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Modeling Single Atom Catalysts

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One of the objectives of electronic structure theory is to predict chemical and catalytic activities. This is a challenging target due to the large number of variables that determine the performance of a heterogeneous catalyst. The complexity of the problem has reduced considerably with the advent of single atom catalysts (SAC), new systems consisting of a single transition metal stabilized on a solid matrix. SACs offer great potential advantages compared to more conventional supported metal nanoparticles in terms of selectivity and of material needs in order to prepare the catalysts. A lot of attention has been given in particular to graphene-based SACs for electrocatalytic reactions such as the oxygen reduction (ORR), the oxygen evolution (OER) and the hydrogen evolution (HER) reactions. In this context we assist to a rapidly growing number of theoretical studies based on density functional theory (DFT) and of proposals of universal descriptors that should provide a guide to the experimentalist for the synthesis of new catalysts. In this talk we critically analyze some of the current problems connected with the prediction of the activity of SACs based on DFT: accuracy of the calculations, neglect of important contributions in the models used, physical meaning of the proposed descriptors, inaccurate data sets used to train machine learning algorithms, not to mention some severe problems of reproducibility. It follows that the “rational design” of a catalyst based on some of the proposed universal descriptors or of the DFT screening of large number of structures should be considered with great caution [1-4].

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“There’s plenty of room at the” border between classical mechanics and quantum chemistry

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A significant part of the experimental observables (structural, dynamic, thermodynamic, kinetic and spectroscopic) of interest for the theoretical-computational chemistry, comes from the condensed phase: either solid or liquid. In particular the modeling of liquid phase-systems, where a large part of chemistry has traditionally developed, has always represented a challenge since most of the related observables (regardless of the energy and timescale in which they emerge) represent a convolution, i.e. typically averages, of properties involving classical and quantum degrees of freedom. In this respect, for the study of these systems, a strong interplay between quantum-chemistry and classical statistical mechanics is mandatory and, paradoxically, it often requires that approximations rather than certainties be more accurately dealt. Our laboratory has been involved in the study of these systems for almost two decades and in this talk I will review some of our most significant results in the field of chemical reactions thermodynamics [1], kinetics/dynamic [2] and spectroscopic properties [3]. The intrinsic features, the advantages and drawbacks of our “point of view” will also represent a focus of the talk in order to assess its possible coupling and interplay with other theoretical-computational approaches developed in the last years by many investigators.

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First principles methods for photo-induced phenomena and non-equilibrium dynamics

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Time-dependent electronic structure theories can model the subpicosecond evolution in time of excited electronic states from first principles. Among non-perturbative approaches to mean-field quantum electronic dynamics, Real-time time-dependent density functional theory combined with ab initio molecular dynamics have shown to be very powerful, providing a molecular interpretation of a plethora of transient photo induced phenomena, such as the interplay between initial photoexcited states, exciton and polaron formations.[1]

Real-time propagation and ab initio molecular dynamics combined with an innovative time-resolved electronic and vibrational analysis protocol are presented to disentangle the most relevant features underlying both linear and non-linear effects, capturing the resulting spectroscopic fingerprints of charge transfer, exciton formation, and long-lived charge species.

Excited state photo dynamics of prototypical molecules in gas phase along with more complex systems in solution will be used as test cases, showing the molecular basis of the temporal evolution of the electronic and vibrational signatures upon the excitation. In this contribution is presented a designed protocol of analysis for real-time electronic dynamics to be applied to time evolving electronic density related properties to characterize both in time and in space CT dynamics in complex systems, proposing easy to be read cross-correlation maps. As case studies to test such tools, we present the photoinduced metal-to-ligand charge-transfer electronic dynamics in water solution of $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]^{4+}$, dcbpy = (4,4' -dicarboxy-2,2' -bipyridine), or "N3⁺", a dye sensitizer for solar cells and relaxation dynamics of a non-covalent CT complex. [2-5]

Such analysis tools and the presented case studies can help to unveil the influence of the electronic manifold, as well as of the finite temperature-induced structural distortions and the environment on the ultrafast charge motions.

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CRYSTAL: a Program for Solid State Physics and Chemistry

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Crystal23[1] is the latest release of the CRYSTAL program,[2] a long-lasting project for the development of scientific instrument for quantum-mechanical simulations of materials. The particularity of CRYSTAL, in the field of solid state physics and chemistry, derives from the use of atom-centered basis functions within a linear combination of atomic orbitals (LCAO) approach and from the corresponding efficiency in the evaluation of the exact Fock exchange series. As generally recognized, the inclusion of a fraction of Fock exchange in the exchange-correlation potential of the density functional theory is key to a better description of many properties of materials (electronic, magnetic, mechanical, spintronic, lattice-dynamical, etc.).

In this presentation, we will summarize the main features of CRYSTAL and examine some of the novelties of this latest version, i.e. spin-orbit coupling,[3] topological analysis of electron density for lanthanides and actinides,[4] multiwall nanotubes,[5] together with their most noteworthy applications. Finally, this will be the occasion to briefly present the new Born-Oppenheimer molecular dynamics module currently present in the beta version of the code.[6]

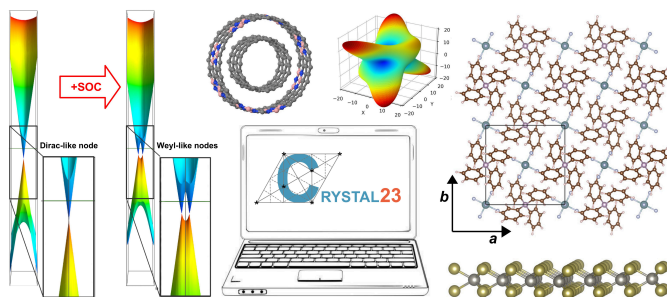


Figure 1: CRYSTAL23, graphical abstract of the last release of the code.

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Unveiling exotic chemistry and molecules in the interstellar medium: The role of quantum-chemical calculations

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The chemistry of the interstellar space occurs under extreme conditions, with temperatures ranging between 10 and hundreds of K (with a few exceptions such as shocked regions), very low number densities varying from 1 to 10^8 cm^{-3} , and ionizing radiation. Because of such extreme conditions, the chemical reactions that involve either ions or radicals as one of the reactants are effective and efficient. These reactions are unusual or even unfeasible under terrestrial conditions. The interstellar medium (ISM) is also characterized by turbulence and shocked regions. Shock-wave-driven chemistry contributes to widen the unusual chemical reactivity and leads to the onset of both transient and stable molecular species, with different shock-wave velocities triggering different chemical processes [1]. In short, the ISM is characterized by a chemistry that can be defined as exotic (with respect to the terrestrial standard) and can lead to the formation of unstable and/or highly reactive molecules, which can be broadly denoted as exotic. These are radicals and ions, but also closed-shell unsaturated systems such as imines and carbon chains. Owing to the very low density of the ISM, these reactive species survive long enough to be detected.

The strategy developed at the ROT&Comp Lab (Department of Chemistry “Giacomo Ciamician”, University of Bologna) to tackle the challenges of the characterization of such an unusual chemical reactivity and species [2-5], is presented by means of significant examples, the emphasis being on the computational methodology to be exploited. Illustrative systems range from potential prebiotic species such as (*Z*)-1,2-ethenediol [6,7] and allylimine [8] to radical species [9], passing through a long carbon chain [2], and substituted benzene [10]. As far as chemical reactivity is concerned, the focus will be on the general reaction mechanism for methanimine (CH_2NH) reacting with a radical species [11,12], and effective gas-phase formation routes for the CH_2SO isomers [5].

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Atomistic simulations of chiral polymers and low-dimensional perovskites

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In recent years, photoactive chiral materials are attracting considerable interest owing to relevant applications in optoelectronics as well as high resolution imaging. Luminescent chiral materials include soft chiral organic assemblies [2], together with inorganic chiral frameworks [3]. In these regards, hybrid materials are skyrocketing the field of material science for optoelectronics because they can tune the properties of soft and inorganic assemblies. A recent interesting class of luminescent chiral materials is represented by chiral hybrid perovskites, since they are showing prominent circularly polarized emissions without any need of expensive ferromagnets or extremely low temperatures. Indeed, the chiral source impacts specific non-covalent interactions occurring within the chiral scaffold, which in turn affect the efficiency of the chiral emissions. Modern multiscale modeling and simulations nowadays have an unprecedented level of accuracy, enabling an efficient chiral design of luminescent materials. Recent simulations of soft organic and hybrid materials, as helical polymers [4] and chiral hybrid perovskites [5,6] will be presented. The chiral design concepts are based on enhanced sampling simulations and TD-DFT calculations from the predicted free-energy basins. This simulation strategy enables to consider a variety of contributions including molecular rotations within the chiral framework, that may affect the generated chiroptical properties.

