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Book of Abstracts

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2 Contributions from Invited Speakers

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S. Corni Exploring quantum chemistry on quantum computers.

M. Corno Cyclodextrin-based nanosponges (CD-NS) as drug delivery systems: a novel computational approach.

T. Marino Computational Enzymology: A Challenge for Multiscale Approaches.

M. Pagliai Hydrogen Bond Structure and Dynamics in Liquid Water under Pressure.

G. Raos Polymers interacting with surfaces: insights and surprises from simple models.

Computational approaches for biocompatible ionic liquids.

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ABSTRACT

Biocompatible ionic liquids[1] are based on the combination of amino acids anions with cations such as choline. The computational description of these substances is far from being trivial and requires the use of an array of diverse techniques to model a surprisingly rich chemistry due to phenomena such as polarization, charge transfer, proton transfer and isomerization reactions. In this presentation I review the difficulties that arise in attempting a computational modelling of these systems that are a clear example of how a seemingly simple system can hide an unexpected complexity. Part of their structure, and of their bulk properties are strongly influenced by collective phenomena such as the occurrence of isomerization reactions and proton transfer[2]. For example, and quite surprisingly, these liquids are characterized by an unusually large degree of like-charge ionic association whereby intra-molecular proton transfer leads to the appearance of zwitterionic and neutral forms that shape not only their nanoscopic structures, but also their ability to act as gentle solvent for biological matter, as media for green chemistry[3] and as peculiar electrolytes[2].

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3. S. Onofri, A. Le Donne, H. Adenusi, E. Bodo* CO_2 Capture in Ionic Liquids Based on Amino Acid Anions With Protic Side Chains: a Computational Assessment of Kinetically Efficient Reaction Mechanisms, ChemistryOpen, 9, 1153 – 1160 (2020).

Exploring quantum chemistry on quantum computers

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ABSTRACT

Quantum computer hardware is rapidly evolving thanks to the efforts of major enterprises such as IBM and Google and dedicated startups. It was proposed early that quantum computers may be particularly suitable to simulate quantum systems [1], with an emphasis on quantum chemistry [2]. This spurred an intense research activity on algorithm development and software implementation, mostly focusing on calculating ground and then excited state energies. In this talk I shall present our first works in this field, related to the implementation on digital quantum computers of quantum optimal control algorithms [3] and the extension of electronic structure calculations on quantum computers to include solvent via an implicit description [4]. Quantum computing can also be used for classical Theoretical Chemistry problems [5]. The emphasis of the presentation will be mostly on the barriers and difficulties we have encountered (and we are encountering) to enter in this intellectually stimulating field.

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Cyclodextrin-based nanosponges (CD-NS) as drug delivery systems: a novel computational approach

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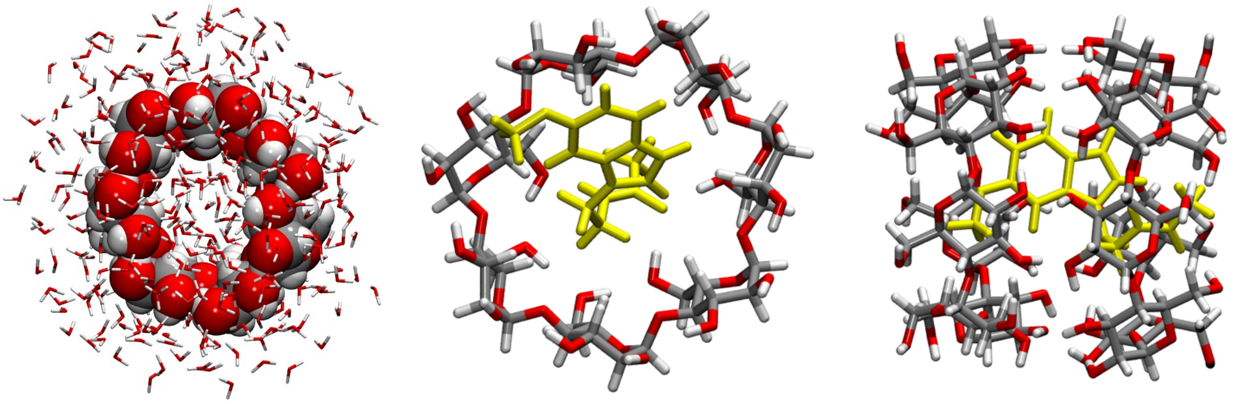
In recent years, the interest in both the theoretical description and the structural modeling of cyclodextrin-based nanosponges (CD-NS) as carriers for a variety of guest molecules has risen. To this extent, previous studies have investigated the formation of non-covalent complexes between a guest molecule and β-cyclodextrin monomers, by applying different computational methods and different levels of theory. Among these, classical mechanics and semi-empirical levels were explored, as well as Density Functional Theory (DFT) methods, lastly.[1]

Due to the increasing complexity of these systems and their derivatives, especially considering β-cyclodextrin three dimensional networks, i.e. nanosponges,[2] it is necessary to employ a method combining the accuracy of density functionals with the computational cheapness ensured by force-field-based methods and standard semi-empirical ones. A promising candidate, aimed at bridging this gap, is the recently developed semi-empirical xTB-GFN2 method, proposed by Grimme's group. xTB-GFN2 has been employed in a large variety of systems, including different host molecules.[3,4]



Left: β-cyclodextrin with explicit H_2O; center: melatonin/β-CD complex; right: melatonin/β-CD dimer complex.

Among several possible pharmacologically active molecules, we have chosen melatonin (MT) and investigated the melatonin/β-cyclodextrin inclusion complex as a testing ground for this novel method.[5] Its validation has concerned structure, energetics, and IR spectra predictions in comparison with more standard DFT-based approaches. Specific attention has been paid to solvent effects, for water, with implicit and explicit solvation. The aim was to define a robust, accurate and, at the same time, low-cost methodology to investigate these complexes. So far, results have indicated that the xTB-GFN2 method provides accurate computed observables, paving the way for modeling cyclodextrin-based nanosponges.

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Computational Enzymology: A Challenge for Multiscale Approaches

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ABSTRACT

Enzymes are an extraordinary machinery, indispensable for life in the vegetal and animal kingdoms, able to act as efficient catalysts with high selectivity, fast kinetic constants and with low energy demands. Their importance has increased tremendously in recent decades encompassing several fields in addition to the life sciences, such as agribusiness, environmental and green chemistry, and various areas of modern industry. In this scenario, knowledge of their working mechanisms at the atomistic and electronic levels is very important and is a matter of frontier research from both experimental and theoretical viewpoints. Multiscale approaches (QM, QM/MM, MD and SMD) can help to shed light on all the various phases involved in the catalytic activity of an enzyme. Examples will be presented in this contribution that emphasize the importance of the various stages of enzyme catalysis and the role that theoretical and computational tools can play in each.

Hydrogen Bond Structure and Dynamics in Liquid Water under Pressure

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ABSTRACT

Liquid water has a fundamental role in most of the biological, chemical, physical, geological, and environmental processes occurring in nature. Water molecules interact through hydrogen bonds, which determine the tetrahedral arrangement of the first solvation shell and characterize the tridimensional network in condensed phase. The relation between structure and dynamics of the hydrogen bond is essential to understand the behaviour of liquid water [1, 2, 3].

The application of computational methods to study the hydrogen bond interactions in liquid water has allowed to rationalize the results of experimental measurements in different pressure and temperature conditions and to identify the low and high density forms [1, 2, 3]. A direct correlation between computational and experimental results has been obtained by the analysis of molecular dynamics trajectories. The low-high density turning point at ambient temperature has been determined by the variation of the isothermal compressibility coefficient with pressure [4].

To improve the agreement with the spectroscopic properties, a new polarizable model, based on the Chemical Potential Equalization (CPE) principle, is currently being developed. Although the model requires further improvements, the first results are very encouraging [5].

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Polymers interacting with surfaces: insights and surprises from simple models

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ABSTRACT

The interaction of polymer melts and networks with solid surfaces is important for many applications, such as polymer adhesion, friction, and the mechanical reinforcement of rubber by colloidal nanoparticles (e.g. carbon black).[1,2] In recent years, my group has undertaken a systematic study of the effect of surface chemical heterogeneities on the properties of adsorbed or confined polymer films.[3-6] To do so, we have adopted a simple coarse-grained model, in which a surface consists of a “mixture” of weakly and strongly interacting sites, which may distributed randomly or according to specific morphologies. We have found that the dynamical and mechanical properties of the polymer films (chain diffusion coefficients, work of adhesion) depend in a non-trivial way on the compositional and morphological variables of the surfaces. The last part of my talk will illustrate results from a recent extension of the model, showing the effect of chemical bonding (of the polymer to the surfaces) and cross-linking (within the polymer) on the mechanical properties of the films.

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3 Contributions from Oral Presentations

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M. Bertani Extending the simulation of NMR parameters of oxide glasses to large models via machine learning.

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M. Vanzan Energy transfer to molecular adsorbates by transient hot-electron tunnelling.

Capturing the recognition dynamics of para-sulfonato-calix[4]arenes by cytochrome c: towards a quantitative free energy assessment

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ABSTRACT

Calix[n]arenes selective recognition of protein surface covers a broad range of timely applications [1-4], notably to control protein assembly and crystallization. Here, the interaction of para-sulfonated calix-[4]-arenes with cytochrome c is investigated by all-atom, explicit water molecular dynamics simulations which allow to characterize two binding sites in neat agreement with experimental evidences [1,4]. Free energy calculations based on the MM-PBSA and the attach-pull-release (APR) [5,6] methods highlight key residues implicated in the recognition process and provide binding free energy results in quantitative agreement with the isothermal titration calorimetry. MD investigation allows, through the QHMB [7] method, to probe also an allosteric reinforcement of several per-residues interactions upon calixarene binding, which suggest a more complex mode of action of these supramolecular auxiliaries. This study paves the way towards an automated procedure for predicting computationally supramolecular protein–cages association, with the possibility of a computational screening of new promising derivatives for controlled protein assembly and protein recognition surfaces processes.

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Extending the simulation of NMR parameters of oxide glasses to large models via machine learning

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ABSTRACT

Multicomponent oxide glasses are key materials in many technological fields like energy, medicine, and advances communication systems[1]. The understanding of the composition-structure-properties relationship is hampered by the disordered nature of these materials which makes the interpretation of experimental data, such as NMR spectra, very complicated. To overcome this problem, Molecular Dynamics (MD) can be used to simulate structures from which compute the NMR spectra[2]. The main limitation to this approach is the high computational cost of the DFT calculations needed for NMR computation which restricts its application to small systems (max ~800 atoms) limiting the accessible information.

Machine Learning (ML) methods can be a reliable tool to extend the NMR calculations to large systems with low computational cost and high accuracy[3]. They are based on the training of complex models with accurate input-output couples coming from the fingerprinting (descriptors) of small structures and NMR parameters derived from DFT calculations.

In this contribution the application of a Leas-Square Support Vector Regression based on Kernel Ridge Regression (LSSVR-KRR) on Na_2O-MgO-SiO_2 systems will be presented. The structures, containing 400 atoms of five glasses have been obtained from MD simulations using three different interatomic potentials[4-6] at 0, 300, and 1000K. The local environment of each atom has been encoded into Smooth Overlap of Atomic Position (SOAP)[7] descriptors. A 5-fold cross-validation approach has been applied to optimize the SOAP and LSSVR parameters and to train the model, obtaining excellent agreement with DFT data on an external test set (for example, the mean absolute error on ^{29}Si σ_{iso} was 1.4 ppm)

The trained model has been applied to larger simulation boxes, containing 800, 4000, and 20000 atoms and averaged to the full low-temperature trajectory of the MD simulation (300 structures) to simulate NMR parameters and ^{29}Si MAS NMR spectra. Such big simulation boxes are not accessible with DFT calculations, but they can be easily used with the trained ML model. The calculation of NMR parameters with the ML model for the 300 structures containing 20000 atoms took almost 2 hours on one CPU, while almost 2 days were necessary for the DFT calculation on one structure containing 400 atoms using 40 CPUs.

