vertical Detachment Energies (VDEs) were extracted for all the states, thus representing an ideal set of reference values for testing theoretical approaches. On the other hand, Adiabatic Detachment Energies (ADEs) were only determined for the ground state, due to limitations of the experiment. We decided to test some approaches for the prediction of VDEs for the states of neutral AuH_2 by accounting for the role of relativistic effects, orbital relaxation and electron correlation. Our results [2] clearly suggest that both the energy order of the experimental bands and the experimental VDE values are correctly reproduced only when SOC and electron correlation are included in the calculations with a high degree of accuracy. By applying the IP-EOM-CCSD approach in its relativistic formulation [3], we are able to gain complementary results with respect to the experiments, such as the optimized geometries of all the states and the corresponding ADE values that could not be determined experimentally. Our approach confirms that the ground and first excited state lie very close in energy and for this reason vibronic coupling effects may take place which can be evaluated through the scan the Potential Energy Surface not only in the direction of the bending, but also in the direction of the asymmetric stretching. Eventually, we find the ground state to be also affected by a symmetry breaking in the asymmetric stretching direction due to the Pseudo-Jahn-Teller Effect (PJTE). This last finding makes the intriguing gold dihydride, to the best of our knowledge, the first reported heavy-metal-containing molecule to be affected by PJTE.

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POSTER PRESENTATIONS

Inclusion of three-body interactions as a way to improve empirical force-fields for the molecular dynamics simulation of oxide glasses

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ABSTRACT

Multicomponent oxide glasses play a key role in addressing major global challenges in energy, medicine, and advanced communications systems [1,2] and are thus among the more used materials in the related industries. Unfortunately, the development of new glass compositions with tailored properties is hampered by the lack of a complete understanding of their structure. Among the physics-based methods, classical Molecular Dynamics simulations based on empirical interatomic potentials have emerged as a powerful and efficient tool to gain insight into the composition-structure-properties relationship of a wide range of amorphous and glassy materials [3,4]. However, the accuracy and reliability of classical MD results strongly depend on the interatomic potential used and thus it is of great importance to develop new, accurate and transferable, force-fields. In this contribution, the self-consistent PMMCS potential [5], a widely used force field for the simulation of silicate, aluminosilicate and phosphate glasses based on two-body cation-oxygen and oxygen-oxygen interactions computed with Morse functions, has been revised and hugely improved by the inclusion of two types of three-body interactions acting between T-O-T bridges (T = Si and P) and network formers – network formers repulsive interactions. We will show that the new force-fields, called BMP-harm and BMP-shrm, better reproduce the T-O-T bond angle distribution and network former – oxygen distances. As a consequence, the prediction of Qn distributions (Q stands for quaternary species and n is the number of bridging oxygens around it), neutron total distribution functions (TDF), solid-state NMR spectra of spin active nuclei (^{29}Si, ^{17}O, ^{31}P, ^{27}Al) and the density have also been hugely improved. We will also highlight the strong correlation between the T-O-T bond angle distributions and the other short and intermediate structural properties in oxide glasses, which has been largely neglected in the past. In addition to the improvement of the structure, the new FF has revealed to reproduce fairly well also the ionic conductivity in mixed alkali aluminosilicate glasses and the elastic properties.

To better show the accuracy and reliability of our new potential models in the simulation of glass properties, we will report a systematic comparison with other interatomic potential models, including the polarizable core-shell one.

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Multi-scale QM/MM investigation on the mechanistic features of the water oxidation reaction center

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ABSTRACT

In the field of enzymatic mechanisms the ones related to the Photosystem-II (PSII) are among the most debated nowadays. This enzyme is located at the end of the energy funnel of the light absorption proteins in the photosynthetic machinery and is eventually able to carry on the water oxidation, converting two water molecules in molecular oxygen, protons and electrons [1]. The water oxidation reaction is one of the most important reactions for humankind, both because it is at the very base of life and because it could be a key point for producing renewable energy if a robust artificial photosynthesis would be achieved.

While the last phases of the water oxidation, which involve the oxygen-oxygen coupling and final oxygen release, are elusive from the experimental point of view due to lack of any stable intermediate, insight at the molecular level can be obtained by means of hybrid QM/MM approaches. Here, I will present mechanistic information obtained by canonical QM/MM Molecular Dynamics (MD) calculations and validated by the good agreement with the time constant measured for the reaction [2, 3]. In particular the flexibility of the hydrogen bond network, which is well represented using MD simulations, is fundamental for the fulfillment of both the oxygen coupling and oxygen release. Also, the presence of a strong template effect of the metal cluster, core of the reaction center, have been observed, which providing a starting point for the study of the cluster formation.