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Oral Communications

- O1. Lorenzo Briccolani-Bandini (Università degli Studi di Firenze)
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- O4. Andrea Lombardi (Università degli Studi di Perugia)
Enhanced molecular networks by invariant shape coordinates
- O5. Ilaria Barlocco (Università di Milano-Bicocca)
Does the Oxygen Evolution Reaction follow the classical OH, O*, OOH* path on single atom catalysts?*
- O6. Yasi Dai (Università di Bologna)
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- O7. Guido Raos (Politecnico di Milano)
Breaking polymer chains, networks and films, with a computer
- O8. Dario Frassi (Università di Pisa)
Photoisomerization dynamics of spiropyrans
- O9. Riccardo Cortivo (Università degli Studi di Padova)
A multiscale approach to coupled nuclear and electronic dynamics: quantum-stochastic Liouville equation
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- O11. Riccardo Conte (Università degli Studi di Milano)
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- O15. Abderrahmane Semmeq (Università degli Studi dell'Aquila)
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- O16. Edoardo Buttarazzi (Scuola Superiore Meridionale)
The real-time interplay between the ultrafast charge dynamics and nuclear vibrations in dyes for solar cell technologies
- O17. Giacomo Salvadori (Università di Pisa)
Transient Intermediates in a Bacteriophytochrome Photocycle Revealed by Multiscale Simulations
- O18. Adriano Pierini (Università di Roma "La Sapienza")
Mechanistic study of redox mediators in Li-O₂ batteries
- O19. Anna Ranaudo (Università di Milano-Bicocca)
Guiding competitive binding assays using protein-protein interaction prediction: the affitin-Her2 use case
- O20. Annalisa Pallini (Università degli Studi di Modena e Reggio Emilia)
Aluminosilicate Glasses: Thermal and Mechanical Properties Simulations
- O21. Pierraffaele Barretta (Università della Calabria)
An activatable photosensitizer for Photodynamic Therapy: mechanism of NO photo-release and free radical generation
- O22. Giulio Poli (Università di Pisa)
An in silico platform for evaluating the potential pathogenic impact of hRPE65 missense mutations
- O23. Roberto Paciotti (Università di Chieti-Pescara)
The FMO-GRID based scoring functions to predict the binding energy of ligand-receptor complexes containing metals

Concerted vs. Stepwise Proton Transfer reactions in the [2,2'-bipyridyl]-3,3'-diol molecule: a static and dynamic ab-initio investigation.

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The double proton transfer PT reaction was investigated in the [2,2'-bipyridyl]-3,3'-diol, where the tautomerization involves a significant rearrangement of the electronic structure on the conjugated bipyridyl rings. Different reaction mechanisms have been proposed for the ground state: concerted and step wise [1]. In the concerted PT, two protons are transferred with different degrees of synchronicity, whereas in the stepwise PT, the two transition states are separated by a keto-enol intermediate.

To this end, a static exploration of the Minimum Energy Path was conducted in conjunction with the analysis of the Free-Energy Surface, with both being evaluated at the Density Functional Theory level adopting different exchange-correlation functionals. On the basis of the calculation the simultaneous PT mechanism has been discharged while the characteristics of the stepwise and asynchronous concerted PT significantly depends on the chosen functionals.

The computational results show how different functionals, even those belonging to the same family, result into distinct mechanisms that influence the chemical interpretation of the investigated process. Thanks to the comparison with reference post-HF data obtained for the static approach, it was possible to correlate the discrepancies between the functionals and the reference data to the Self Interaction Error [2,3,4]. Indeed, the capacity of the functionals to accurately describe localized, zwitterionic, and delocalized electronic structures has a significant impact on the small energy barriers and overall relative stability of the different tautomers. Functionals that are significantly more affected by SIE tend to overstabilize the delocalized electronic structures of the keto-tautomer and keto-enol intermediate, providing a qualitatively distinct picture than all others.

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Exploring Machine Learning Techniques for Molecular Property Prediction

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In recent years, machine learning has revolutionized the field of drug discovery and molecular property prediction, offering powerful tools to accelerate the identification and design of novel therapeutics [1].

It is a technique that combines computational power and experimental data, benefiting from this union. In fact, by leveraging vast amounts of data, machine learning algorithms can extract valuable insights, uncover hidden patterns, and make predictions about molecular behavior, toxicity or simply predict molecular properties such as solubility, reduction potential or electronic properties. Through the integration of diverse molecular descriptors [2], feature engineering and advanced modeling techniques, machine learning enables the rapid screening of a vast chemical space, guiding the selection of potential drug candidates for further exploration. Overall, machine learning represents a breakthrough in the field of drug discovery, revolutionizing the way molecules are analyzed, predicted and optimized in ever shorter time frames. Here we present the results of the application of machine learning to the prediction of key molecular properties of metal containing compounds as anticancer drugs.

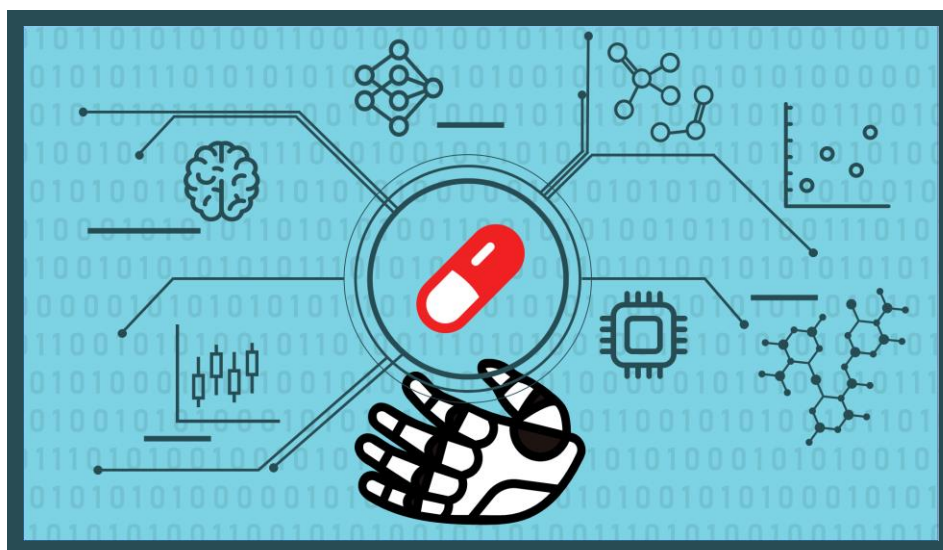


Figure 1 The use of machine learning in translational medicine

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On the study of thermoresponsive (adsorbent) species at the nanoscale: the case of polyoxazolines

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Polyoxazolines (POAs) are a class of thermoresponsive polymers characterised by a lower critical solution temperature (LCST) in water. The thermoresponsiveness makes POAs smart materials that can be exploited in the design and development of thermosensitive nanoscale devices. Recently, POAs-based nanodevices have been used in environmental remediation to remove heavy metal ions from water.[1] By changing the chemical nature of the groups attached to the POA backbone, different polymeric systems can be designed to both adsorb diverse cargos, and undergo controlled solubility transitions in response to thermal triggers. The ability to control and tune both polymer-cargo and polymer-solvent interactions offers the potential to develop a wide range of effective - and potentially selective - smart nanoadsorbers. The simplest case of thermoresponsive POA (namely polyisopropylloxazoline or PiPOx) in water has recently been studied using atomistic simulations.[2] Our data show that the thermoresponsive behaviour of PiPOx is dominated by intermolecular interactions leading to the experimentally observed liquid-liquid phase separation (LLPS). We also found that the system behaviour can be well modelled by remapping the polymer chains into effective ellipsoids.[3] Such a simplified description allowed us not only to observe that in the LLPS phase the average distance between polymer chains mirrors the experimental lattice spacing measured on crystalline phases, but also to suggest the presence of a liquid crystalline phase in the polymer rich region, at high temperatures.[4]

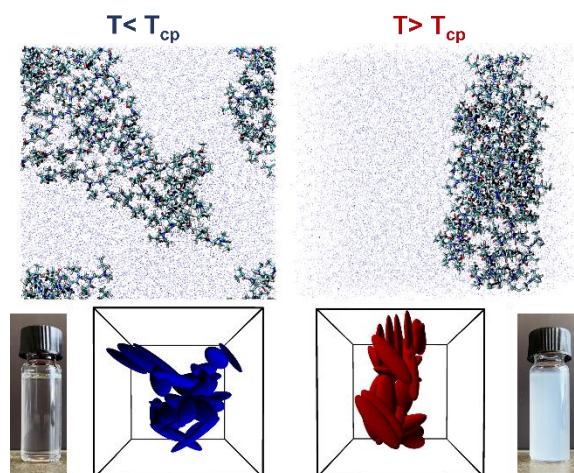


Figure 1 Representative snapshots from the atomistic MD simulations of aqueous PiPOx at temperatures (T) below and above the transition (T_{cp}), the same systems represented by means of the corresponding effective ellipsoids are also shown, along with real-case pictures.

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Enhanced molecular networks by invariant shape coordinates

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Representations of large molecules, typically proteins or DNA, are commonly obtained by molecular networks, for the purpose of classification and machine learning applications. These are usually made up by sets of specific centers (or nodes) that identifies atoms of the molecule (e.g. C_α atoms for proteins) plus a neighbourhood criterium, that allows to generate links between the nodes [1]. The nodes plus the links produce a graph or network, whose properties can be conveniently described in the framework of graph theory. Here we propose an approach to generate enhanced molecular networks, by embedding in the graph parameters that contain invariant structural information of the molecules [2]. These can be shape coordinates and deformation indexes, borrowed from the generalization of hyperspherical coordinates to the classical N-body problem [3]. The approach will be illustrated and its application to large protein structure sets shown.

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Does the Oxygen Evolution Reaction follow the classical OH*, O*, OOH* path on single atom catalysts?

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The Oxygen Evolution Reaction (OER) is a key part of water splitting. On metal and oxide surfaces it usually occurs *via* formation of three intermediates, M(OH), M(O), and M(OOH).^[1] The last step consists of O₂ release. Generally, it was assumed that the same path occurs on single atom catalysts (SACs).^[1] However, the chemistry of SACs may differ substantially from that of extended surfaces and is reminiscent of that of coordination compounds.^[2,3] This raises the question of whether on SACs the OER follows the classical mechanism or not. Indeed, a set of 30 SACs were prepared by anchoring a metal atom (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Pd and Pt) in a carbon matrix (graphene, nitrogen-doped graphene and carbon nitride). Conventional and unconventional pathways, see Figure 1, were then considered,^[4] and in all cases at least one unconventional intermediate was found to be more stable than the classical one.