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Multi-Scale Modeling of Mechanistic Promiscuity in Glu-ER Mutants Electron-Donor-Acceptor

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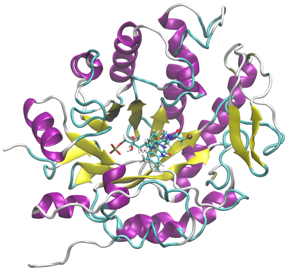
ABSTRACT

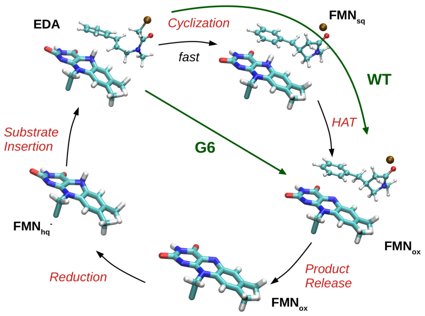
An Electron Donor Acceptor Complex (EDAC) is a transient species formed by two molecules, one electron donor and the other electron acceptor. Excitation under visible light of an EDAC can be used to catalyze chemical functionalization also of non-activated substrates [1]. A protein-based EDAC is an ideal kind of catalyst due to the intrinsic regio- and stereo-selectivity. Additionally, in the excited state the protein-based EDA complexes can fulfill reactions that are precluded to the ground state of the protein, as for example in Flavin mononucleotide (FMN) ene-reductases [2]. The transient nature of a protein-based EDAC and its dependence on the fluctuating and anisotropic protein environment makes its characterization very challenging.

Herein, we employ a multiscale methodology based on molecular dynamics simulation and the Perturbed Matrix Method [3,4] to study the possible mechanisms of the enantioselective radical cyclization of α-chloroacetamide-(1) within FMN-dependent ene-reductases.

In particular, the wild type GluER and the mutant named G6 (GluER-T36A-K317M-Y343F), that was engineered to have a faster catalytic rate [1,2], are here considered. In the wild-type, the mechanism suggested by kinetics experiments consists of: i) light-induced exit of the Cl anion with formation of the semi-oxidized intermediate of FMN, ii) radical cyclization and iii) termination through an hydrogen atom transfer (HAT).

In the mutant, the mechanism is still unclear and most probably very different from the one of the wild type because of the absence of the FMN semi-oxidized intermediate. We have hypothesized an early HAT in the mutant, possibly concerted with the exit of the Cl anion, followed by the slower cyclization step. Preliminary calculations show a decrease of the energy difference between the ground and the excited state in the mutant catalytic cyle, suggesting that the mutated protein environment might favor a diabatic crossing, therefore shortening the reaction timescale.





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PyMM: An open-source Python program for QM/MM Simulations based on the Perturbed Matrix Method

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ABSTRACT

Quantum-Mechanical/Molecular-Mechanics (QM/MM) methods[1] are important tools in molecular modelling as they are able to couple an extended phase space sampling with an accurate description of the electronic properties of the system. In this work we present a software package written in Python3, called PyMM, which has been developed to apply a QM/MM approach, the Perturbed Matrix Method[2-4] (PMM), in a simple and efficient way. PMM has been applied successfully to describe systems of biological interest[5,6], but software that supports this method is still not publicly available. PyMM requires a classical atomic trajectory of the whole system and a set of unperturbed electronic properties of the ground and of the electronic excited states for the QM region. The software output includes a set of the most common perturbed properties, such as the electronic excitation energies and the transitions dipole moments, as well as the eigenvectors describing the perturbed electronic states which can be then used to estimate whatever electronic property (see Figure 1). The software is composed of a simple and complete command-line interface, internal input validation, and three additional modules focusing on i) the analysis of the perturbed eigenvectors behavior, ii) the calculation of the electronic absorption spectrum and iii) the estimation of the free energy differences along a reaction coordinate.

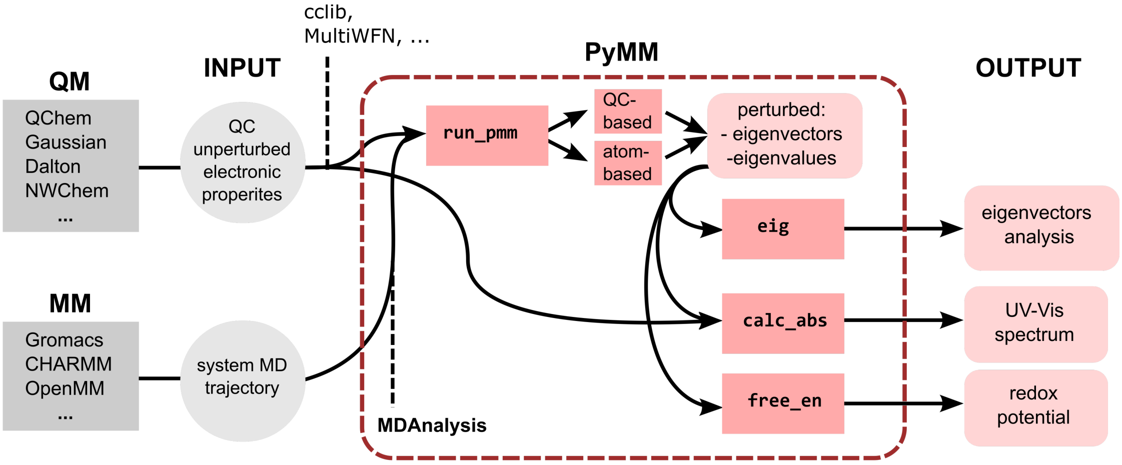

Figure 1: Structure of PyMM within the framework of a PMM simulation.

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Predicting G Protein-Coupled Receptor dimers 3D structures in native-like environments

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ABSTRACT

G Protein Coupled Receptors (GPCRs) represent ~34% of marketed drug targets[1]. Recent fluorescent data support their existence in native tissues[2] and animal models[3,4] as homo-/hetero-dimers and higher order oligomers. Accruing evidence suggests that hetero-dimers are the appropriate drug target to treat depression, pain, Parkinson's disease (PD) and drug addiction[5-8]. From a drug design perspective, dimers represent an unmet challenge as their properties cannot be inferred from the existing knowledge on monomers. A major setback to the design of dimers modulators is the lack of methods to predict their three-dimensional (3D) structures. Here we present a computational protocol for the prediction of dimers 3D structures in native-like environments. The protocol was validated retrospectively using the CXCR4 homo-dimer as test case, and is currently being exploited to identify the interface of the opioid mu (MOP) and N/OFQ (NOP) receptor hetero-dimer (MOP-NOP). MOP-NOP interaction in native tissues was recently proved[9] and bivalent ligands - namely Dermorphin-N/OFQ (DeNO) and Dermorphin-UFP101 (De101)- are available[10].

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Into the dynamics of a metal surface via machine learning of atomic environments

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ABSTRACT

The surfaces of solids become mobile at temperatures well below the melting point, with facile diffusion observed at much lower temperatures.

For transition metal surfaces the onset of surface mobility has been detected at temperature of 1/3 of the melting point, called ”Huttig temperature”. Most metallic surfaces involved in catalysis are active at temperature above this value, meaning that they are dynamic entities during the reaction with potential implications on the activity.

In this work we focused on the study of the dynamic behavior of copper (Cu), an important catalyst in the conversion of CO2 to methanol. To have an accurate description of the Cu surface dynamics we constructed an ab initio quality potential with machine learning techniques; to do this we rely on DeePMD-kit[1], a software that interpolates inter-atomic potentials through deep neural network, training on information obtained at a higher accuracy level, precisely DFT.

We then employed a data-driven approach built on Smooth Overlap of Atomic Position (SOAP)[2] to compare and classify the dynamics of different surfaces.

The calculation of the soap environments of each atom in the system allows us to catalog all the environments that appear in the system and in particular to analyze how quickly and to what extent each atom remains in the same state or jumps from one state to another in dynamic equilibrium. This permits us to completely reconstruct the inter-conversion dynamics between all the states that exist in the system, and their transition rate.

Finally, the creation of a dataset containing all the atomic environments present in various types of Cu surfaces offers us the possibility to verify the stability of the same and to what extent, during the thermodynamic equilibrium at certain temperatures, the surfaces are transformed and reconstruct environments that are typical of other types of structures, how stable they are, how much they are in communication with each other and the origin of such a dynamic. This approach offers a remarkable tool to classify the dynamic behavior present even within solid structures and its flexibility allows to compare the different behaviors that each structure exhibits.

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Solvatochromic Emission from the “Dark” Double-Exciton state of a Polyhalogenated Thiele Hydrocarbon: a quantum-chemical investigation

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ABSTRACT

Recently there has been a considerable interest in the exploration of organic neutral radicals for various applications including optoelectronics.[1] Radical-based OLEDs can reach values of internal quantum efficiency of 100%,[2] but two major unresolved problems affect these devices: a severe roll-off and a device lifetime of few minutes.[1,3] An alternative to free radicals, potentially capable to overcome these problems, is represented by luminescent diradicaloids. Here we present a computational investigation on the luminescence properties of the first example of an inert and photostable non-perchlorinated Thiele[4] hydrocarbon (TTH) recently synthesized.[5] This molecule exhibits an intense solvatochromic emission with a large Stokes shift of ca. 0.66 eV. Diradicals have attracted considerable attention due to their potential applications in optoelectronic devices[6,7] and in singlet fission process[8]. A distinctive character of these molecules is to exhibit a dark low-lying double-exciton (DE) state dominated by the doubly excited H,H □ L,L configuration. In fact, such state has been shown to be the lowest-lying singlet excited state for molecules exhibiting medium to large diradical character (y_0)[9,10]. Accordingly, the luminescence properties of TTH have been interpreted with quantum-chemical calculations demonstrating the key role of its moderate diradical character in determining the unconventional fluorescence properties. Quantum-chemical calculations have been carried out at DFT, TDDFT and with multi-reference multi-configurational approaches such as DFT-MRCI and CASSCF + NEVPT2. Specifically, the calculations suggest that the observed solvatochromism is determined by twisting of exocyclic CC bonds in the DE excited state, accompanied by charge separation as a result of sudden polarization[11]. We believe that understanding the luminescence mechanism in TTH will contribute to design p-QDM derivatives and related conjugated diradicaloids with increased luminescence efficiency.

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Reconstructing Reactivity in Dynamic Host-Guest Systems at Atomistic Resolution

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ABSTRACT

Spatial confinement is widely employed by Nature to attain unique efficiency in controlling chemical reactions. Notable examples are enzymes, which selectively bind reactants and exquisitely regulate their conversion into products. In the attempt to mimic natural catalytic systems, supramolecular metal-organic cages capable of encapsulating guests in their cavity and of controlling/accelerating chemical reactions under confinement are attracting increasing interest. However, the complex nature of these systems, where reactants/products continuously exchange in-and-out the host, makes it often difficult to elucidate the factors controlling the reactivity in dynamic regimes.

We have developed a flexible computational framework, useful to build structure-dynamics-property relationships for a variety of reactive host-guest systems and we discuss here two applications.