Another fundamental step in the photosynthetic process involves the chemical species which is able to produce the fuel, i.e. the oxidation equivalents to the reaction center of the water oxidation: the special pair P680, which is composed by a pair of chlorophyll A.

The reduction potential of the P680 is the highest among all the biological systems and is finely tuned by its complex environment. Using a different QM/MM approach based on MD simulation and the Perturbation Matrix Method, which already provided good results on other similar systems [4-5], we are in the process of understanding the dynamical effects exerted by the protein and the water molecules on the reduction potential and the UV-VIS absorption properties.

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Investigating ultrafast two-pulse experiments on single DNQDI fluorophore: a stochastic quantum approach

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ABSTRACT

Together with ensemble approaches, as two-dimensional electronic spectroscopy, single- molecule techniques have been recently developed.[1] In particular, ultrafast two-pulse ex- periments are invaluable tools to investigate the microscopic dynamics of a fluorophore.[2] The first pulse generates electronic or vibronic coherence, the second pulse probes the time- evolution of the coherence. We set up a protocol based on a quantum mechanical description of the fluorophore coupled to the simulation of the real-time dynamics of the system wave- function. The vibronic structure of the molecule is included in terms vibronic states energy and transition dipole moments.[3] The molecule is described as an open quantum system and its dynamics is computed through the stochastic Schrödinger equation (SSE) within the Markovian limit.[4] This protocol[5] has been applied to DNQDI fluorophore, previously investigated experimentally,[6] whose energies and transition dipole moments have been computed with DFT/TDDFT methods. We find a good agreement with the experimental outcomes and provide a microscopic and atomistic interpretation.

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Modeling interstellar amorphous solid water grains by tight-binding based methods

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ABSTRACT

The Interstellar Medium (ISM) is comprise of Complex Organic Molecules (iCOMs) [1] formed in the gas phase of the ISM but also at the surface of water ice grains via chemical recombination. These interstellar grains are submicron in size, composed of a silicate-core covered in multiple layers of amorphous ice, and are believed to work as a reaction catalyst for the formation of molecular species that cannot happen in the gas phase such as the formation of H2 the most abundant molecule in the ISM [2]. Thus, the model of interstellar grain used to study the formation of iCOMs and their binding energy (BE) in the solid phase using computational chemistry is crucial. In this work we propose a methodology that aims at modelling water ice grains and their hydrogen bonds cooperativity by building a cluster of dozens of water molecules. This methodology uses the semiempirical quantum mechanical methods (SQM) made available in the GFN-xTB program from the Grimme's group [3,4,5,6]. The GFN methods are at least two orders of magnitude faster than conventional density functional theory (DFT), and in a previous work we showed that they were highly accurate with small water clusters even when compared to CCSD(T) results for GFN2 [7].

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Mechanochemical treatment of TADF molecules

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ABSTRACT

Thermally activated delayed fluorescence (TADF) plays a key role in the design of high efficiency organic light-emitting diodes. The mechanism of the process consists in both, direct fluorescence (25%) and delayed fluorescence produced after thermal transformation of triplet to singlet excited states (75%), known as reverse intersystem crossing (rISC). Increasing the triplet-singlet states energy degeneracy, facilitating the rISC, the efficiency of the system increases.[1] In this regard, we aim to use mechanochemistry (that is the application of an external force) as a versatile tool to modulate the properties and enhance the efficiency of TADF systems.

In particular, we have selected PTZ-DBTO$_2$ as the system under study (Figure 1). First we have improved a previously used method[2] to calculate the force that optimally decreases or increases the energy difference between two electronic states. Additionally, with this method the three key energy changes between the electronic states have been evaluated. In the first place, the most important is to evaluate the force that decreases the energy difference between the first triplet (T1) and singlet excited state (S1). Then, we have to calculate the forces that make triplet states as far in energy as possible, which in this case increases the coupling of T1 with S1 (increasing the whole efficiency). Finally, the modulation of the emission energy of TADF systems could be a worthwhile achievement, as few examples of systems giving red emission have been reported. Hence, we have also calculated the forces decreasing the S1-S0 energy difference, red-shifting the emission.
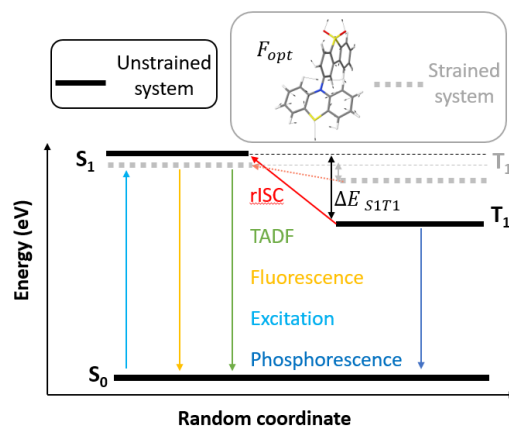
Figure 1. Scheme of TADF mechanism for the unstrained (black) and strained (grey) system.