This demonstrates that the assumption done in modelling OER on bulk materials can not be transferred to the SACs as it is. Completely different prediction on the activity of SACs in OER can be made if one follows the assumption that only a sub-set of intermediates can form. Indeed, only once all the possible intermediates are considered, one can speculate about the preferred reaction pathway. The pathway followed to form O₂ from H₂O is metal and support dependent underlying the complexity of this “simple” reaction. As an example, on Ti@DV-Gr, only one unconventional intermediate forms, η²-O₂*. Different is the case of Fe@C₃N₄, where the entire pathway is characterised by the formation of unconventional intermediates. Considering Sc@4N-Gr, two intermediates are “classical” and two are unconventional. Finally, on Pd@C₃N₄ the classical and the unconventional paths lead to completely different predictions about the reactivity of the SAC.

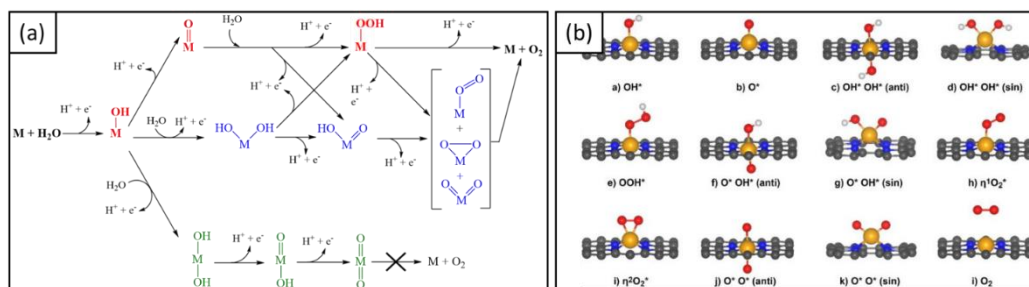


Figure 1: (a) Oxygen evolution reaction (OER) scheme where all the possible pathways are shown including the formation of all possible “classical” (in red) and “unconventional” intermediates (blue and green) and (b) Possible OER intermediates on SACs embedded in 2D carbon nanostructures (N-doped graphene is reported as an example). Similar structures have been considered on the other supports.

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Ambipolar charge transport in organic semiconductors: the role played by diradical character

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π -conjugated diradicals are organic semiconductors featuring a certain degree of unpaired electrons. Thanks to their small HOMO-LUMO gap, they exhibit NIR absorption, amphoteric electrochemical redox behavior [1] and favourable p-type and n-type conduction. Such intrinsic electronic properties make them promising for applications in spintronics, organic batteries and optoelectronics [2]. A key process in these devices is charge transfer. By reference to the semiclassical Marcus theory, the charge transfer efficiency is governed by the combination of **intramolecular reorganization energy** and **intermolecular electronic coupling**. In particular, a small reorganization energy and/or large electronic coupling favor the charge hopping rate.

In two recent studies on two classes of conjugated diradicals with medium diradical character [3], we showed that the amphoteric redox behavior and ambipolar conductance in OFETs, based on some of these diradicaloids, is assisted by rather small computed intramolecular reorganization energies. We showed that such small reorganization energies are related to the presence of the partial open-shell (OS) nature, generating a pseudo-hole and pseudo-electron character in the neutral forms that, upon charging, provide similar conditions for the stabilization and transport of holes and electrons resulting in ambipolar charge transport.

In this presentation, I will show how the diradical character, that can be quantified by the diradical index y_0 [4], impacts the geometrical and electronic structure of neutral species which in turn control the magnitude of reorganization energies for both charge carriers. To this end, a more extended library of diradicaloid molecules is considered [5]. The reorganization energies are calculated with the four-points adiabatic potential method [5], at R(U)B3LYP/6-311G* levels, considering both a limiting reference closed-shell (CS) representation and the more realistic OS structures. Based on computed geometries of neutral and charged species, a simple scheme to rationalize the small, computed reorganization energies for both n-type and p-type charge transport is proposed (Figure 1). The study is supplemented with the calculation of intermolecular electronic couplings for selected diradicals, supporting the ambipolar character of the investigated diradicals.

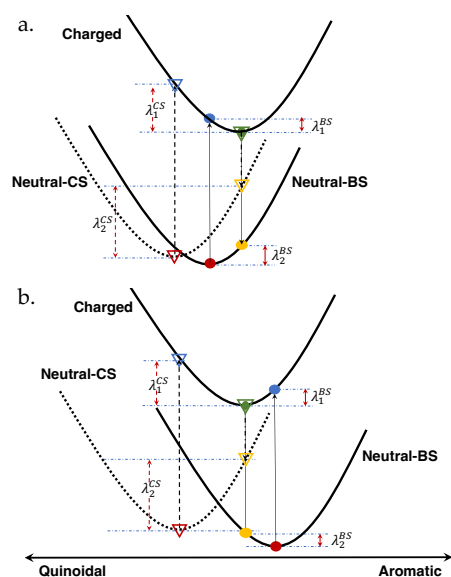


Figure 1. Schematic representation of the impact of diradical character and the consequent geometry change on the intramolecular reorganization energy.

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Abstract for DCTC 2023, Pisa.

Breaking polymer chains, networks and films, with a computer

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Polymers are markedly different and in many ways superior to other materials, when it comes to their mechanical properties. They can be light, highly deformable, mechanically tough, depending also on their chemical structure and physical processing. These mechanical properties depend on the possibility to stretch a polymer chain to several times its unperturbed random coil dimension, storing a great amount of elastic energy and releasing it as heat when it eventually breaks. We have simulated this phenomena both on single chains, using a fully atomistic reactive force field, and at the level of adhesive polymer networks using a coarse-grained model. Our simulations shed light on the role of polymer stereochemistry in chain scission, and the density and location of cross-links in adhesive films. We will also discuss the challenges that arise when dealing with energy dissipation (i.e, thermostating) in non-equilibrium molecular dynamics simulations of polymer breakup.

Raos, G. and Zappone, B., 2021. Polymer Adhesion: Seeking New Solutions for an Old Problem. *Macromolecules*, 54(23), pp.10617-10644.

Photoisomerization dynamics of spiropyrans

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Spiropyrans are a broad class of compounds widely used in materials science due to their pronounced photochromic properties. The excitation of spiropyrans in the UV range converts them into the open and colored merocyanine form. Despite the large use of these molecular switches, the exact mechanism of the photoisomerization reaction is not fully understood and appears to be strongly dependent on the substituents and the environment [1]. For these reasons, we want to study the excited-state dynamics of two spiropyrans labeled as BIPS and nitro-BIPS (Figure 1) through “on the fly” surface hopping nonadiabatic dynamics simulations using the FOMO-CI method in a semiempirical AM1 framework [2,3]. We considered the modifications of the lowest-lying excited state PESs of BIPS induced by nitro substitutions, and their impact on the nonadiabatic dynamics. Furthermore, to bring the solvent effects out on the BIPS excited state dynamics, we ran simulations in three different environments (chloroform, methanol, and ethylene glycol) and we compared these results with previous simulations carried out in vacuo [4].

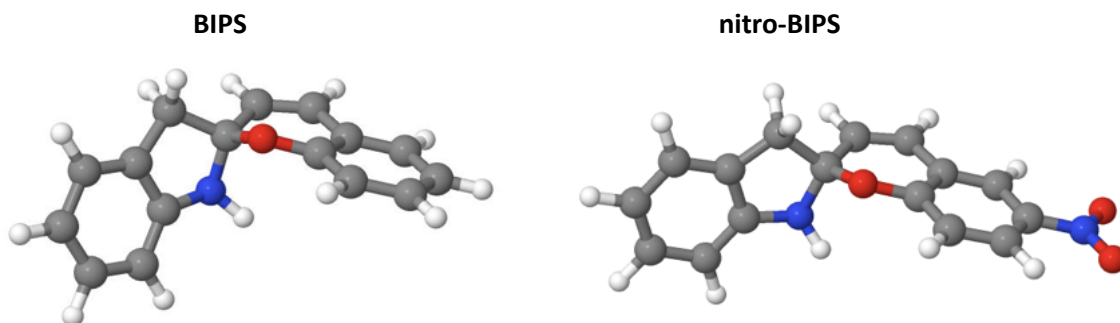


Figure 1. Spiropyrans labeled BIPS and nitro-BIPS

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A multiscale approach to coupled nuclear and electronic dynamics: quantum-stochastic Liouville equation

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Multiscale methods are based on a hierarchical partitioning of the degrees of freedom (d.o.f.) of the system, so that each set can be treated in the most computational efficient way. In the context of coupled nuclear and electronic dynamics, a multiscale approach can overcome current computational limits in fully treating complex systems at quantum mechanical level, such as biological macromolecules in explicit solvent. Based on the pioneering work of R. Kapral and G. Ciccotti [1], this presentation is intended to show a nonadiabatic theory that describes the evolution of electronic populations coupled with the dynamics of the nuclei under the basic approximations of the quantum-classical Liouville equation. The two elements of novelty that are here introduced are: i) the casting of the theory in the natural, internal coordinates, which recall chemists' description of molecular structure and dynamics; ii) the projection of the nuclear d.o.f. which can be treated as a thermal bath, leading to a quantum-stochastic Liouville equation (QSLE) [2,3]. Some tests on a simple 1D model are presented to demonstrate the main features of the method. Finally, the cis-trans photoisomerization of azobenzene (Figure 1) is shown as an example of a real system application of the QSLE.