Firstly, we have employed molecular models to probe the isomerization of azobenzene guests within a Pd(II)-based coordination cage host in water. Atomistic molecular dynamics and metadynamics simulations allowed us to characterize the flexibility of the cage, the (rare) guest encapsulation and release events, and the relative probability/kinetics of light-induced isomerization of azobenzene analogues in these host–guest systems, allowing us to reconstruct the mechanism of azobenzene switching inside the cage cavity.[1]

In the second case, we focused on a coordination cage that can encapsulate amide guests and enhance their hydrolysis by favoring their mechanical twisting towards reactive molecular configurations under confinement. We designed an advanced multiscale simulation approach that allowed us to reconstruct the reactivity in such host-guest systems in dynamic regimes, characterizing the amide encapsulation/expulsion in/out the cage cavity (thermodynamics and kinetics), coupling such host-guest dynamic equilibrium with the characteristic hydrolysis reaction constants. All computed kinetic/thermodynamic data were then combined, obtaining a statistical estimation of reaction acceleration in the host-guest system that is found in optimal agreement with the available experimental trends.[2]

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Novel explicitly correlated composite schemes for the accurate thermochemistry and kinetics of gas-phase reactions

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ABSTRACT

Gas-phase reactions are involved in processes occurring in the interstellar medium or ruling the evolution of Earth exoplanetary atmospheres, thus playing a central role in global climate changes or in the build-up of chemical complexity in space. The formation rates of these species are crucial in order to build reliable global kinetic schemes, but both experimental and brute-force computational approaches face a number of difficulties. The computation of accurate rate constants of key elementary reactions mainly depends on two pillars: the transition state theory (TST) model used and the accuracy of the structural and energetic properties of the stationary points ruling the reaction potential energy surface (PES). Unfortunately, the most accurate quantum chemical methods (providing results with sub-chemical accuracy for very small systems) are plagued by a very unfavorable scaling with the size of the system analyzed.[1] On the other hand, the approaches in current use for larger systems[2] include some empirical parameters and/or employ geometries which are not fully reliable especially for the transition states and non-covalent complexes ruling the entrance channels of most reactions of astrochemical and atmospheric interest. Based on these premises, we are developing a new family of cheap composite schemes (ChS)[3,4,] based on explicit correlation methods,[5] which allow to obtain accurate energetic and structural parameters with non-prohibitive computational requirements for the medium-sized molecular systems of current astrochemical and/or environmental interest. The latest versions of these schemes employ optimized basis sets derived from the so-called “calendar” basis sets[6] or from the Peterson’s correlation consistent cc-pVnZ-F12 counterparts.[7] The issuing basis sets have comparable size and, above all, retain the ‘hierarchic’ property, which allows to perform reliable complete basis set (CBS) extrapolations. These schemes will be validated with reference to the results of the most accurate state-of-the-art quantum chemical models for the hydrogen abstraction reactions of water and hydrogen sulfide (H_2S) with small radicals (e.g., Cl, OH). The computed structural and energetic parameters will be employed in the framework of the ab-initio TST / master equation approach including tunneling effects[8] with the aim of unveiling the thermochemical and kinetic features of such processes, which this prototypical heavy-light-heavy atom reactions, which play a key role in different environments.

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Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction

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ABSTRACT

The hydrogen evolution reaction (HER) has a key role in electrochemical water splitting. Recently a lot of attention has been dedicated to HER from Single Atom Catalysts (SAC).[1] The activity of SACs in HER is usually rationalized or predicted using the seminal model proposed by Nørskov and co-workers in 2005,[2] where the free energy of an H atom adsorbed on an extended metal surface M (formation of a MH intermediate) is used to explain the trends in the exchange current for HER. SACs differ substantially from metal surfaces, and can be considered analogs of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable dihydride or dihydrogen complexes (HMH) can form.[3,4] We show that the same can occur on SACs and that the formation of stable HMH intermediates, in addition to the MH one, may change the kinetics of the process.[5] Extending the original kinetic model to the case of two intermediates (MH and HMH) one obtains a three- dimensional volcano plot for the HER on SACs. DFT numerical simulations on 55 models demonstrate that the new kinetic model may lead to different conclusions about the activity of SACs in HER. The results are validated against selected experimental cases. The work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds.

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Harvesting triplet excitons in TADF emitters with negative singlet-triplet gap: The path towards highly efficient OLEDs

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ABSTRACT

Organic light-emitting diodes (OLEDs) are already widely available and typically used in television and mobile screens. Nevertheless, their technology is still not optimal and an improvement of their efficiency would have huge economic impact, leading to an important reduction in consumption. Indeed, most of the efforts are focused on boosting OLEDs internal efficiency by optimal harvesting of (non-emissive) triplet excitons. To this end, a possible strategy is based on the phenomenon called Thermally Activated Delayed Fluorescence (TADF) [1-4]. The crucial requirement for TADF emitters is a small singlet-triplet gap ΔE_{ST} that enables a thermally driven reverse intersystem crossing (RISC) from the triplet to the singlet manifolds and subsequent fluorescence. While ΔE_{ST} is typically positive, recent experimental [5] and theoretical [6,7] studies have shown that several N-doped triangle-shaped organic molecules have the first excited singlet state lower in energy than the first triplet state. This inversion of states has been proposed as a pathway to greatly improve RISC rate, thus leading to optimal TADF emitters. From a theoretical point of view, commonly used quantum chemistry excited state methods, like TDDFT, miserably fails in describing negative ΔE_{ST} [6,7].

In this contribution, we present an exploratory study of the energy ordering within the excited singlet and triplet manifolds of different azine and heptazine derivatives described in terms of the fully correlated Pariser-Parr-Pople (PPP) model.

This project received funding from the European Union Horizon 2020 research and innovation program under Grant Agreement No. 812872 (TADFlife) and benefited from the equipment and support of the COMP-HUB Initiative, funded by the “Departments of Excellence” program of the Italian Ministry for Education, University and Research (MIUR, 2018–2022). We acknowledge the support from the HPC (High Performance Computing) facility of Parma University.

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Integration of Quantum Chemistry, Statistical Mechanics and Artificial Intelligence for Computational Spectroscopy: the UV-vis spectrum of TEMPO radical in different solvents

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ABSTRACT

The ongoing integration of quantum chemistry, statistical mechanics and artificial intelligence is paving the route towards more effective and accurate strategies for the investigation of the spectroscopic properties of medium-to-large size chromophores in condensed phases. In this context we are developing a novel workflow aimed at improving the generality, reliability and ease of use of the available computational tools.

In this contribution we report our latest developments with specific reference to unsupervised atomistic simulations employing non periodic boundary conditions (NPBC) followed by clustering of the trajectories employing optimized feature spaces. Next accurate variational computations are performed for a representative point of each cluster, whereas intra-cluster fluctuations are taken into account by a powerful perturbative approach. A number of novel methodological improvements have been introduced including, e.g., more realistic reaction field effects and corrections of wrong coordination numbers at the outer boundary of the simulation sphere, automatic definition of the feature space by continuous perception of solute-solvent interactions, full account of solvent polarization and combined coupled-cluster/DFT electronic computations.

After its validation, this new approach is applied to the challenging case of solvatochromic effects on the UV-vis spectra of a prototypical nitroxide radical (TEMPO) in different solvents.

The reliability, effectiveness and robustness of the new platform is demonstrated by the remarkable agreement with experiment of the results obtained through an unsupervised approach characterized by a strongly reduced computational cost as compared to that of conventional QM/MM models.

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Polarons in organic conjugated materials: interplay between electronic and vibrational properties.

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ABSTRACT

Polarons (i.e., excess charges localized within the nuclear structure) play a crucial role in governing charge transfer, thermo-electric and redox mechanisms in organic functional materials.[1,2] An accurate description of their electronic structure and electron-phonon couplings is mandatory to assess their response and transport properties.[3,4]

Here, we report a comprehensive investigation of polarons in conjugated polymers, by studying both ladder- and not-ladder-type architectures.[1-5] The firsts are characterized by a planar polymer structure, missing intra-molecular torsional degrees of freedom, while the seconds show a distorted (not flat) polymer structure, leading to a distribution of intra-molecular torsional angles. Such structural diversity impacts the polaron properties, by affecting the electronic, optical and transport mechanisms.

By combining broken-symmetry density functional theory (BS-DFT), fragment orbital density analysis (FOD), and multireference methods (e.g., CASSCF/NEVPT2), we revealed the poly-radicaloid character of the electronic structure of polarons in both ladder and not-ladder type polymers. We found that negative (electron) and positive (hole) charges relax on localized states of the polymer chain, featuring different structural and electron-phonon coupling properties.

Multi-charged species, up to two charges per polymer repeat unit, revealed complex electronic structures, as characterized by quasi-degenerate states showing various spin multiplicities (e.g., doublet, triplet, quartet, quintet) and response properties.

Vibrational (IR and Raman) and electronic (UV-Vis) spectra of both electron and hole multi-polarons were computed and compared with experimental data, the latter collected on highly doped solid-state polymer films.[2]

Our computational studies provide insights towards the understanding of doping processes and insulator-to-conductor transitions for the last generation of organic conjugated polymers, active materials for opto-electronic, energy-saving and biomimetic applications.[6,7]

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Theoretical predictions of chiral hybrid perovskites

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ABSTRACT

In recent years, hybrid organic–inorganic perovskites (HOIPs) have covered a broad area of research open to several breakthrough discoveries for innovative devices, emerging as excellent candidates for solar cell applications.[1] A particular class of HOIPs is represented by the chiral HOIPs, featured by a structural asymmetry. The chiral bias usually starts from the chiral organic ligand inducing a chiral screw-sense to the entire inorganic lattice, thereby generating a set of interesting chiroptical properties, as well as ferroelectric and chiral spintronic features.[2]

However, to date the mechanism through which the chiral bias is generated from the chiral organic ligand to the inorganic lattice is unclear. Furthermore, for chiral perovskites ab-initio spectra simulations together with molecular dynamics predictions are still in their infancy.[3] In this scenario, theoretical approaches can draw new design rules to boost the research for innovative technologies beyond photovoltaics and based on chiral HOIPs.

We herein present a bespoke simulation protocol implemented for lead- and tin-based chiral perovskites, where we investigated how the chiral bias is generated and how it is propagated in the inorganic polyhedra.

The chiroptical features for lead- and tin-based chiral HOIPs enantiomers, as S- and R-$(MBA^+)_2PbI_4$[4] and S- and R-$(MBA^+)_2SnI_4$,[5] have been predicted within the density functional theory (DFT) framework and its time-dependent extension (TD-DFT) and explored through ab-initio Born Oppenheimer Molecular Dynamic (BOMD) simulations. The molecular orbitals mainly involved during the transitions suggest a metal-ligand charge transfer (MLCT) character, in higher extent for lead-based perovskites compared to the tin-based counterparts. The accuracy of the simulation protocol was assessed through the UV-vis and ECD spectra predictions, both showing good agreement with the experimental ones available in literature.[5,6]

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Functional groups in chemistry: molecular dynamics experiments

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ABSTRACT

When it comes to identify the building blocks of middle sized organic molecules, chemists mainly think in terms of functional groups. Is that picture truly representative of the dynamics of molecules?

We try to answer this question with an experimental mindset: we run simulations that artificially “decouple” pairs of atoms and see how the system as a whole reacts to that. In practice, if an atom A perceive a strong force from an atom B, we soften up the perceived force and examine how much this artificial decoupling influences the whole system. With that in mind, we propose a perturbed Hamiltonian function, namely $H_{dec}(q,p,\alpha) = H(q,p) + D(q,\alpha)$, where the second is a decoupling function, which is a potential energy contribution that depends on the “pair-softening parameters” α.

In the limiting case of no decoupling it is easy to establish that, for a tiny decoupling $\partial\alpha$, the system looses energy approximately as $\partial E \approx \frac{1}{2} V_{ij}^{''} \delta q_i \delta q_j \partial\alpha$, which is proportional to the off-diagonal entries of the hessian matrix $V^{''}$. Non-equilibrium contributions are recovered with a classical MD sampling. We can draw molecular graphs that quantitatively shows that the “functional groups picture”, at a quasi-classical level, is often a good description of the molecule’s dynamics, yet unexpected subgroups often appears.

However, when the decoupling is finite, we cannot make reliable estimates. Therefore we rigorously derived a family of simple integration algorithms to simulate the dynamics of the pair-decoupling Hamiltonian for any value of α, to confirm and extend our investigation. The integration algorithms are proven to be symplectic for harmonic/bilinear potentials.