Once calculated these optimal forces, we are going to introduce different substituents into the molecule at different positions that generate certain structural changes with respect to the original system but without actually producing electronic changes in the states. So that the substituent can be seen as an external mechanical force acting on the original system.

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Preliminary computational studies of membranes probed by [129]Xe NMR

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Satisfy the demand for an increasing computational power became easy, thanks to the computer industry which fulfils the needs of the Information Age, in which we still live. Advancing in machine architecture and computer technology led to notable milestones in the past decade. Performing simple simulations are, nowadays, tasks that everyone could attempt just with an ordinary personal computer. However, doing simulation isn't just pressing buttons of black boxes. Computational chemists' expertise relies on evaluates numbers, thus answering the question: "How good are the numbers that have been calculated?" [1] could be sometimes tricky, because this implies knowing how's the black box made and what are the mechanisms working inside it.

This work focuses on Mixed Matrix Membranes (MMM) with ionic mesogens (ILC) employed as fillers. It aims to bridge the experimental knowledge [2] with the computational counterpart. Nevertheless, such complex systems aren't straightforwardly modelled: the overall properties depend on a sum of contributions. ILC' structure and morphology are investigated experimentally using Xenon-129 Nuclear Magnetic Resonance (NMR) spectroscopy [2]. In these materials, Xe atoms reside in the lipophilic moiety, often constituted by a long alkyl chain. To model and calculate accurately [129]Xe NMR properties for such material is compulsory to rightly model, first, [129]Xe NMR spectra in simple alkanes, whose experimental data exist in literature [3,4], and discern which contributions have more weight and thus, have to be treated more carefully.

The first steps in this work are: choosing a suitable Force Field (FF) for modelling alkanes, in molecular dynamics simulation, and selecting an appropriate level of theory for quantum mechanical DFT calculations which generates NMR spectra. AMBER-94 [5] FF and L-OPLS-AA [6] are used in Molecular Dynamics (MD) simulations. The latter better represents the conformational space explored by alkanes and it better reproduces the transition temperatures from solid to liquid of these substances. For the NMR calculations relativistic corrections should be included; QZ4P basis is employed in modelling Xe, while three different bases (DZP, DZ, SZ) are evaluated in modelling C and H atoms.

[129]XeNMR spectra are, also, exploited in the morphological and structural determination of inorganic membranes made of certain Zeolites [7]. In this case, Xe loading, and thus its concentration, create clusters of Xe in the zeolite's cavity. This evidence is not deeply understood and the reasons that rule these systems are not fully clear up to now.

The sub-microscopic lens of simulation could improve our knowledge of this issue and gives insights on mechanisms working inside these systems.

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General formulation of polarizable embedding models and of their coupling

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ABSTRACT

Polarizable embedding models, such as polarizable continuum models (PCM) or polarizable QM/MM models, can provide accurate properties in a simple way. However, their use introduces an additional degree of freedom in the problem, that is the polarization density. Depending on the energy definition, we distinguish variational and non variational polarizable embeddings models. In the first kind the polarization density is a minimizer of the energy, so the expressions for the properties are simple as the terms containing the derivatives of the energy with respect to the polarization density vanish. In the second kind, the expressions for the properties are in principle more complex, however by introducing an appropriate set of Langrange multipliers and by solving for them, the properties can be obtained again in an easy way[1].

Further difficulties arise when one wants to couple two polarizable embedding models in a multilayered strategy, such as those employing a QM method for the interesting part, a polarizable MM description for the molecules close to the QM part and a polarizable continuum model for the outer shell[2]. In particular, the expressions for the energy and the properties can become complex if one or both the employed models are non variational.

In this work, we propose a general formalism for polarizable embedding models that can be applied to either continuum or atomistic polarizable models[3]. After deriving such a formalism for both variational and non-variational models, we address the problem of coupling two polarizable models among themselves and to a quantum mechanical (QM) description in the spirit of multiscale quantum chemistry. We discuss general, model-independent coupling hypotheses and derive coupled polarization equations for all combinations of variational and non-variational models and discuss the embedding contributions to the analytical derivatives of the energy, with a particular focus on the elements of the Fock or Kohn–Sham matrix. We apply the general formalism to the derivation of the working equations for a three-layered, fully polarizable QM/MM/continuum strategy using the non-variational atomic multipole optimized energetics for biomolecular applications polarizable force field and the domain decomposition conductor-like screening model.