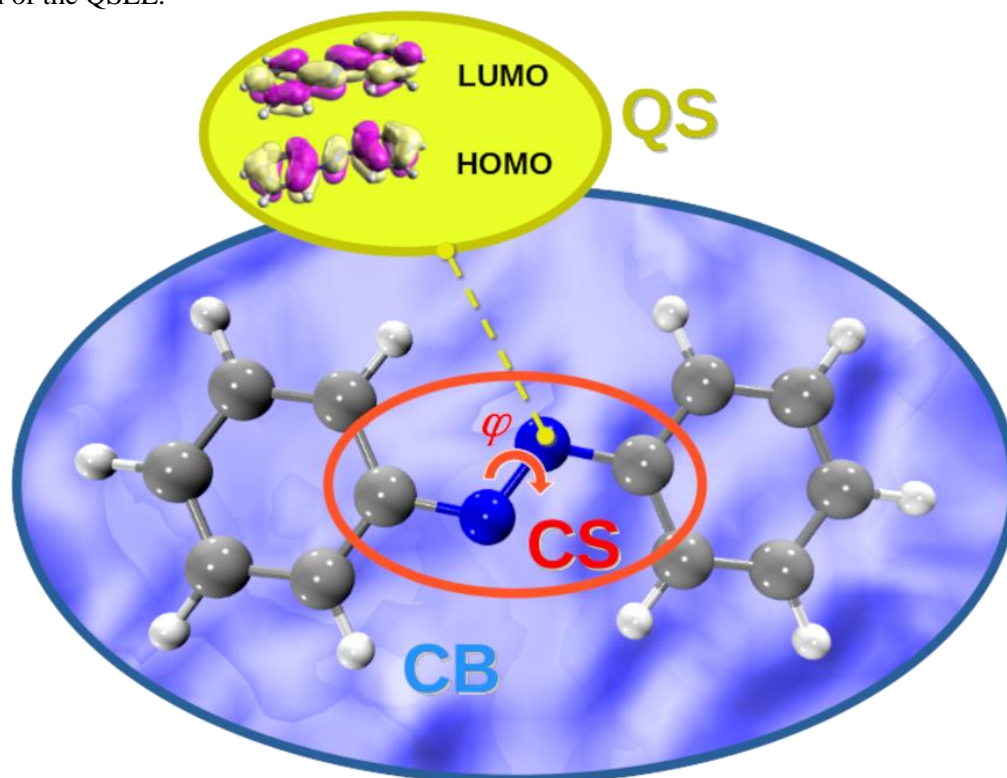


Figure 1 A possible scheme for partitioning the coordinates to study the photoswitching properties of azobenzene with the QSLE. Here, the quantum degrees of freedom of the system (QS) are the electrons, especially those responsible for the HOMO and LUMO orbitals (for this picture, obtained at B3LYP/6-31G* level in the optimum geometry). The relevant classical internal coordinates (CS) are the rigid body rotations and the dihedral angle (φ) highlighted with a red arrow in the picture. All the other molecular internal degrees of freedom and the solvent coordinates (represented as a blue surface in the background) constitute the set of irrelevant bath coordinates (CB).

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Charge and Energy Transfer Kinetics in Ternary Organic Solar Cells

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Photovoltaic (PV) represents one of the most important renewable-energy technology. Lately, research efforts have been focused on low-cost solar cells based on organic materials (OSC). Unfortunately, OSC power conversion efficiency (PCE) is still much far from the theoretical Shockley-Queisser limit of 33% for single junction devices and from the efficiency of inorganic devices. This can be imputed to very fast radiative and non-radiative decays to the ground state. In fact, it was the removal of non-radiative decay channels the real breakthrough for achieving high efficiency in GaAs based solar cells[1].

Thus, characterizing the kinetics of all processes is of paramount importance in order to recognize both beneficial and detrimental processes affecting the PCE of OSCs. This task requires the computation of the rates for all charge and energy transfer processes occurring in the device. To that end, we developed a theoretical method for computing the rates (k) based on the framework of the Fermi's Golden Rule (1), where V is the electronic coupling and $\rho(\Delta E, T)$ is the Franck-Condon Weighted Density of States (FCWD)[2].

$$k = \frac{2\pi}{\hbar} |V|^2 \rho(\Delta E, T) \quad (1).$$

Since it is widely recognized that the morphology interface deeply influences the rates, we started our study performing MD simulations. The most significant MD configurations were extracted from dynamics and then characterized at the DFT level to compute the electronic couplings for all processes. FCWD was evaluated, introducing the harmonic approximation, by the generating function approach (GF). The GF has indeed several advantages because it permits to take into account all the vibrational modes and also includes thermal effects.

We tested our method on the very challenging case of a ternary OSC (TSC). There, the occurrence of several concomitant processes at three different interfaces, strongly complicate things with respect to binary devices. For the TSC composed of FG3, FG4 and Y6, two small molecules donors (FG) and one acceptor [3], we computed the rates of photo-electron transfer (PET), photo-hole transfer (PHT), charge recombination (CR) and Förster resonance energy transfer (FRET) using our newly developed methodology.

Preliminary results strongly indicate FRET as the most beneficial process and predict an efficiency substantially higher than the one of the binary devices counterparts. In fact, simulations of the OSC obtained by removing one of the donors (thus resorting to the binary device) predict a substantially lower efficiency, in good agreement with experimental results.

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Semiclassical vibrational spectroscopy from small molecules to solvated biomolecules

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The hallmark of semiclassical dynamics is the ability to get quantum effects starting from classical trajectories.[1] Therefore, the main challenge semiclassical methods have to face is to demonstrate their accuracy and possibility to be applied even to large and complex systems.[2]

I will show that semiclassical dynamics can be straightforwardly interfaced to different descriptions of the potential energy surface (PES), ranging from *ab initio* PESs[3-5] to force fields[6,7] and QM/MM schemes. This allows one to apply semiclassical spectroscopy to the calculation of the quantum vibrational features of very different systems, including not only small molecules characterized by elusive Fermi resonances, like ethanol, or hard-to-assign experimental spectra, like proline, but also large systems like solvated biomolecules. Finally, ongoing efforts to reproduce also the intensity of absorption in the framework of semiclassical dynamics will be illustrated.[8]

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Accuracy meets Feasibility for Structural and Spectroscopic Investigations: The Study of DNA Basis Tautomers by Novel Parameter-Free Approaches

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Most molecular bricks of life (amino acids, nucleobases, sugars, etc.) undergo either conformational or tautomeric equilibria, which are tuned by both intrinsic stereo-electronic and environmental effects. The refinement of a general strategy to handle the above-mentioned features poses a pioneering challenge in the field of electronic structure quantum chemistry. In fact, even the most refined computations performed till now employed geometrical structures and force fields of limited accuracy, thus compromising any unbiased comparison with the results of high-resolution spectroscopy. In order to face these intricacies, a general parameter-free protocol for the accurate computation of structural and spectroscopic properties of biomolecule building blocks in the gas phase has been developed and validated for tautomeric equilibria. The main features of the new model are the inclusion of core-valence correlation in geometry optimizations by a double hybrid functional and the systematic use of wave-function composite methods in conjunction with cc-pVnZ-F12 basis sets [1] with separate extrapolation of MP2 and post-MP2 contributions. The resulting Pisa composite scheme (PCS) [2] can be employed both for geometry and energy refinements and represents a further improvement over the already highly successful jun-Cheap model [3,4]. The PCS, employing conventional or explicitly-correlated approaches, is applied to the challenging problem of DNA basis (e.g. cytosine and guanine) tautomers in the gas phase. The results are in remarkable agreement with the experimental structures, relative stabilities and spectroscopic signatures of different tautomers. The accuracy obtained at a reasonable cost through black-box parameter-free approaches paves the way toward systematic investigations of other molecular bricks.

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Combining High Accuracy and Chemical Insight with Local Coupled Cluster Methods

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Local correlation techniques exploit the short-range nature of dynamic electron correlation to reduce the inherent steep scaling of wavefunction-based methods. In this contribution, we explore the application of local coupled cluster methods to study reactivity and interactions of large and complex chemical systems with challenging electronic structure. Emphasis is placed on discussing recent theory advancements enabling: (i) the calculation of benchmark-quality energies for large systems [1] and (ii) the in depth-chemical interpretation of the coupled cluster results. [2,3] Thus, our research offers a powerful toolbox for achieving at the same time high accuracy and chemical insights. [4,5,6]

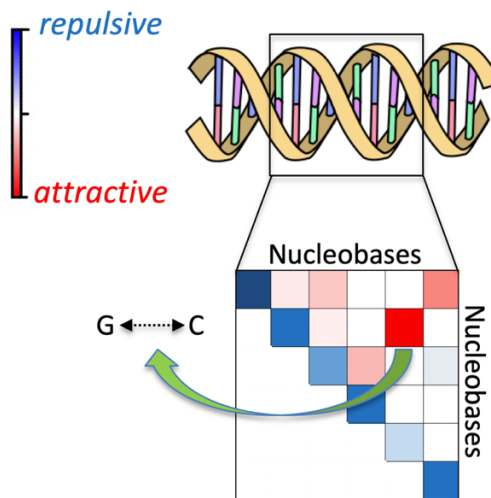


Figure 1. A recent local coupled cluster study on a large DNA duplex model (1001 atoms, 13998 contracted basis functions) provided an in-depth characterization of the key inter- and intra-strand interactions responsible for the stability of human DNA. [5]

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Boosting hybrid kernel TDDFT with STO by Resolution of Identity: implementation and application to a series of ligand protected nanoalloys

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Nowadays, the tuning of electronic and optical properties of thiolated noble metal clusters by doping them with transition metals has gained much interest [1,2]. By simulating their optical response we should be able to better rationalize the experiments and give important insights about the design of such systems. However, the availability of fast and robust computational schemes for this task is still limited. The polTDDFT [3] (a complex damped polarization method) proved to be particularly well suited for such a task, when hybrid functionals are involved, also thanks to the use of the Hybrid Diagonal Approximation [4] in its new “fitted” fashion. As a matter of fact, the use of Resolution of Identity technique to convert numerical exchange-correlation integrals into a sum of analytical ones allows a speedup factor of 30 of the simulations. The accuracy of this scheme is validated by the agreement between the calculated and low-temperature experimental photoabsorption spectra of $[\text{Ag}_{25}(\text{SR})_{18}]$, $\text{Au}_{24}\text{Pt}(\text{SR})_{18}$ and $[\text{Ag}_{24}\text{Pt}(\text{SR})_{18}]^{2-}$ clusters. For these systems the principal spectral features are analyzed in terms of molecular orbitals contributions and Independent Component Map of Oscillator Strength. Therefore, combining the polTDDFT together with the fitted-HDA, we obtain a computationally accurate and affordable approach suitable to study the optical properties of large metal clusters.