CASSCF energy and properties with the Cholesky Decomposition of the two-electron integrals

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ABSTRACT

CASSCF calculations can be used to get a qualitatively correct description of multireference systems, including transition metal complexes, transition states, excited states and open-shell systems. Such calculations are, however, hindered by two intertwined, major computational burdens. First, they require one to solve a full CI problem in an appropriate active space. Given the exponential scaling of this step, it is either rather inexpensive, for active spaces of 14 electrons in 14 orbitals or less, or insurmountable. In the former case, the computational cost is dominated by the optimization of the orbitals that, when done by using a second-order procedure, requires a $O(N^5)$ integral transformation. We present a second-order CASSCF implementation that makes use of the Cholesky decomposition[1,2] of the two-electron integral matrix to reduce the computational cost associated with the orbital optimization. Such an implementation can handle, with standard computational resources, a few thousands of basis functions, offering good performance and robust convergence. Electric and magnetic response properties, the latter obtained using Gauge-including Atomic Orbitals, can also be computed by solving the coupled-perturbed CASSCF equations[3].

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In silico Design of Biocompatible Carborane Carriers for Boron Neutron Capture Therapy

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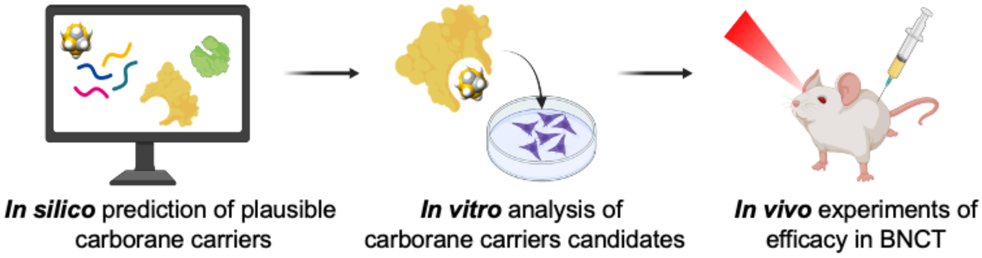
ABSTRACT

Boron Neutron Capture Therapy (BNCT) is a non-invasive, therapeutic approach for the treatment of different types of cancers. The effectiveness of BNCT is based on adequate and selective accumulation of 10B in the tumor tissue (approximately 10^9 atoms/cell), which is still on of the major obstacles in drug development for BNCT. Nowadays only two drugs, BPA (boronphenylalanine) and BSH (sodium borocaptate), are clinically used in BNCT. Icosahedral closo-carboranes ($C_2B_{10}H_{12}$) promise to be good candidates in BNCT because of the presence of 10 boron atoms and the lipophilic character that eases the cross of hydrophobic membranes. Nevertheless, their insolubility in water requires the design of delivery vehicles able to carry closo-carboranes to the target (drug delivery system). Biocompatible, water soluble and non-immunogenic transport systems are the best candidates for this task.

Amino acids, peptides, protein, and macrocyclic structures were selected as plausible carriers and their affinity for the carborane cage is investigated, by means of Molecular Docking, Molecular Dynamic (MD) simulations followed by binding affinity computations performed by Molecular-Mechanics Generalized-Born Surface Area (MM-GBSA) analysis. This protocol quantifies the binding affinity of each complex, defining the non-covalent interactions (hydrogen bonding, hydrophobic, aromatic, cation- π, anion-π, surfactant-like, electrostatic) that govern the binding.

The results reported here are part of a computational-experimental project funded by AIRC (Italian Association for Cancer Research) and supported by PRACE-ICEI aimed to identify new vehicles for boron delivery in BNCT.



Oxygen redox activity in high-energy Na-ion battery cathodes unveiled from first principles

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ABSTRACT

Na-ion batteries (NIBs) are rapidly emerging as promising post-Lithium technology for large-scale applications, thanks to the wide availability and low cost of raw materials [1]. Design and optimization of highly efficient active materials are major issues for their effective deployment [2]. Layered transition metal oxides (Na_xTMO_2) have shown outstanding performances as high-energy cathode materials in NIB cells and exhibited the chance to attain larger specific capacity by enabling anionic reactions at high operating voltage [3, 4]. This represents a new paradigm in the development of positive electrodes, but the $O^{2-}/O_2^{n-}/O_2$ redox processes need to be finely controlled to prevent the release of molecular oxygen and thus huge capacity loss. We report a first-principles investigation of P2-type Mn-defective layered oxides with different metal doping at the TM site by means of PBE+U-D3(BJ) calculations. Structural and electronic features are dissected for each redox-active element in $Na_xTM_{0.25}Mn_{0.68}O_2$ (TM = Ni, Fe, Ru) materials as function of sodiation degree corresponding to different states of charge. We address the oxygen redox activity by considering the formation of oxygen vacancies and dioxygen metal complexes at low Na loads (*i.e.,* high voltage range). Low-energy superoxide moieties with different coordination geometries are predicted to be formed at x Na = 0.25 in Mn-deficient sites, while the x Na = 0.125 content enables the release of molecular O_2 via preferential breaking of Ni-O bonds. Mechanistic insights show that dioxygen formation is driven by the TM-O covalency and unveil that O_2 loss can be effectively suppressed by Fe and Ru doping. Our findings pave the route for the rational design of high-energy Na_xTMO_2 cathodes that feature enhanced reversible capacity and thus boost the development of efficient NIB devices. These outcomes are subject of recent scientific publication on *ACS Energy Letters* and *Journal of American Ceramic Society* [5, 6].

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A computational approach for modelling Electronic Circular Dichroism of solvated chromophores

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ABSTRACT

The theoretical modelling of Electronic Circular Dichroism (ECD) has attracted much attention in recent years because of the possibility to ascribe the absolute structure of chiral compounds by comparing the calculated ECD with the experimental one[1]. Nowadays, the ECD spectra can be calculated by using the Time Dependent Density Functional Theory (TDDFT) and accurate enough exchange-correlation functionals (e.g., the hybrid B3LYP). However, it is noteworthy that the ECD is extremely sensitive to the conformations[1], which are themselves further sensitive to the solvent presence, especially when intermolecular interactions (i.e., H-bonds) are involved. Therefore, a valid protocol should require not only an accurate electronic scheme, but the inclusion of the conformational and solvent effects as well[2, 3].

For this purpose, we present a computational protocol which can be divided into three steps: (i) execution of Molecular Dynamics simulations (MDS) of the investigated system at the experimental conditions (ii) analysis of the MDS with the Essential Dynamics (ED),[4, 5] a powerful tool for obtaining a reduced, thus affordable, number of internal degrees of freedom (iii) quantum-chemical calculations (i.e., ECD) on the statistically significant conformations.

The theoretical approach was tested on the aqueous cationic tripeptide GAG^+ and the aqueous neutral decapeptide $(GVGVP)_2$, since reliable force-fields (FF) can be used for the MDS (i.e., OPLS-AA FF[6]) and experimental ECD are available at different temperature (T) values[7, 8]. The comparison between the calculated and the experimental results showed first the ability of our protocol to give the proper conformational states of the solute in water, hence we were able to follow the conformational transitions induced by the temperature changes. Secondly, the approach allowed us to extract a certain number of conformations among the most probable ones, reducing the computational effort but maintaining a good accuracy, as resulted from the comparison between the calculated statistically weighted and experimental ECDs at different T. The possibility to consider the relation among temperature, conformations and spectral features was tested in parallel with the capability of this approach to take into account the effect of the explicit solvent on the conformational states and on the optical response.

An affordable computational scheme which treats properly the conformational aspect, and what affects it, in the ECD calculations opens the possibility to study also more complex systems such as metal nanoparticles whose ECD is deeply influenced by the high flexibility of the selected protective ligands.

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Investigation of chemokine receptors dimerization through coarse grained metadynamics

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ABSTRACT

G-protein coupled receptors (GPCRs) are membrane proteins regulating the signal transduction from the extracellular to the intracellular environment. They represent the pharmacologically most relevant protein family, targeted by ∼40% of marketed drugs[1]. Important members of the GPCR family are the chemokine receptors CCR5 and CXCR4, which regulate vital processes like leukocyte migration and are associated to many severe pathologies including cancer, neurodegenerative diseases, and HIV infection. Recently, growing evidence demonstrated that GPCRs are able to work also as dimers and oligomers[2], paving the way to studies on the physiological and pathological role of receptors association.

Here we have disclosed the homo- and hetero-dimerization mechanism of the chemokine receptors CXCR4 and CCR5. Such process occurs on long timescales that are typically elusive to theoretical techniques such as molecular dynamics simulations. For this reason, we employed metadynamics in combination with a coarse-grained representation of the system[3]. In Metadynamics[4] an history-dependent bias is added to selected collective variables (CVs) of the system in the form of Gaussian potentials to fill up the valleys of the energy landscape. In the present case, we defined as CVs the distance between the two proteins and a specifically designed dihedral angle that discriminate the orientation of one promoter relative to the other.

Our results show a symmetric and an asymmetric dimer structure for each of the three investigated systems (CCR5/CCR5, CXCR4/CXCR4 and CCR5/CXCR4). The diverse dimer states differ in the access to the binding sites of the ligand and the G-protein, indicating that dimerization represents an allosteric mechanism to regulate the receptor activation. Our study provides structural basis for the design of ligands able to modulate the formation of dimers and in turn their activity, paving the way to innovative therapeutics in the fight against HIV, cancer and immune-inflammatory diseases related to these chemokine receptors.

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Modelling charge transfer reactions by hopping between electronic ground state minima: application to hole transfer between DNA bases

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ABSTRACT

We present the application of a theoretical-computational approach to model the kinetics of the hole transfer between guanine bases along double-stranded DNA in aqueous solution.
The charge migrations through DNA represent a very interesting subject because they are relevant in different areas, ranging from biochemistry to technology. In fact, the understanding of the charge fluxes occurring within DNA can help to describe, among others, cell oxidative damage processes as well as to design DNA-based sensors [1,2].
The theoretical-computational approach used in this study is the Perturbed Matrix Method (PMM) that allows to describe the molecular electronic properties in complex systems through a mechanical-statistical treatment, from which it is possible to extract thermodynamic and kinetic properties [3,4]. In the present case, we determined the kinetic rate constants for the inter- and intra-strand hole transfer between two guanine bases in several fully solvated double strands (Figure 1) and compared them with the available experimental data [5].
In almost all the cases, our model reproduces the observed trends of the kinetic rate constants as a function of the length and type of the sequence between the electron donor and acceptor. Moreover, we found out that the solvent plays a key role in promoting the hole transport.

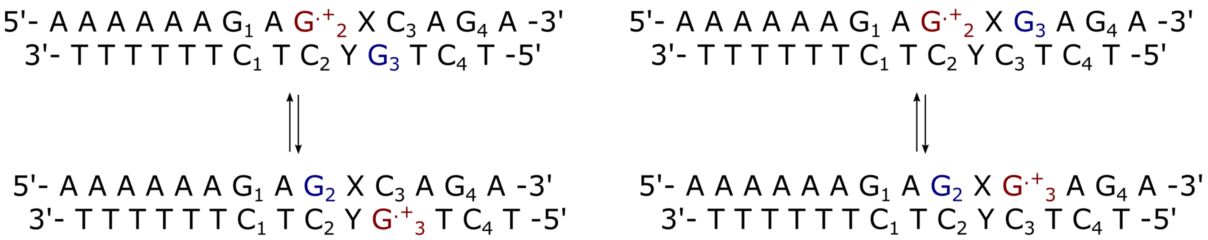

Figure 1. Schemes of the inter- (left) and intra-strand (right) hole transfer between the hole donor (in red) and acceptor (in blue) guanine bases. The double strands presenting the bridges X = {A, AA, AAA, T, TT, TTT} were considered. Y represents the complementary sequence of X in each case.

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A New Self-Consistent Empirical Potential Model for Multicomponent Borate, Borosilicate and Aluminoborate Glasses

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ABSTRACT

A new self-consistent empirical potential model for the simulation of multicomponent glasses of technological interest, such as borate, borosilicate and aluminoborate ones, has been developed.