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A NEW APPROACH TO INCREASE THE ACCURACY OF ADMP EXTENDED LAGRANGIAN MOLECULAR DYNAMICS.

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ABSTRACT

Ab initio molecular dynamics techniques are widely employed to simulate equilibrium and non-equilibrium properties of molecular systems. [1] In particular, the so-called extended Lagrangian methods are a good compromise between accuracy and computational cost. In the Atom-centered Density Matrix Propagation (ADMP) approach, the one-electron density matrix is treated as a (classical) dynamical variable and propagated along with the nuclei. [2-5] Therefore, a fictitious electronic mass has to be introduced. This parameter has a fundamental role in governing the degree of adiabaticity between the (fictitious) electronic and (real) nuclear degrees of freedom.

A rational way to non-uniformly attribute masses to the density matrix elements in an orthonormal atomic basis is here proposed. To this end, a projection operator onto several molecular orbital subspaces is constructed. Both light and heavy atoms (treated as all-electron as well as with pseudopotentials) can be modelled with consistent accuracy. A detailed analysis of improvements and limits of the method performances is then presented. This approach can enhance adiabaticity between the electronic and nuclear degrees of freedom and allows for the employment of a wide range of time steps, without loss in accuracy. [6]

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Computational investigation of anticancer activity, DNA-binding and photodynamic properties of a N^C^N-coordinated Pt(II) complex

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ABSTRACT

The fundamental discovery of the cytotoxic activity of cisplatin and the subsequent clinical approval of its carboplatin and oxaliplatin analogues worldwide efforts to develop new anti-cancer platinum(II) complexes have been remarkably stimulated. Cyclometalated platinum(II) complexes containing tridentate π-conjugated organic ligands have been receiving an increase of interest as they display rich and diverse photoluminescent properties that are sensitively affected by the local environment. Alongside photoluminescent properties, such complexes have attracted, in the last few years, a lot of interest for application as potent anticancer agents and several groups have studied their antitumor properties[1]. These complexes can exert their cytotoxic action via either classical covalent binding, both intra and inter strand cross-linking, to the DNA base pairs or reversible interactions such as intercalation. Indeed, the planar motifs of these platinum(II) complexes can render them DNA metallointercalators capable of inserting between adjacent DNA base pairs and establishing non-covalent ligand–ligand π–π stacking interactions. More recently[2], the investigation of the antiproliferative properties of that kind of complex has demonstrated that they are promising photosensitizer under visible light capable to produce singlet oxygen in organic solvents. Inspired by such findings we have undertaken a detailed theoretical investigation, using several computational tools, of the cytotoxic activity of complex Pt(N^C^N)Cl, where the N^C^N ligand is 2,6-dipyrido-4-methyl-benzene, its modes of interaction with DNA, the effect on its spectroscopic properties of such interactions and the possibility that induced DNA damage is the consequence of its photosensitizer nature.
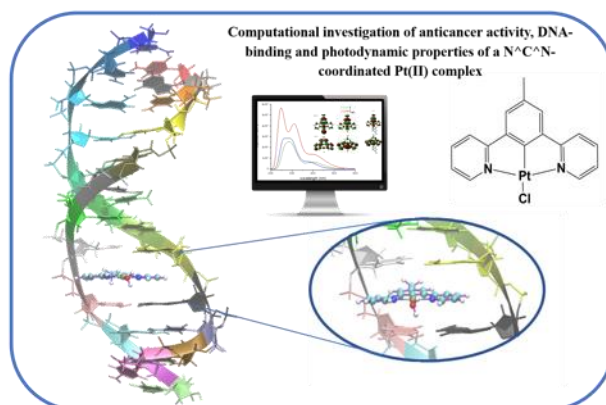
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Ammonia binding energies distribution strategy on amorphous models of water ice by ONIOM ab-initio calculations

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ABSTRACT

In the denser and colder (£ 20 K) regions of the interstellar medium (ISM), near-infrared observations have revealed the presence of sub-micron sized dust grains covered by several layers of H_2O-dominated ices and "dirtied" by the presence of other volatile species [1]. Whether a molecule is in the gas or solid-phase depends on its binding energy (BE) on ice surfaces. Thus, BEs are crucial parameters for the astrochemical models that aim to reproduce the observed evolution of the ISM chemistry. In general, BEs can be inferred either from experimental techniques or by theoretical computations. In this work, we present a reliable and a new computational strategy to evaluate the ammonia BE distribution on amorphous solid water (ASW). This new flowchart is based on three different level of theory in order to perform accurate BEs into the ONIOM procedure framework [2,3,4,5].

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