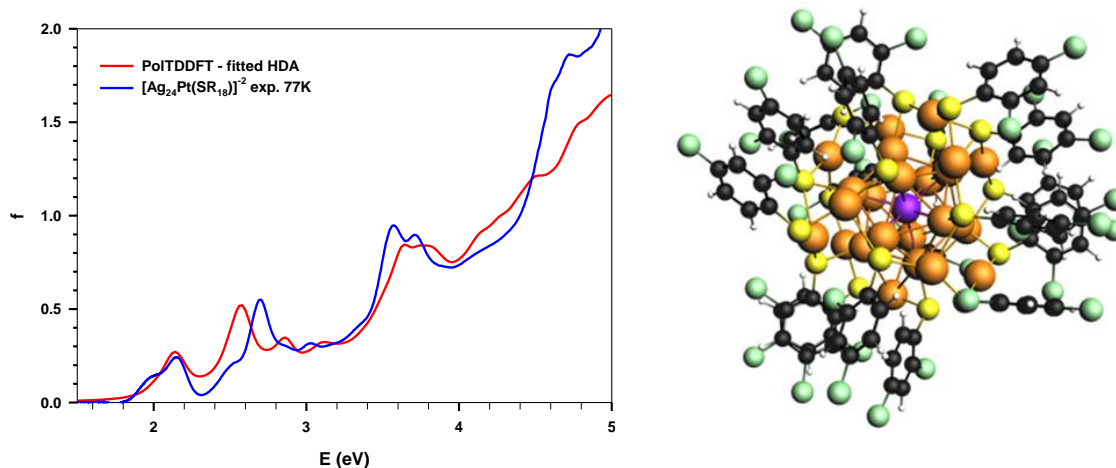


Figure 1 comparison between experiment and simulated spectrum using fitted-HAD for bimetallic nanocluster $[\text{Ag}_{24}\text{Pt}(\text{SR})_{18}]^{2-}$ (left panel), the geometry of it (right panel).

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Dye-encapsulated zeolitic imidazolate framework (ZIF-71) for fluorochromic sensing, insights from Molecular Dynamics and TDDFT

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Fluorochromic materials provide a photoluminescent response to an external physical or chemical stimuli, among them, Luminescent metal–organic frameworks (LMOFs) are an emerging class of these materials with high versatility and functionality [1]. In particular, Guest@MOF systems are considered as promising candidates for multimodal and ultrasensitive sensing of pressure [2,3]. Recently, LMOFs based on Rhodamine B (RhB) and Tetraphenylethylene (TPE) incorporated in the zeolitic imidazolate framework (ZIF-71) were shown to exhibit ultra-sensitive sensing properties. In the case of mechanochromism, RhB@ZIF-71 and TPE@ZIF-71 displayed a linear relationship between the emission peak wavelength, and the applied pressure as well as emission intensity in the case of TPE@ZIF-71. However, the driving mechanisms of the fluorochromic sensing properties of Guest@MOF systems are not understood, and the theoretical background is lacking due to the complex environment of the Guest@MOF. Indeed, this environment is challenging for the available theoretical methods. In this study, we propose a computational approach relying on both Quantum calculations and classical molecular dynamics by developing an ad hoc force field [4]. This latter is derived from quantum calculations for the ground and excited states in the aim of addressing the effect of nanoconfinement on the optical properties of the guest fluorophore, as well as providing a theoretical understanding of the experimentally observed linear relationship between the emission spectra and the external mechanical stimuli.

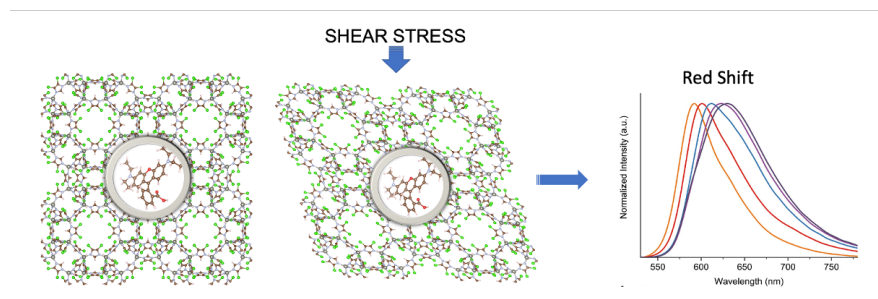


Figure 1 Schematic representation of the Mechanofluorochromic effect exhibited by RhB@ZIF-71, under shear stress the caging effect increases and the emission peak of the compound display a redshift in linear relationship with the applied stress

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The real-time interplay between the ultrafast charge dynamics and nuclear vibrations in dyes for solar cell technologies

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Dye-sensitized solar cells (DSSCs) have gained significant attention in recent years as a promising alternative to traditional silicon-based solar cells. Ruthenium-based dyes have emerged as highly efficient light-absorbers (even in the near-infrared spectral region) indeed, relying on metal-to-ligand charge-transfer (MLCT) excitations, very efficient for the electron injection into the semiconductors in the DSSCs. One of the most efficient dyes for DSSCs is the $[\text{Ru}(\text{NCS})_2(\text{dcbpy})_2]^{4+}$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine), also known as N3^{4+} and its variants have been already largely studied and employed in the DSSC devices [1,2]. N3^{4+} undergoes complex charge transfer (CT) which can be dictated by structural rearrangement and solvent environment [3,4,5], although a complete comprehension on the molecular scale of such ultrafast phenomena is still missing. Ultrafast excited state dynamics of N3^{4+} has been theoretical investigated through Real Time-Time Dependent DFT (RT-TDDFT) simulations [5,6], finding compelling evidence of ultrafast (< 30 fs) inter-ligand electron-transfer (ILET) mechanisms of N3^{4+} that can be activated through visible-range radiation and with no requirement of vibrational motions. On another hand, a full analysis of the electronic manifold coupled with nuclear vibrations can be useful to understand the competitive non-radiative pathways and the resulting overall absorbing dye performances in the light harvesting process (electron injection).

In this contribution [7] we analyze several nuclear motions, infrared active, that can generate modifications of the electronic energy separation and of the electronic distribution, such as the stretching modes of NCS^- ligands along the Ru-N bond. The vertical excitation energies of several electronic transitions of N3^{4+} from the ground state to higher states under different vibrational displacements to understand how the dense electronic manifold are investigated and is also studied how they can change the energetic order of MLCT states and their interplay with other adjacent electronic states. To unveil the ultrafast CT dynamics and the mutual influence of such nuclear motions we collected several RT-TDDFT [8,9,10] electronic dynamics on displaced geometries along such infrared relevant modes and we used natural transition and molecular orbital representations to better interpret our data.

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TRANSIENT INTERMEDIATES IN A BACTERIOPHYTOCHROME PHOTOCYCLE REVEALED BY MULTISCALE SIMULATIONS

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Phytochromes are photoreceptors responsible for sensing red and far-red light in plants, fungi, and bacteria[1,2]. They can switch between the resting state (Pr) and the biologically active state (Pfr), which differ in both chromophore stereochemistry and protein structure (Figure 1). Their photoactivation is initiated by the photoisomerization of an embedded chromophore, which triggers large conformational changes in the entire protein[3]. Despite decades of studies[4-7], a comprehensive understanding of the photoactivation mechanism of phytochromes is still far from being achieved.

In previous computational work[7], we obtained atomistic details on the photoactivation mechanism of *Deinococcus radiodurans* bacteriophytochrome through an integrated multiscale approach of nonadiabatic and adiabatic molecular dynamics and IR spectroscopy simulation. In particular, we showed the ps-timescale mechanism of chromophore photoisomerization and how a histidine residue can control the kinetics of the process. The initial photoproduct evolves rapidly into an early intermediate (early Lumi-R) that relaxes on the ns-to- μ s scale to a late intermediate (late Lumi-R), characterized by a more disordered binding pocket (Figure 1).

The transition to the Meta-R intermediate occurs on a timescale of tens of microseconds[5,6]. Therefore, we relied on enhanced-sampling methods to investigate such a mechanism and the role of the environment. Our simulations show how the stability of our putative Meta-R is strongly influenced by the interactions between the chromophore and the nearby residues.