The new potential is based on a pair-wide interatomic potential terms where the cation – oxygen and oxygen – oxygen interactions are described by Morse functions and of T-O-T (T = Si, P, and B) three body and network former – network former repulsive interactions.

Exploiting a Bayesian Optimization approach we have derived B-O and T-T interatomic potentials parameters.

To reproduce correctly the complex chemistry of boron a composition-dependent model for the *D* parameter of the B-O interaction has been built. In particular, in this model D is a function of the R ratio (defined as R = $[Na_2O]/[B_2O_3]$ for borate and borosilicate glasses and as $[Na_2O]-[Al_2O_3])/[B_2O_3]$ for aluminoborates) and the K ratio (K = $[SiO_2]/[B_2O_3]$). This model allows to better simulate the structure (fraction of BO_4 (N_4) species, non-bridging oxygen (NBO) speciation, coordination numbers and bond distances) and properties (density, ^{11}B and ^{17}O MAS NMR, and elastic properties) in a wide range of compositions.

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Exotic hexagonal structured NaCl films on a methylammonium lead iodide substrate: a first-principles study

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ABSTRACT

Sodium chloride NaCl is a ionic compound that is used in heterogeneous junctions for tuning the electronic properties of the interface. In photovoltaics, NaCl is often used in perovskite solar cells as interlayer between the photoactive material and the charge transport layers.[1] Despite its simplicity, unexpected complex NaCl interfacial structures can be found at high pressure or low dimensions. The most stable surface facet of cubic NaCl is the (100), nevertheless recent experiments found different surface termination depending on the chemical nature and the structure of the substrate, for example a hexagonal surface of NaCl has been found on the diamond (110) surface.[2] In this framework, this contribution explores the interface between NaCl and the prototypical lead halide perovskite (MAPI) with first-principles calculations at the DFT level of theory. Our results show different possible NaCl surface reconstructions depending on the MAPI terminations and the nature of the interactions at play. Effects on MAPI electronic structure (work function, band edge potentials) are also discussed. These findings will help the design of new and better performing perovskite solar cells.

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Unveiling ultrafast charge transfer in Ruthenium-based metal complexes through ab initio electronic dynamics

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ABSTRACT

Ru-based $Ru[(dcbpy)_2(NCS)_2]^{4-}$ (“$N3^{4-}$”) complex is a popular dye-sensitizer for dye-sensitized solar cells. Following a strong absorption in the 370-500 nm region, $N3^{4-}$ photophysics is characterized by a peculiar excited-state relaxation dynamics, involving an intersystem crossing from the initially excited singlet metal to ligand charge transfer ^{1}MLCT states to triplet ^{3}MLCT ones. [1]

The dynamic electronic evolution of the N3 MLCT photo-excited singlet states most vibronically coupled with the triplet one [1] was investigated in the ultrafast time-scale through real-time time-dependent density functional theory (RT-TDDFT) approach, which allows the propagation of the electronic density starting from a given initial excitation. [2-4] Finite temperature and solvation effects [5] were also indirectly included and characterized. After the initial exciton formation, the hole and the electron reveal a quite different behaviour. In particular, ultrafast transfer of the photo-excited electron between the acceptor bpy-like ligands are observed after 15 fs from the excitation. Remarkably, this inter-ligand electron transfer process appears to be a consequence of a purely electronic relaxation within the dense electronic manifold in the visible region, not requiring dynamic electron-nuclear couplings in this ultrafast time regime. [6]

The comprehension from first principles of the electronic density reorganization following light absorption in molecular dyes is fundamental for the interpretation of time-resolved spectroscopic data [7] and for a rational design of improved light-harvesting systems.

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Computational modeling of electron-transfer reactivity in aprotic metal-oxygen batteries

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ABSTRACT

The race to electrification is leading many societal sectors in a forced march toward decreased carbon emissions; hence, a huge relevance in research is put on the development of next-generation batteries with increasingly higher energy density. Metal-oxygen batteries (MOBs) present, on the one hand, an outstanding potential in terms of enhanced storage capacity and environmental sustainability; on the other hand, they are still plagued by severe limitations in cycle-life and efficiency (in particular Li-O_2 batteries). The main reason for this is the presence of uncontrolled parasitic reactions. Experimental evidences for electrolyte degradation and evolution of excited-state singlet oxygen have been reported[1,2], but the fundamental chemical mechanisms underlying these phenomena are still poorly understood.
Electronic structure calculations have proven to be a great aid in attempting to unravel the complex chemistry of reduced oxygen species in aprotic environment[3,4]. In this contribution we show that the use of theoretical method for exploring ground- and excited-state potential energy surfaces (PESs) can be a suitable approach for tackling the hard task of understanding electron-transfer reactivity of discharge products in MOBs. In particular, we employed correlated multiconfigurational quantum chemistry methods in order to describe the electronic PESs and their crossing points for superoxide and peroxide species involved in the chemistry of MOBs, with specific reference to: i) the disproportionation reaction of superoxide anions, in presence of different cations[5,6]; ii) the existence of low energy oxygen-to-lithium charge-transfer states in the peroxide products[7,8]; iii) the oxidation of peroxide discharge products by means of dissolved homogeneous redox catalysts (redox mediators). Based on the multiconfigurational approach, possible reactive pathways leading to the formation of singlet oxygen are discussed. Also, ground-state density functional theory was used for predicting the reaction thermodynamics. The results provide a novel insight into the chemistry of aprotic MOBs cycling, and an example of a computational approach only seldom applied to the study of electrochemical systems.

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Novel Ru(II)-based compounds active in PDT and PACT cancer therapy: theoretical study of the photophysical properties and photoactivity .

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ABSTRACT

The transition metal complexes containing metal ions such as Pt (II), Pt (IV), Os (II), Re (I), Ir (III) and Ru (II), thanks to their tunable photophysical, photochemical and redox properties, are promising candidates for PDT (Photodynamic therapy) and PACT (photoactivated chemotherapy) .[1-3]

Currently cancer research is primarily focused on the design of ruthenium systems. These complexes are generally considered less toxic respect to platinum-based drugs, show high chemical stability and appear to follow a different mechanism of action. In particular, Ru(II)-polypyridyl complexes are today the most studied compounds for their possible use in PDT and PACT.[4-5]

In this work, Density Functional Theory and its time-dependent extension (DFT, TDDFT) have been employed to check the properties of a series of new Ru(II)-polypyridyl complexes for their application in PDT and PACT. In particular, the photophysical and chemical properties of such complexes have been theoretically explored. The investigation of the electronic structure in the ground and excited states and the calculation of the excitation energies, intersystem spin crossing viability and spin-orbit coupling constants (SOCs) have been carried out. In addition, the mechanism of photoactivation has been theoretically explored.

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Modelling amino-acid based ionic liquids with polarizable force field

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Ionic liquids and deep eutectic solvents have increasingly attracted a huge research effort due to their application in many fields of technology like solvents, catalyst or electrolytes [1,2]. In recent years it has been assessed that the “green” nature of ionic liquids is a complex question, realizing that most of them are toxic and less environment-friendly than supposed.[3]

The very recent implementation of ionic liquids based on choline and ammino acids (AAILs) is particularly relevant for their intrinsic biocompatibility. Despite their growing use in many technological setups, the physico-chemical mechanism in which AAILs interact with biological matter is still largely unknown [3].

Polarizable molecular dynamics simulations represent a powerful tool for understanding these mechanisms and provide a “best balance” option between the accuracy of ab-initio that is too computational demanding to sample adequate timescale and classical parametrized dynamics which is too simple to accurately model electrostatic interactions. Some of the crucial ingredients of the interaction energy in ionic liquids are polarization and induction, so that the simulations of dynamical processes in ionic liquids has long been recognized by the community to need an electrostatic model as accurate as possible. Due to ionic nature of the materials, these effects are particularly important, and they will affect dynamic quantity like fluidity, ionic mobility or conductivities which are all heavily underestimate by non-polarizable models [4].

New polarizable force field parameters have been determined and especially designed to describe the nanoscopic behaviour of AAILs and this new force field can be considered an extension of AMOEBA model to biocompatible AAILs. It has been parametrized with high quality ab-initio data and is able to accurately reproduce the structure and the interaction energies.

The new force field can be used to gain a detailed understanding of the bulk structure and dynamics of AAILs and to rationalize in which way these systems act as solvents of biomolecules.

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Manifold Al-Coordination as Nano-Pivots in Porous Cement Nanoclusters

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Abstract: Modern cements are high in strength, and endeavor to the long-term toughness of ancient Roman structures. However, the atomistic structure and nanoscopic role of each element in cement remains poorly understood; the Calcium-(Alumino-)Silicate-Hydrogel (C-(A-)S-H) phase in particular, as well as Aluminium's role in toughening. [1-4] Molecular cluster C-(A-)S-H nanoparticles (~1—3 nm^3) were therefore investigated by high-level Density Functional Theory (DFT) complemented by *Ab initio* molecular dynamics simulations (AIMD) to resolve their nano structures and dynamical flexibilities. The configurational ordering of Al at terminal (Q1) vs. bridging (Q2) positions was also investigated. It was found that Al assisted in retention of higher chain-length and that the increased flexibility of Al-O-X bond angles (X = Si, H, Al) was sustained by Al, serving as hinge-points in the networks. Structurally, alumino-silicate units with differing Al-coordinations (4-, 5- and 6- coordinate) were characterised, with 5-coordinate facilitating distortion and interconversion, equating to increased flexibility and potential for dispersion of mechanical stresses. The Al-doped structures were amorphous with irregular pores with an overall increased free volume (Vf), relative to Al-poor ones, evidencing Al's role in the stabilisation of dry and hydrated pore architectures. The findings suggest atomistic contributions of Al-atoms to toughening in cements and may promote Al-tailored structuring and applications towards reproducing the damage tolerances observed in heritage cements.

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Exploring the surface chemistry of Boroxine-containing frameworks via computational core-electron spectroscopies

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ABSTRACT

On-surface synthesis of 2D organic structures is a convenient bottom-up approach for tailoring both the chemistry and the morphology of surfaces and for the synthesis of complex hybrid interfaces of potential interest in the development of organic based devices [1]. Whereas the condensation of molecules with two boronic groups allows for obtaining extended 2D structures[2], the use of single-terminated precursors leads to the formation of boroxine-containing molecular moieties [3]. We have shown that the interaction between boroxine and Au(111) surfaces is characterized by the presence of interface electronic states, which are preferential channels for ultra-fast charge delocalization [3]. We therefore suggested that the employment of boroxine molecules as platforms for the hosting of guest molecules is able to mediate charge transport at the interface between organic films and metal substrates. The latter property is key for an effective implementation of these systems in organic electronics.

In this talk I will illustrate the results of computational core-electron spectroscopic studies, namely X-ray Photoemission and X-ray absorption, which are used to understand the surface chemistry of several boroxine containing compounds. This work has been carried out in close collaboration with experimental groups of the ELETTRA Synchrotron in Trieste.

The theoretical description of B 1s core-excitations of boronic and B-B containing systems proves a challenging task, both in the gas phase [4,5], and as adsorbates on the Au(111) surface [3]. Gas-phase studies reveal that static correlation effects between different excited states need to be taken into account, while studies on adsorbates highlight the unexpected creation of a complex B-Au interface.

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Energy transfer to molecular adsorbates by transient hot-electron tunnelling

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ABSTRACT

In the last ten years the study metallic nanoparticles gained a lot of interest because of their opto-electronic features and especially because of the presence of Localized Surface Plasmon Resonance (LSPR). This peculiar effect makes these nanosystems suitable for a broad variety of applications in biomedicine, catalysis, electronics, optics and more. [1,2] A relatively new and highly promising way by which LSPR can be exploited is hot-carriers photocatalysis. As the LSPR 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 nanoparticle 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. Our work aims 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 hot-electrons (HEs) and a small molecule at the real time Time Dependent Density Functional Theory (rt-TDDFT) level. We represented the hybrid metallic nanostructure-molecule system through a minimalistic model composed on a linear chain of metal atoms interacting with a small molecule 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 vibrational modes, with an efficiency strongly dependent on the molecular species and on the HE energies. Our work suggests that, regardless their energy, all generated HEs can compete to the activation of the motion involved in the photocatalyzed reaction and this process can cooperate with the currently accepted mechanism involving a direct electron transfer. [7]

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4 Poster Contributions

P. Barretta Mechanism of action of an iridium (III) complex for H_2O_2 – responsive anticancer therapy. A computational study.

G. Cardoso Gomes Computational Study of dicationic ionic liquids.

R. Cortivo Exact and approximate evaluation of transition rates for quantum-stochastic master equation dynamics.

V. D'Annibale Theoretical evaluation of the thiol/disulfide interchange energy barrier as a model for proteins interaction.

M.L. De Sciscio Asn deamidation and Met oxidation: an hybrid QM/MM study.

C. Nania Hydrodeoxygenation of isoeugenol on platinum cluster: DFT insights into HYD and DDO mechanisms.

R. Palombo Picosecond Excited State Dynamics Reveals the Coexistence of Stereochemically Distinct Reactive and Non-reactive Isomerization Paths in Heliorhodopsin.

V. Piacentini Polarizable Molecular Dynamics of Aprotic Electrolytes with Lithium Salts in Li-O2 batteries.

A. Ranaudo Validation of a protein – protein docking approach through Molecular Dynamics simulations.

E. Rossi Modelling of ATP-Zn^{2+} coordination as a key element for ATP-fueled self-assembly.

A. Rovaletti Solving the puzzle about the CO oxidation reaction mechanism of Mo/Cu CO dehydrogenase by means of QM/MM calculations.

G. Schifino How molecular chirality affects the supramolecular chirality in the self-assembly of TPPS 4 porphyrin aggregates.

V. Vigna Machine Learning for Drug Discovery.

Mechanism of action of an iridium (III) complex for H_2O_2 – responsive anticancer therapy. A computational study

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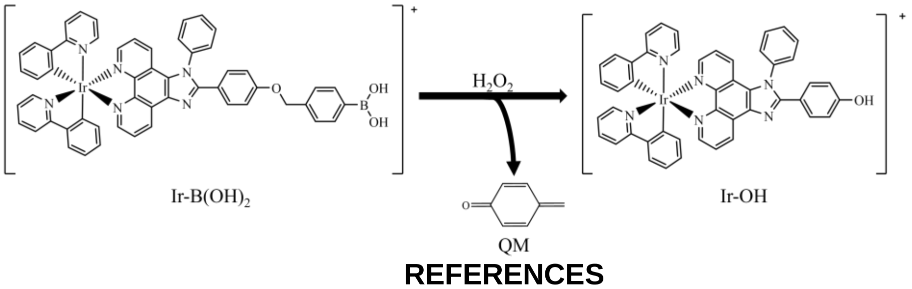
ABSTRACT

Photodynamic Therapy (PDT) is a promising therapeutic methodology which could replace the classic cancer treatments. The operator chooses where and when activate the photosensitizer drug (PS), increasing the selectivity and safety and reducing the therapy's side effects. The methodology is based on the *in situ* production of Reactive Oxygen's Species (ROS), that are cytotoxic and kill diseased tissues. It is noteworthy that cancer cells already have high concentration of ROS that are neutralized by the antioxidant systems that allow their survival. The most abundant redox couple in maintaining cellular redox balance is the Glutathione system (GSSG/2GSH), which is able to neutralize the ROS produced by the treatment reducing the effectiveness. Indeed, one of the strategy recently proposed provides the design of molecular systems able to decrease the amount of the ROS-scavenger GSH exploiting the high concentration of one of the ROS naturally produced by cancer cells, H_2O_2. It can be utilized as target agent, because it selectively reacts with biocompatible moieties like boronic esters producing methylquinone (QM) as by-product QM is a well-known GSH scavenger and could prevent GSH-mediated ROS quenching. Such a reaction between boronic acid and H_2O_2 can, thus, be utilized to improve the selectivity and the effectiveness of the therapy[1,2].

A recent work reports the combination of a cyclometalated iridium(III) complexes as PS for the PDT and aryl boronic acids as prodrugs for the H_2O_2-responsive anticancer therapy [3]. DFT and TD-DFT approaches have been, here, employed to study the (QM) release reaction mechanism from a prodrug, named Ir-B(OH)$_2$, composed of a complex of Ir(III) bonded to an boronic ester, which can selectively reacts with H_2O_2. In addition, the photophysical properties of both starting IrB(OH)$_2$ and released complex, Ir-OH, have been fully elucidated .



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Computational Study of dicationic ionic liquids

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ABSTRACT

Ionic liquids (ILs) gain a high relevance in the last decades and have been extensively studied as alternatives solvents due to their properties such as negligible vapor tension, thermal and chemical stability, and the possibility to recycle [1]–[4]. In this context, we use the computational technic to characterize and determine the stability of the IL-based on the two imidazolium rings connected by a xylene spacer with ortho (**Figure1a**), meta (**Figure1b**), and para (**Figure1c**) isomers with bromide, tungstate (**Figure1d**). The program gaussian 16 [5], XTB [6] and LAMMPS [7] was used for the analyses.

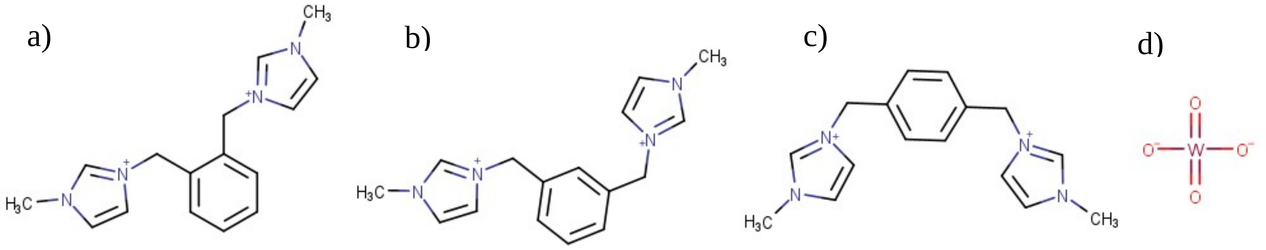

Figure 1: Structure a) orto; b) meta, c) para and d) tungstate anion.

The characterization using the gaussian program with the DFT theory, method B3PW91 and the base SDDall to calculate the IR and RMN spectrums from the IL with both anions. The simulation using molecular dynamics founded that the system based on WO_4^{2-} anion are more stable than those with the Br^- anion. These calculations demonstrate that the presence of the WO_4^{2-} anion creates strong ionic bonds between the cation and the anion leading to stable ionic pairs. The simulation using the LAMMPS was made for 1ns using the OPLSS-AA [8] force field to simulate the system using a cheaper method and comparer both methods.

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Exact and approximate evaluation of transition rates for quantum-stochastic master equation dynamics

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ABSTRACT

Simulations of the coupled dynamics of nuclei and electrons represent an important challenge in theoretical and computational chemistry to interpret measured quantum properties that can be modulated by nuclear motions. A possible solution is the quantum-classical master equation, the multiscale approach derived by R. Grunwald and R. Kapral from quantum-classical Liouville dynamics.[1,2] The key idea is to use the Liouville formalism to describe the coupled evolution of the classical probability density of the nuclei and the quantum density matrix of the electrons. The target system is partitioned into a quantum-classical subsystem that interacts with a classical bath. The nuclear coordinates are expressed in natural internal coordinates.[3] Finally, the degrees of freedom of the bath are projected out, leading to a stochastic Markovian evolution of the diagonal elements of the subsystem density matrix. The resulting system of equations can be interpreted as the adiabatic evolution of the classic probability density interspersed with transitions between two potential energy surfaces. An exact and an approximate protocol to calculate the transition coefficients are here presented and applied to a two-level model system, which resembles the behaviour of a photoswitching rotating molecule. Comparisons between the two results are illustrated, and the conditions under which the approximations hold are pointed out.

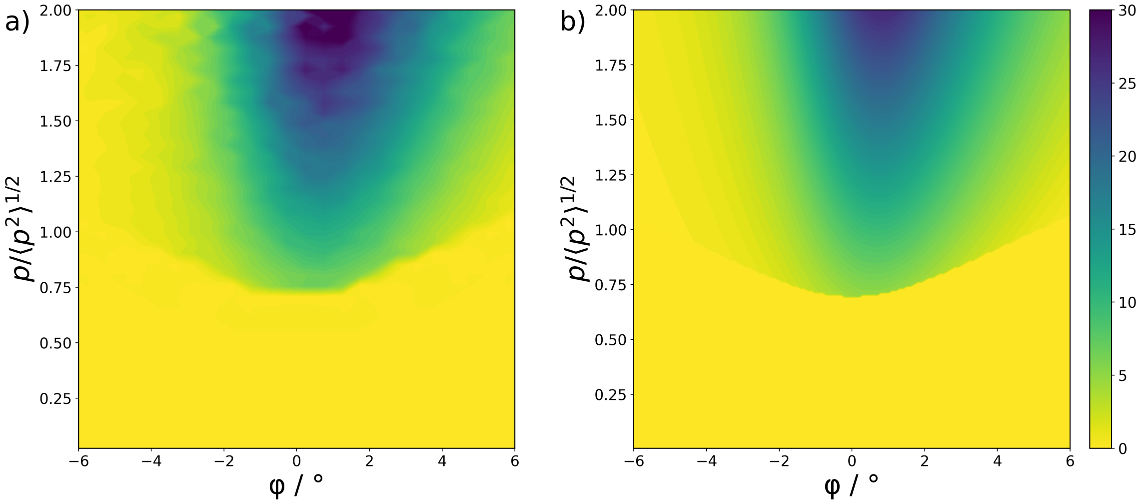

Figure 1. Plot of the transition rate coefficient from ground state to excited state (expressed in ps^{-1}) vs dihedral angle (φ) and conjugated momentum (*p*). In particular, the calculation is made by (a) the exact protocol, and (b) the approximate protocol.

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Theoretical evaluation of the thiol/disulfide interchange energy barrier as a model for proteins interaction

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ABSTRACT

Thiol/disulfide interchange is a reaction that regulates many biological processes, due to the presence of Cysteine residues in proteins. In this reaction, the deprotonated thiolate form could exchange its role with an oxidizing disulfide bridge [1][2], by means of a nucleofilic attack. The reversible and covalent bond formation between two sulfur atoms shows, in proteins or in small molecules, a free energy barrier of around 15 kcal/mol [3].

Here, we present a theoretical-computational study, based on a QM/MM method (the *Perturbed Matrix Method*), to model the thiol/disulfide interchange reaction in different solvents. By such an approach, we were able to evaluate the free energy barriers for this reaction, using mercaptoethanol and buthanethiol as model molecules, in a polar protic (water) and aprotic (DMF) solvent. The results obtained, in very good agreement with experimental values reported in literature [3] (Table 1 and Figure 1), show that our approach, able to combine Quantum-Mechanical description of the reactive center to an extended phase space sampling, as provided by Molecular Dynamics simulations, can be successfully applied to model chemical reactions in solution.

Table 1 : Comparison between computed (PMM) and experimental ([3]) data in DMF and water.