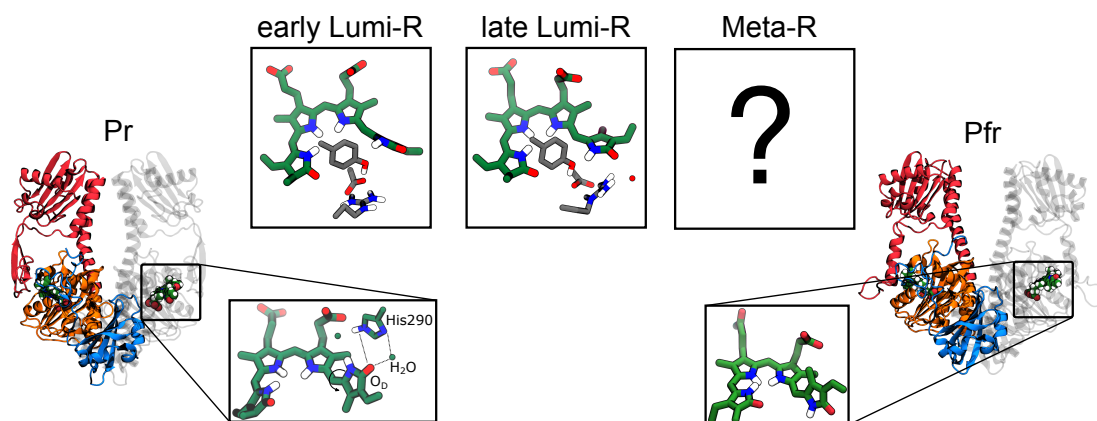


Figure 1 Representation of the Pr and Pfr photoproducts, with a zoom on the chromophore. The structures of the chromophore and the nearby residues for the early and late Lumi-R intermediates are reported (top panels).

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Mechanistic study of redox mediators in Li-O₂ batteries

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The research on lithium-oxygen batteries (LOBs) is an active field in the quest for next-generation batteries with larger energy density [1]. The addition of redox mediators (RMs) is seen as the most promising strategy in order to contrast the two main problems which still hinder LOBs in performance and durability [2]: the high degree of parasitic reactivity and the large charging overpotentials, which are strongly interrelated by the formation of reactive, excited-state singlet oxygen [3, 4].

We studied the oxidation process of lithium peroxide discharge products by different redox mediators through computational modeling, then combined the results with in-operando and post-mortem experimental analysis to understand how the choice of the mediator redox couple and of the solvent does impact on the thermodynamic reaction pathways and the release of singlet oxygen.

A simplified cluster model was used to estimate reaction energies of discharge products with different oxidation states of the RMs at a double-hybrid DFT level, evaluating the effect of solvent's polarity by means of implicit solvation. Also, we performed relativistic spin-orbit DFT calculations in order to investigate the effect of spin-orbit coupling, as induced by the heavy nuclei of iodine- and bromine-based RMs, in promoting spin transitions from singlet electronic states to the triplet ground-state, which is of paramount importance to mitigate the impact of singlet oxygen release on the cell chemistry.

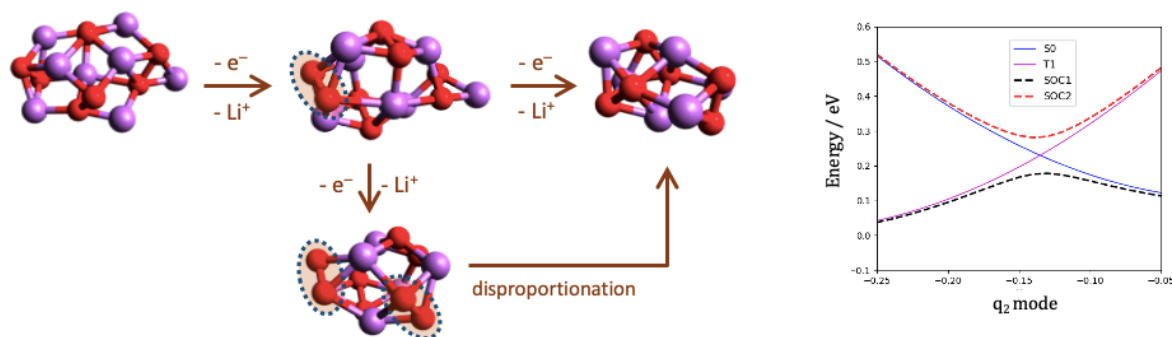


Figure 1. On the left, a scheme of the oxidation routes of Li₂O₂ clusters. On the right, the avoided crossing arising from SOC of singlet and triplet states during the electron transfer.

The results, combined with experimental data from EPR and IR spectroscopy and SEM microscopy, allow to better understand the reactive mechanisms of RMs from an electronic structure point-of-view, helping to improve the screening of optimal electrolyte/redox mediator combinations for future LOBs.

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Guiding competitive binding assays using protein-protein interaction prediction: the affitin-Her2 use case

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The human epidermal growth factor receptor 2 (Her2), overexpressed in several forms of tumoral pathologies, is a well-established molecular target both for diagnostic and therapeutic purposes. Monoclonal antibodies (Abs) such as Trastuzumab and Pertuzumab have now been used for more than a decade for cancer treatment. In the last years, small-sized, synthetic proteins have been explored to overcome Abs drawbacks [1]. In this perspective, affitins, which are 7kDa proteins engineered from the wild-type protein Sac7d [2], have been considered too.

In the present work, the stability of two engineered affitins as a function of the 14 mutations introduced in the sequence was studied by Molecular Dynamics (MD) simulations. MD showed that Sac7d fold is mostly conserved, and it is not significantly affected by the sequence. The second step consisted in the individuation of the more likely areas of Her2 involved in the binding of the two considered affitins (Figure 1). Docking calculations were thus performed with ClusPro web server [3]. As previously carried out competitive binding assays showed that both affitins do not compete with Trastuzumab and Pertuzumab, Her2 residues involved in the interaction with the two Abs were masked during the docking process. Moreover, the mutated residues of the affitins were selected as the ones responsible for the recognition of Her2. The analysis of the docking models obtained was addressed with different approaches. MD simulations were performed, followed by the calculation of the DockQ parameter [4], which describes the overall stability, and thus quality, of the models. The latter were also compared with the regions more prone to bind a partner, as predicted by Matrix of Local Coupling Energies (MLCE) method [5].

The approach employed led to the identification of Her2 binding sites that have a higher likelihood of binding to affitins compared to others. Interestingly, these identified regions overlap with experimentally known binding regions of Her2 with other protein partners. Using this information, competitive binding assays could be conducted between the affitins and these established partners of the target Her2. Consequently, the results obtained by the modeling process could serve as a valuable guide for the upcoming experimental tests, that are yet to be performed.

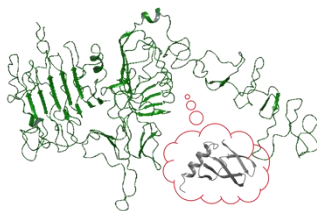


Figure 1- The two proteins involved in the present study: Her2 (in green) and an affitin (in gray).

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Aluminosilicate Glasses: Thermal and Mechanical Properties Simulations

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The computational simulation has been a great tool in the last decades to improve the efficiency of R&D in glass industry: many sources and wastes have been saved thanks to the development of accurate empirical force fields [1] and to the massive study of glass' properties.

According to the milestones that industry has nowadays to satisfy all its purchasers' requests, this case of study is focused on obtaining specific performances and values of thermal and mechanical properties.

To study those features, we have decided to consider aluminosilicate crystals of sodium and calcium that belong to the series of plagioclase feldspars: albite and anorthite.

From the crystals we have also investigated the glasses with the same compositions, considering different sizes of the simulation box and the quenching rate. To study the effect of the modifier on the properties, both thermal and mechanical, another feature which has been considered is the composition of the glasses. For this reason, we have decided to also simulate four intermediate compositions from the albite-like to the anorthite-like ones. [2] This choice was also due to the relevant role that such glasses has for their engineering properties: they withstand very high temperatures, and they are used as advanced materials for aircrafts, constructions, electronic packaging, and many others.

Starting from the linear thermal expansion coefficient (LCTE) simulations, we have simulated and analysed also Elastic Moduli (such as Young Modulus and Bulk Modulus) [2] and the indentation mechanism. As long as it concerns indentation, we decided to study albite-like glass and its counterpart obtained by the substitution of all the alumina with silica; we have also decided to anneal those glasses at different pressures, in order to simulate as much as possible the experiments.

All the simulations have been performed with a molecular dynamics approach: we have performed all our calculations with LAMMPS and DL_Poly codes and using BMP potential (2020) [3] to describe the interactions between atoms. The analysis of Elastic Moduli [4] and LCTE has followed a still tried and tested approach, even if we have introduced and new empirical parameter to study the correlation between the properties of interest and the fraction of modifier oxides. On the other hand, the analysis of the indentation simulations has given very interesting results and was performed studying the changes in various shells surrounding the indenter's tip and the changes between bulk and surface, with self-made programmes.