Molecule	Solvent	ΔG_{exp} $(kcal/mol)$	$\Delta A_{calc}(kcal/mol)$
$\mathrm{OHCH_2}CH_2S^-$			
	DMF	11.5	10.1
	$\mathrm{H_2}O$	16.2	17.3
$\mathrm{CH_3}CH_2CH_2CH_2S^-$			
	DMF	11.1	11.28

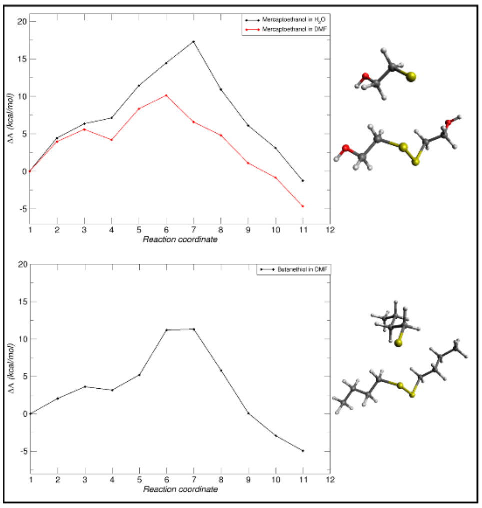

Figure 1:Energy barrier for mercaptoethanol (in water and DMF) and buthanethiol (in DMF) disulfide interchange reaction.

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Asn deamidation and Met oxidation: an hybrid QM/MM study

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ABSTRACT

Chemical stability is a major challenge in the development of safe and effective biotherapeutics drugs. Among post-translational modifications (PTMs) of proteins, Met oxidation and Asn deamidation are the most common non-enzymatic degradation pathways, both affecting biodrugs biological activity. Therefore, a deep understanding of reaction mechanisms and associated free energy barriers is needed to avoid and prevent them[1].

In light of such evidences, we performed an hybrid QM/MM study of both Asn deamidation and Met oxidation by means of the Perturbed Matrix Method (PMM), a QM/MM theoretical-computational procedure. In the PMM scheme the perturbed Hamiltonian operator (H) of the quantum center (QC), i.e. the reactive subpart of the system, is expressed as the sum of the unperturbed QC-H and a perturbation term provided by the perturbing electring field generated by the environment atomic charges at each MD frame[2].

Asn deamidation proceeds through a multi-step reaction, involving succinimide formation, with kinetics affected by neighbouring amino acid (n+1 position). Here, we focused our study on the ring-closure step, using two model pentapeptides, GGNGG and GGNIG, with very different experimental half-times. Calculation of the reaction energy surface along selected degrees of freedom allowed us to identify (unperturbed) energy pathways, which have been perturbed by means of PMM to reconstruct the free energy profiles (Fig.1). Our data point out that the effect of the perturbation, as provided by the environment, has a stronger stabilizing effect on GGNGG than GGNIG, leading to an estimated $\Delta\Delta A^{\ddagger}$ in good agreement with the experimental data (4.2 kcal/mol *vs* 3.6 kcal/mol)[3].

Regarding Met oxidation by hydrogen peroxide, no protein backbone involvement has been reported and, so, the reaction has been studied on a single Methionine. The perturbed free energy barrier (Fig.1), successfully reproduces experimental data (14.9 kcal/mol *vs* 15.5 kcal/mol)[4] . Noteworthy, PMM well describes the water-mediated stabilizing effect as provided by classical molecular dynamics simulations, i.e. it does not require to explicitly treat the water molecules at QM level, as previously reported[5,6].

In conclusion, Asn deamidation and Met oxidation have been successfully exploited in simple model systems by our theoretical-computational procedure, thus allowing for future investigations on more complex systems of pharmaceutical relevance.

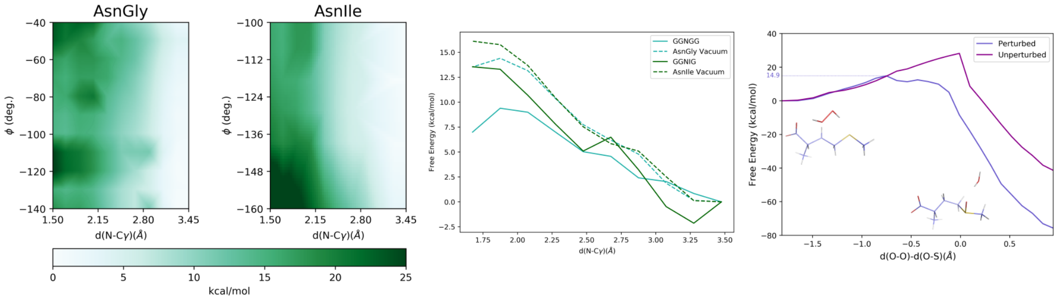

Figure 1. On the left, 2D PES of Asn Deamidation and perturbed free energy profiles (center). On the right, Met oxidation free energy profile vs vacuum profile.

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Hydrodeoxygenation of isoeugenol on platinum cluster: DFT insights into HYD and DDO mechanisms

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ABSTRACT

In a scenario of declining fossil resources and increasing demand for renewable and sustainable alternatives, biomass is the only source able to offer an easy and gradual transition in the use of current energy technologies based on the exploitation of carbon derivatives. Its conversion to liquid fuels has oriented our study towards the computational mechanistic analysis of the catalytic hydrodeoxygenation (HDO) reaction of isoeugenol[1], which is currently considered one of the most challenging routes for the upgrading of biomass-derived bio-oils[2,3]. For this purpose, a subnanometric platinum cluster (Pt_{10})[4] was chosen as the catalyst model, being this noble metal a computational reference for catalytic hydrogenation, and isoeugenol as a model for typical species of biomass origin. One of the most relevant aspects in the study of HDO process concerns the order in which the hydrogenation and deoxygenation steps are carried out. Both are necessary to obtain biofuels, but deoxygenation has a primary role[5]. It involves the removal of oxygenated groups (such as −OH, $-OCH_3$) which are responsible for the instability of bio-oils. Generally, two types of deoxygenation mechanisms have been proposed: (a) hydrogenation-through-deoxygenation (HYD) in which aromatic ring hydrogenation occurs first and is followed by the removal of oxygen via C-O hydrogenolysis from the satured hydrocarbon ring; (b) direct deoxygenation (DDO) which involves the direct cleavage of the Ar-O bond via hydrogenolysis without ring saturation. DFT calculations revealed that the energy barriers related to the cleavage of $C(sp^2)$-O bonds in the DDO mechanism are significantly lower (by about 45 kJ mol^{-1}) than those in the HYD mechanism in which $C(sp^3)$-O bond breaking from saturated ring occurs. This evidence suggests that isoeugenol deoxygenation on Pt_{10} occurs more readily through direct removal of the oxygenated components, i.e., by DDO mechanism. Furthermore, the results obtained identify for this mechanism the formation of the 4-propylphenol intermediate as the rate determining step and as the pivotal point for one of the most important branching step leading to 4-propylcyclohexan-1-ol as a secondary product.

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Picosecond Excited State Dynamics Reveals the Coexistence of Stereochemically Distinct Reactive and Non-reactive Isomerization Paths in Heliorhodopsin.

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ABSTRACT

In 2018 a new family of rhodopsins called heliorhodopsins was discovered using functional metagenomics and readily detected globally in many aquatic environments. This third and new family of rhodopsin offers a further possibility to study of how organisms has exploited the reaction of the photoisomerization of the retinal protonated Schiff base chromophore (rPSB) for targeting biological tasks and adapt to different environments. Despite first experimental evidences have shown similarities with the reaction in microbial rhodopsins, the precise reaction mechanism in one member of heliorhodopsins has not been established, yet. Here we studied the reaction mechanism in one member of the family that is expressed in the *Thermoplasmatales archaeon* (*Ta*HeR) by analysing the sub-picosecond evolution of hundreds of hybrid quantum/classical trajectories. In order to provide a reference and also to show mechanistic differences and similarities, the same analysis is also carried out on the largely studied visual pigment rhodopsin expressed in the *Bos Taurus* (Rh). The results testify the extremely faster and efficient nature of the reaction in Rh, but reveal a diverse and possibly adaptive mechanism that controls its quantum efficiency in *Ta*HeR that is based on the internal competition between reactive and unreactive excited state deactivation paths acting on different double bonds of the rPSB chromophore.

Polarizable Molecular Dynamics of Aprotic Electrolytes with Lithium Salts in Li-O2 batteries

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The innovations that are occurring in many strategic industrial sectors towards green technologies heavily rely on the constant improvements of energy storage devices. Aprotic lithium-oxygen batteries (aLOBs) are the so-called-generation 5 energy storage devices and will displace current technologies in the mid-term. aLOBs can outperform current lithium-ion batteries in terms of theoretical energy density (about 3500 Wh/kg vs 150 Wh/kg), and can disclose outstanding improvements also in terms of costs and safety.[1] Despite these fascinating opportunities, many missing pieces are still preventing these systems from achieving their theoretical figures, as aLOBs suffer from low round-trip energetic efficiency, poor reversibility and materials instability. One of the most important drawbacks that affects aLOBs is the degradation of electrolyte components (salts, organic solvents, redox mediators) during the discharge and charge processes.

The aim of this communication is to illustrates innovations in materials design for Li-O2 battery systems from experimental and theoretical perspectives. More precisely, theoretical calculations employing a polarizable force field, AMOEBA[2], have been used to simulate the bulk conditions of the solvent and to obtain information the dynamical and transport properties of the electrolyte. The need to use a polarizable force field lies in the requirement to accurately represent the chemical surroundings of the (charged) electrolyte. From the experimental side we present new measurements of the conductivity and transport numbers of lithium in solutions as well as Raman spectra that can aid the characterization of the solvation state of the electrolyte and that can be directly compared with the calculation. The combination of the results of theory and experiments will be used as the basis for future calculations and provide guidelines for designing of aprotic electrolyte solutions for Li-oxygen batteries.

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Validation of a protein – protein docking approach through Molecular Dynamics simulations

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ABSTRACT

Protein – protein recognition is a complex problem that needs to be addressed with computational methods, especially in absence of experimental information. Among them, protein – protein docking procedures can help in finding possible binding geometries of a complex consisting of two or more proteins. Starting from the crystallographic structures of the protein partners, these methods foresee the sampling of the possible binding modes and the use of scoring potentials, which differ among the specific docking approaches, for ranking the putative binding geometries. The main limit of protein – protein docking approaches is that the dynamical behaviour of proteins is not included, or it is only partially. Thus, the refinement of the docked binding poses should also take into account proteins flexibility. This can be achieved through Molecular Dynamics (MD) simulations.

In the present work, we apply a protocol [1] that allows through MD simulations to discriminate among near-native and non-native docking poses, i.e. poses which are close or not to the known crystallographic structure of the complex. The protocol has been applied to a series of complexes made-up by affitins (a class of engineered proteins) and different protein partners, such as an endoglucanase, a lysozyme, the tyrosine-protein kinase Fyn, the retinol binding protein 4, and the wild-type and a mutated form of K-ras.

The protocol is based on the idea that near-native poses are more stable during MD simulations. Stability is determined by monitoring some parameters calculated with respect to the docked pose. They include the three CAPRI evaluation parameters [2]: i) the fraction of native contacts, i.e. the number of native (correct) residue–residue contacts during the MD divided by the number of contacts in the reference structure; ii) the ligand-RMSD, i.e. the root-mean-squared deviation of the backbone atoms of the smaller protein after the fitting on the same atoms of the bigger protein in the reference structure; iii) the interface-RMSD, i.e. the root-mean-squared deviation of the backbone atoms of the interface residues, defined as the ones having at least one atom within 10 Å of an atom on the other protein. These three parameters sum up to DockQ [3], a value ranging from 0 to 1 that describes the overall quality of the model. Other parameters that are monitored are the number of hydrogen bonds, the buried surface area, and the protein – protein and protein – solvent interaction energies.

The results obtained on affitins complexes show that DockQ values, together with the above-mentioned parameters, are usually able to discriminate among native and non-native poses, thus suggesting that this approach could be used for the reranking of docked binding poses of possible complexes between affitins and other protein partners.