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An activatable photosensitizer for Photodynamic Therapy: mechanism of NO photo-release and free radical generation

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Photodynamic Therapy (PDT) is a non-invasive methodology for cancer treatment: the selectivity and the safety are increased, respect classic chemotherapy, because the operator in principle can choose when and where activate the photosensitizer drug (PS). The methodology is based on photo-catalytically conversion of $^3\text{O}_2$, normally present in biological tissues, in Reactive Oxygen Species (ROS) (type I) and $^1\text{O}_2$ (type II), that are cytotoxic. This strategy is strongly dependent on the presence of $^3\text{O}_2$ in the tissues, but cancer cells are often in hypoxic conditions. This problem can be overcome by the type I reaction that involves the production of toxic free radical not only of the oxygen, but also of other elements like nitrogen or hydrogen. A lot of studies show, for instance, how the NO radical plays a key role in normal physiological processes, but in cancer biology too [1,2]. Sun J. and coworker have recently synthesized a dual action organic PS, called DANO [3]. In presence of Glutathione (GSH), DANO can photo-release NO• converting itself to DAPS that can act as PS for type II reaction, generating $^1\text{O}_2$, and react with GSH to produce H•, which is extremely rare in PDT. The H• produced can trigger a cascade reaction with oxygen that first generate $\text{HO}_2\bullet$, secondly $\text{O}_2^{\bullet-}$ that can react with NO• photo-released from DANO to produce ONOO^- (Fig. 1). All these species can destroy the diseased tissue and improve the efficiency of PDT.

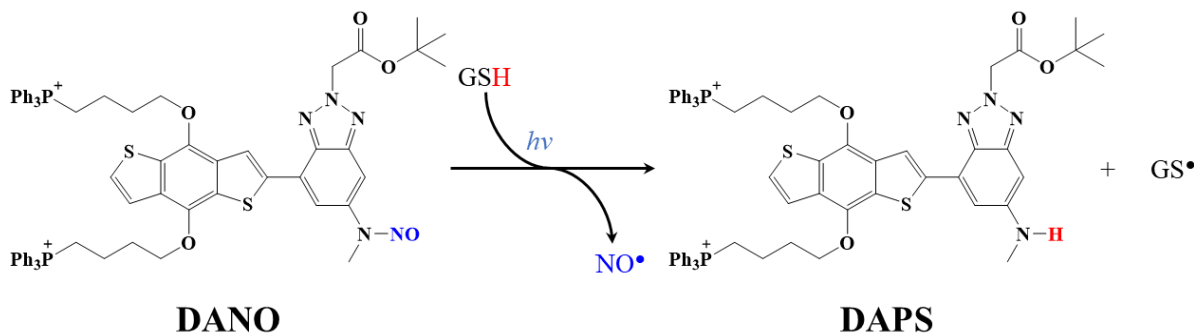


Figure 1 Mechanism of action of DANO

A combined DFT and TD-DFT study has been undertaken to clarify the whole NO release mechanism mediated by light in presence of GSH. For this purpose, the photophysical properties of both DANO and DAPS have been elucidated and all the excited states potentially involved in the photodissociation have been characterized to shed light on the whole mechanism of action.

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An *in silico* platform for evaluating the potential pathogenic impact of *hRPE65* missense mutations

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The human retinal pigment epithelium-specific 65-kDa protein (*hRPE65*) plays a key role within the retinoid visual cycle and many different mutations affecting either its enzymatic function or its expression level are associated with inherited retinal diseases such as Retinitis Pigmentosa and Leber Congenital Amaurosis, characterized by a progressive degeneration of retinal photoreceptors and a very severe visual loss. Voretigene neparvovec (LuxturnaTM) is the first gene therapy approved for the treatment of retinal degeneration [1], but confirmation of pathogenic *hRPE65* mutations is essential for identifying patients for whom treatment with LuxturnaTM may be advantageous. Unfortunately, many known *hRPE65* missense mutations, reported in public databases, either lack of a clear pathogenicity classification or are labelled as variants of uncertain significance (VUS). For this reason, the development of new approaches able to decipher the potential pathogenicity of specific *hRPE65* VUS presented by patients may support the evaluation of their eligibility for gene therapy. In this context, we developed a multi-level *in silico* protocol combining: a) thorough structure-based analyses of *hRPE65* VUS, relying on μ s-long molecular dynamics (MD) simulations, to identify the impact of missense mutations on local folding and conformation stability of specific regions of the protein (Figure 1) [2], and b) a *hRPE65*-tailored consensus bioinformatics strategy named ConPath, obtained combining 19 different predictive tools that showed high performance in discriminating between known pathogenic and benign *hRPE65* missense mutations [3]. Our protocol allowed to classify 13 different *hRPE65* VUS into four groups based on their probability of potential pathogenic effect. Moreover, our ConPath approach can be extended to all other *hRPE65* missense VUS helping clinicians assess the eligibility for gene therapy of patients presenting such *hRPE65* variants.

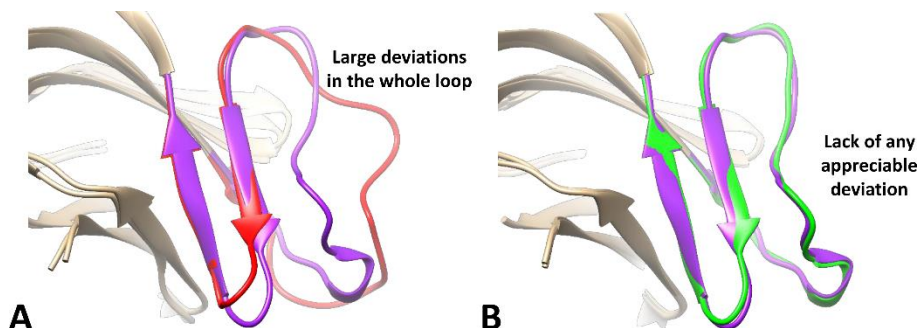


Figure 1 Results of the 5 μ s-long MD simulation analysis performed on the two missense variants A393E (A) and N302I (B) of *hRPE65* predicted to have a deleterious and neutral effect, respectively, on the local folding and conformation stability of the dimerization domain of the enzyme.

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The FMO-GRID based scoring functions to predict the binding energy of ligand-receptor complexes containing metals.

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Polarization, electrostatic and charge-transfer interactions are broadly present in ligand-receptor complexes (LR) containing metals and only quantum mechanics (QM) methods can describe with enough accuracy their contribution to the binding energy. Human Carbonic Anhydrase (hCA) is an important druggable enzyme containing a Zn(II) ion in the active site. In this work, we selected the PDB structures of LR complexes between a set of correlated ligands and hCA II as case study to develop a new scoring function (SC) based on the *ab initio* fragment molecular orbital (FMO) method [1] and on the GRID approach [2] to predict the binding energy of LR complexes involving metals. To build the SC, the following energy values were considered: the fragment efficiency, FE, computed as ratio between ligand pair interaction energies (PIEs) and the heavy atoms [3]; the FMO ligand efficiency, FLE, computed as the ratio of the binding energy computed with FMO method and the heavy atoms [3]; the number of rotational bonds as an evaluation of ligand entropy (n_rot); the -TΔS term computed at the tight binding DFT level of theory; the ligand hydrophobic interaction energy (HIE) [4] computed with GRID method and logP of ligands. We obtained two highly accurate FMO/GRID based SCs. One, based on multi-linear correlation method, combines FE, n_rot, the ligand HIE and logP showing a high correlation with experimental binding energies, $R^2=0.978$ (Figure 1A). We also investigated eventually non linear dependencies between the above mentioned energy terms by using a machine learning (ML) approach (formula generator) [5]. With this method we find a new SC characterized by a high correlation with experimental data, $R^2=0.991$, considering -TΔS, F2LE, HIE and logP as variables (Figure 1B). This procedure represents a fast and efficient QM based computational approach that might contribute to improve the design of new and more effective hCA binders.

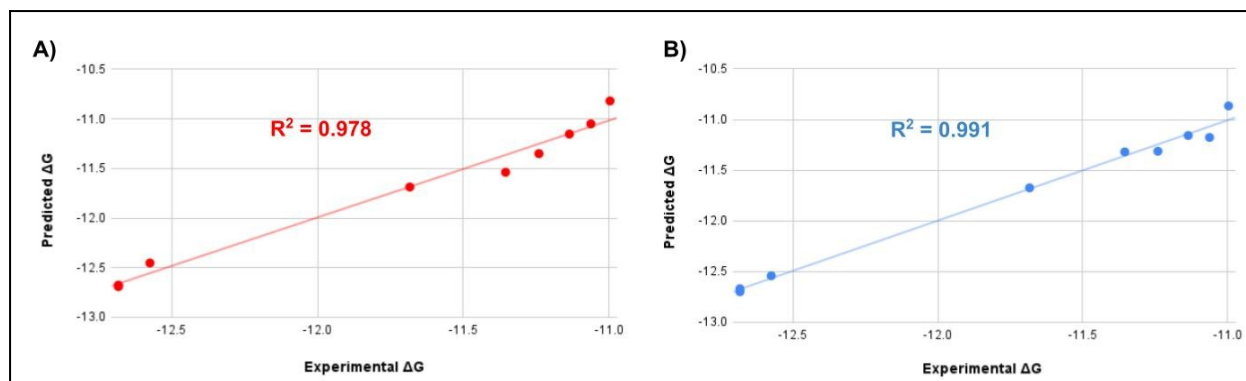


Figure 1 Scatter plots of the experimental binding energies and of the predicted binding energy values computed with SCs obtained by means of the multi-linear regression (A) and ML approach (B)

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Flash Communications

- F1. Patrizia Mazzeo (Università di Pisa)
A Fast Method for Polarizable QM/MM Excited-State Dynamics in Complex Systems
- F2. Gabriele Iuzzolino (Scuola Superiore Meridionale)
Photophysics of a Nucleic Acid-Protein Photo-Crosslinking Model System in Methanol Solution through AIMD simulation
- F3. Alessio Bartocci (Università di Trento)
A multiscale approach to decipher allosteric cannabinoid binding at the glycine receptor α_1
- F4. Michele Casoria (Università degli Studi di Firenze)
Structural properties of N-glycosylated Protein
- F5. Gioacchino Schifino (Università di Catanzaro)
Chiral self-organization of meso-tetrakis(4-sulfonatophenyl)porphyrin assisted by molecular rotations
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Theoretical investigation on S(1D) insertion reactions leading to the formation of S-bearing species in space
- F7. Luigi Crisci (Scuola Normale Superiore)
Toward a black-box computation of accurate rate constants for barrier-less processes: new hints for a challenging problem
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Electronic Current Densities and Origin-Independent Property Densities Induced by Optical Fields

A Fast Method for Polarizable QM/MM Excited-State Dynamics in Complex Systems

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Observing a photoinduced mechanism in complex systems is still a challenging goal. To this aim, molecular dynamics has been coupled with hybrid quantum mechanics/molecular mechanics (QM/MM) models to produce simulations on the excited-state potential energy surface [1]. However, the computational cost associated with these methodologies, such as Time-Dependent Density Functional Theory (TD-DFT) or Complete Active Space Self-Consistent Field (CASSCF), remains prohibitively high. Therefore, the study of complex systems is impeded by the challenges of obtaining statistically significant results.