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Modelling of ATP-Zn^{2+} coordination as a key element for ATP-fueled self-assembly

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ABSTRACT

Following Nature's example, there is currently a strong interest in using ATP as a fuel for self-assembly of functional materials with transient/non-equilibrium behaviour [1,2], which hold a great promise for applications, e.g. in catalysis, in detergent formulation and drug delivery. Crucial to self-assembly is the ability of ATP and in particular of its phosphate group to bind metal ions. Assembly and disassembly are governed by a delicate interplay between entropy and enthalpy, thus, detailed structural and energetic insights on the binding are necessary for a mechanistic understanding. Computational methods can be a valuable means to this purpose. However, the study of ATP-metal complexes in water is challenging, because of quantum mechanical aspects in coordinate bonding combined with entropic effects in hydration and conformational distribution, and long-range electrostatics. Ab initio molecular dynamics (AIMD) with explicit solvent is unpracticable because of its heavy computational cost. On the contrary, classical MD, based on empirical force fields (FFs) with fixed charges, can be used to study also relatively large systems.

In a recent seminal work, binding of ATP to the metallosurfactant zinc hexadecyl-1,4,7-triazacyclononane ([ZnC$_{16}$TACN]$^{2+}$) was exploited to produce ATP-fueled transient vesicles [3]. As a first step to unveil the key elements underlying this process, we investigated the interaction of ATP with Zn^{2+} and [ZnCH$_3$TACN]$^{2+}$. To efficiently sample different coordination modes, we employed well-tempered metadynamics (WT-MTD). We found that the structure of the ternary complex is controlled by ATP coordination to zinc, with a minor role played by the interaction between the nucleotide and CH$_3$TACN which, however, may still be important for the build-up of supramolecular assemblies. Our study highlights the strong impact of triphosphate parametrization (charges, conformation and solvation) on the binding geometry and energetics, and the limits of the currently available FFs [4,5]. We are now performing WT-MTD in AIMD in a restricted configurational phase space to obtain a more accurate parametrization of the ATP-Zn^{2+} interaction.

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Solving the puzzle about the CO oxidation reaction mechanism of Mo/Cu CO dehydrogenase by means of QM/MM calculations

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ABSTRACT

In the atmosphere there are various trace gasses due to both natural sources and anthropogenic emissions. The most abundant of these gasses are hydrogen, carbon monoxide (CO) and methane. Various soil microorganisms have developed high affinity enzymes to consume these small gas molecules, allowing them to "live on air". In fact, the atmosphere has recently been recognized as an important source of energy to support various ecosystems. The enzymes involved in the transformation of CO, called CO dehydrogenases, have a net annual consumption of about 15% of CO present in the atmosphere. Therefore, they perform an important ecosystem regulation service, mitigating the emissions of this highly toxic gas, also known as a climate-altering agent [1]. A particular type of CO dehydrogenase has the rare characteristic of being insensitive to the presence of oxygen, allowing the soil bacteria *Oligotropha carboxidovorans* to take CO directly from the air. This enzyme is called MoCu-CODH to highlight the presence of a particular MoCu bimetallic center in its active site [2]. Over the past twenty years, various experimental and theoretical studies have been dedicated to understanding the mechanism of CO oxidation by this enzyme. However, the proposed mechanisms reported some difficulties in the evolution of the product [3].

By means of a QM/MM model of the enzyme and the employment of the energy refinement BigQM technique developed in our laboratories, we succeeded in presenting for the first time a reaction mechanism for the oxidation of CO catalyzed by the enzyme MoCu-CODH which agrees with the experimental data reported to date [4]. Our novel results will be discussed also in the light of previous theoretical studies we recently carried out on complimentary debated key points regarding the chemistry of such enzymes [5-7].

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How molecular chirality *affects the* supramolecular chirality in the self-assembly of TPPS$_4$ porphyrin aggregates

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ABSTRACT

Understanding chiral mechanisms at a supramolecular level is attracting a considerable interest due to the rapid developments of functional self-assembly strategies. The elucidation of chiral self-assembly from the molecular to the supramolecular level represents an advance of knowledge for the development and design of functional chiral materials. In this background, the spontaneous self–organization of π-conjugated molecules has gained significant attention due to their versatile optical and electronic properties. In this context, meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS$_4$) have shown a particular ability to self-assemble into chiral supramolecular structures, however to date the thorough details of how chirality is imparted in these frameworks remain unclear.

Motivated by the willing in understanding the fundamental principles behind the generation of chirality in self-assembled TPPS$_4$ porphyrin aggregates, enhanced sampling simulations have been performed on TPPS$_4$ atropoisomers, each in its monomeric, dimeric, trimeric and tetrameric aggregate forms. The conformation of porphyrin frameworks can be witnessed by the four torsional pyrrole dihedral angles, each identifying the collective variables (CVs). For this reason, in order to enhance the sampling and the efficiency in exploring and reconstructing the free-energy profiles related to self-assembly, Parallel Bias metadynamics (PB-MetaD) and Multiple Walkers metadynamics (MW-MetaD) simulations were carried out. The free-energy profiles as a function of the improper torsions, the tilted angles between two adjacent monomers and the interplane distances have been reconstructed for all the TPPS$_4$ aggregates allowing us to evaluate how the symmetry or the asymmetry of TPPS$_4$ supramolecular system can be selectively affected by increasing the aggregate dimension.

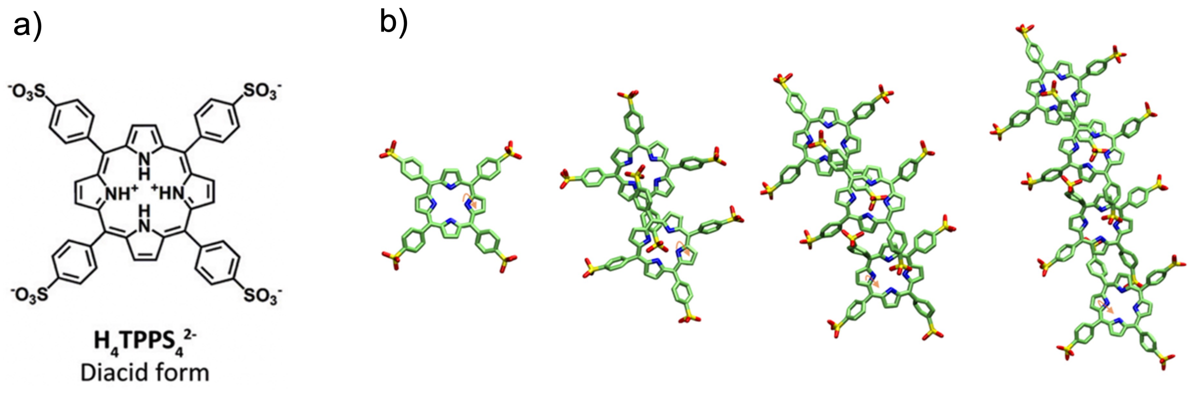

Figure 1: a) Molecular structures of TPPS$_4$ porphyrin in the diacid form that is the object of our theoretical study; b) The monomer, dimer, trimer and tetramer of the TPPS$_4$ system conformations disclosed from enhanced sampling simulations.

Machine Learning for Drug Discovery

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ABSTRACT

Artificial intelligence (AI) is becoming an increasingly important component of drug development. AI is now being applied in various areas of pharmaceutical research and development, including drug repurposing, improving pharmaceutical production, and clinical trials. It is possible to build QSAR models from large experimental databases using Machine Learning (ML) and Deep Learning (DL), which can predict physicochemical properties such as solubility, partition coefficient (logP), and reduction potential, which indirectly affect pharmacokinetics properties of a molecule. Unsupervised learning, on the other hand, is popular in medicinal chemistry, with techniques like hierarchical clustering, Artificial Neural Network (ANN) and principal components analysis (PCA) being used to examine and break down enormous chemical libraries into smaller groups of comparable compounds.

Our aim is to use this arsenal of AI strategies to predict pivotal properties of anticancer drugs, both containing and non-containing transition metals, conjugating them with traditional computational methodologies.

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5 Contributions from Prize Recipients

D. Accomasso *Premio Del Re* Singlet fission dynamics in molecular crystals and covalent dimers.

A.B. Muñoz García *Premio Roetti* A Quantum-Mechanical Journey Across Renewable Energies: a Tale of Stone, Water and Light.

F. Segatta *Premio Scrocco* From quantum chemistry to spectroscopy: systems, methods and insight.

Singlet fission dynamics in molecular crystals and covalent dimers

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ABSTRACT

Singlet fission is a photophysical process whereby a spin-singlet excited state is converted into two lower energy spin-triplet states [1]. The process provides an opportunity to increase the energy conversion efficiency of solar cells from the so-called Shockley-Queisser limit of about 1/3 to nearly 1/2 [2].

Here, we present an extensive computational investigation on singlet fission. First, we show how singlet fission can be affected by extending the delocalization of the excited states beyond two chromophores in a molecular crystal [3]. Next, we present several attempts to design not only new potential singlet fission chromophores [4], but also novel covalent dimers for singlet fission. For the latter case, two different design strategies are proposed. Finally, the most promising covalent dimers obtained by applying such strategies are further investigated by performing simulations of the excited state dynamics [5].

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A Quantum-Mechanical Journey Across Renewable Energies: a Tale of Stone, Water and Light

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ABSTRACT

A sustainable energy future can be achieved only by efficient production, transmission and storage of electricity and fuels using renewable sources. To this purpose, Quantum-Mechanical (QM) methods are great tools for developing multicomponent energy conversion devices, whose performance depends on charge and mass transport across different interfaces made of *hard* and *soft* chemical entities.
In this context, QM simulations of materials and interfaces have the power to extract unbiased atomistic insights that are mandatory for shifting from a trial-and-error to a rational design approach. The complexity of heterogeneous systems calls for the application - and often the integration - of several different QM-based approaches, which must be purposely tailored for the system at hand and the target property to be predicted.
In this talk, examples on how quantum mechanics can identify design principles of energy conversion devices will be outlined, paying particular attention to CO_2 reduction [1] , water splitting [2], perovskite solar cells (PSCs) [3] and state-of-the-art dye sensitized solar cells (DSCs) [4,5]

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From quantum chemistry to spectroscopy: systems, methods and insight

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ABSTRACT

In this contribution, I will summarize some of the results of my research activity, that has been mainly devoted to the development and application of theoretical/computational methods in two fields, namely: *computational quantum chemistry* and *spectroscopy simulation* of molecular and super-molecular systems.

Three *stories* will be presented, retracing the main steps that have led to significant new insight and further development of the employed techniques:

a) In the first story, titled “*A Quantum Chemical Interpretation of Two-Dimensional Electronic Spectroscopy of Light-Harvesting Complexes*”, I will describe our attempt to simulate the nonlinear spectroscopy of large multichromophore aggregates in their environment. Inter-chromophore excitonic couplings (computed for the first time at the CASSCF/CASPT2 level and beyond the dipole-dipole approximation), as well as couplings to intra-molecular vibrations and solvent fluctuations, were combined to simulate the spectra with unprecedented accuracy and insight. The work was conducted in collaboration with Prof. Benedetta Mennucci’s research group.

b) The second story, titled “*In silico ultrafast nonlinear spectroscopy meets experiments: the case of perylene bisimide dye*”, tells about a joint theoretical and experimental study of the perylene bisimide (PBI) dye spectroscopy. Two levels of theory were employed in the simulations, namely CASSCF/CASPT2 and TDDFT. The nonlinear spectroscopy simulation protocol that I contributed developing and refining over the years, is here tested against state-of-the-art ultrafast spectroscopy experimental data, and proved to be extremely reliable. The experimental group of Prof. Giulio Cerullo (PoliMi) and the theoretical group of Prof. Niranjan Govind (PNNL, USA) were key partners in the realization of this project.

c) In the third story, titled “*Soft X-ray Spectroscopy Simulations with Multiconfigurational Wave Function Theory: Spectrum Completeness, Sub-eV Accuracy, and Quantitative Reproduction of Line Shapes*”, I explore the possibility of exploiting all of the knowledge we acquired in quantum chemistry calculations and spectroscopy simulation to describe a completely different window of the electromagnetic spectrum, namely the soft X-ray energy domain. The simulated spectra are again compared to experiments, showing a remarkable (sub-eV) agreement between the two.

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