In this contribution, we present the development of a fast strategy to perform QM/MM excited-state simulations, which combines a SCF description of the excited state (Δ SCF) with the AMOEBA forcefield [2,3,4]. The integration of Δ SCF with a polarizable embedding environment is highly intriguing due to the inherent inclusion of state-specific environmental effect on the excited state [3]. Consequently, this methodology proves to be more accurate than conventional TD-DFT methods when describing excited states with a significant charge-transfer (CT) character. Additionally, we enhance this algorithm by incorporating an extrapolation technique for the excited-state density matrix. Extrapolation addresses two crucial challenges associated with these simulations: maintaining the dynamics on the excited state and reducing the high number of SCF iterations necessary for convergence. This straightforward yet effective approach was applied to the investigation of the photoinduced activation of the AppA Blue-Light Using Flavin (BLUF) photoreceptor. We propagated the dynamics on the CT state (see Figure 1) and we successfully observed the expected proton transfers, showing that the Proton-Coupled Electron Transfer (PCET)-based mechanism that characterizes other BLUF proteins [5,6] is valid also for AppA.

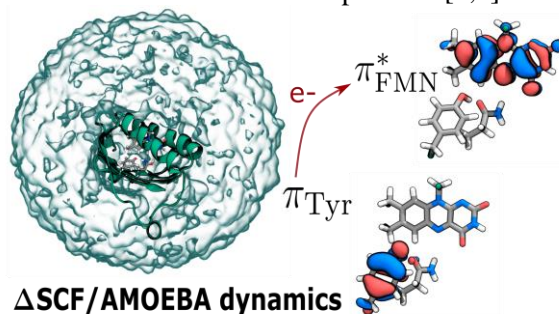


Figure 1 Orbital permutation used to generate the CT determinant for propagating the Δ SCF/AMOEBA dynamics of the AppA photoreceptor.

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Photophysics of a Nucleic Acid-Protein Photo-Crosslinking Model System in Methanol Solution through AIMD simulation.

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A molecular description of the interplay between nucleic acids (NA) and proteins is vital to understand the most basic processes of life, from DNA replication to protein expression and synthesis. Isolation of transient NA-protein complexes in their biological conformation is a challenging task: a promising technique for this goal is to induce *in vivo* NA-protein crosslinking (NPCL) by femtosecond-stimulated UV laser pulses.[1] The photo-addition of phenylalanine to thymine results an exemplificatory reaction of such a class of crosslinking and the photocyclization of 5-benzyluracil (5BU) to 1,2-indaneuracil has been proposed as a model reaction for studying the mechanism of NPCL.[2]

In this context, we present a combined experimental and theoretical study of the ground-state conformational equilibrium and the photophysics of 5BU in methanol,[3] exploiting the framework of the DFT and TD-DFT.[4] We adopted the ADMP[5] method and an hybrid QM/MM ONIOM[6] partition scheme enforcing non-periodic boundary conditions[7]. We recorded the UV absorption spectrum in methanol solution and simulated the band shape from TD-DFT analysis of the AIMD trajectory, finding a good agreement between experiments and simulation. Although previous studies exist based on static-minimum energy structures approaches,[8] we provided unprecedented results and a full characterization of the 5BU absorption spectrum. The first two excited states are indeed the ones responsible for the absorption preceding the photoreaction; we unveil that the brightness of such electronic transitions is strongly influenced by the accessible conformations of the 5BU at room temperature and the microsolvation of its oxygen and nitrogen atoms.

These results suggest a dependence of NPCL on the surrounding environment, as well as the importance of AIMD and an accurate treatment of the solvent to simulate and understand the photophysics of this model system.

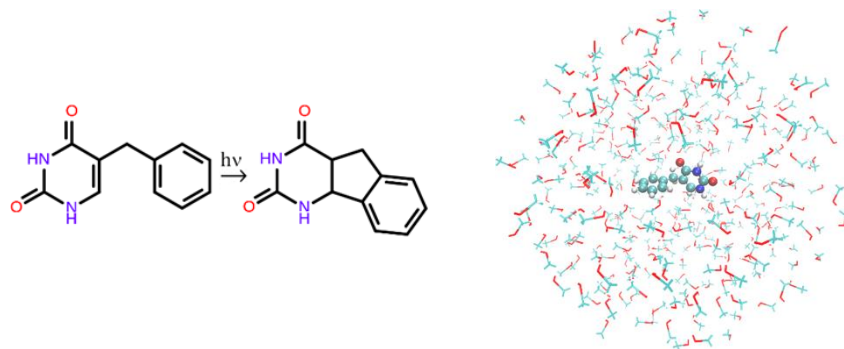


Figure 1 The photocyclization of 5BU (left) and A snapshot from the AIMD of 5BU in methanol (right).

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A multiscale approach to decipher allosteric cannabinoid binding at the glycine receptor α_1

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Pentameric Ligand gated ion channels (pLGICs), as the glycine receptors (GlyRs), can be regulated by small-molecule binding at several allosteric sites [1,2]. Endocannabinoids like tetrahydrocannabinol (THC) and N-arachidonyl-ethanol-amide (AEA) potentiate GlyRs, but their mechanism of action remains unknown. Using millisecond coarse-grained (CG) MD simulations powered by Martini 3 force-field [3,4] it has been possible to characterize their binding site(s) at the Zebrafish GlyR- α_1 with atomic resolution. Based on hundreds of thousand ligand-binding events, cannabinoids are found binding at both intrasubunit and intersubunit sites in the transmembrane domain. For THC in particular, intrasubunit binding is in agreement with recent cryo-EM structures [5], while for AEA binding evidences offer predictions on involved residues to be tested experimentally. The results highlight the complexity of allosteric regulation of synaptic receptors and establish an original simulation protocol for the identification and characterization of allosteric binding sites in the transmembrane region.

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Structural properties of N-glycosylated Protein

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A glycoprotein is a compound containing a carbohydrate covalently linked to a protein; the sugar moiety can be either a monosaccharide or a polysaccharide (glycan). The chemical bond between the sugar and the protein, or glycosidic linkage, is generally of two types: O-glycosidic or N-glycosidic.

The three-dimensional structures of glycoproteins and protein–carbohydrate complexes in the Protein Data Bank (PDB) are a valuable resource for understanding the effects of glycosylation on proteins. Unlucky, the glycan portions of these structures often contain many errors, ranging from minor irregularities to gross errors. PDB-REDO [1] a database of protein structures in which experimental checks have been performed to improve the correctness or accuracy of the deposited structures, can improve, for example, the structure of carbohydrate ring conformations.

Furthermore, the number of computational studies on these systems is quite limited due to the few available Amber-compatible force fields (FFs). [2]

In our group, molecular dynamics simulations on glycoprotein were performed using the open-source software GROMACS; starting from the structure of the protein available in the PDB and the refined one in PDB-REDO. The compound was glycosylated using the doGlycans program [3] which allows the insertion of sugars into the peptide chain and the preparation of inputs for the associated molecular dynamics simulations. However, this program does not match the original experimentally based positions of the sugar moieties.

In this scenario, we planned to develop a user-friendly tool that allows to use the experimental structure for the glycosylation-step in the GROMACS simulation, providing structures in agreement with those present in PDB-Redo database. In addition, we analyze and clusterize the conformations of the glycosyl moiety in the PDB database and use the most common conformers as a starting point for improving the FFs.

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Chiral self-organization of meso-tetrakis(4-sulfonatophenyl)porphyrin assisted by molecular rotations

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In recent years, self-assembly strategies are attracting a considerable interest for the development and design of advanced chiral materials from molecular to supramolecular level. In this background, the spontaneous self-organization of achiral π -conjugated molecules has gained significant attention due to their versatile optical and electronic properties. In this context, meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) have shown a great ability to self-assemble into chiral supramolecular structures. For this reason, understanding the fundamental principles behind the generation of chirality is noteworthy to rationalize the fabrication and control of the chiral assembly-mechanism of TPPS₄ aggregates. Indeed, axial chirality due to the side chain rotations of the sulfonato-phenyl groups, may propagate chiral information through specific interactions along the whole supramolecular structure during the non-covalent self-assembly interactions. Motivated by the interest in designing new chiral material and to elucidate the propagation of the chirality transfer mechanism starting from the atropoisomers of TPPS₄ monomers, enhanced sampling simulations have been performed on TPPS₄ in its monomeric, dimeric, trimeric and tetrameric aggregate forms. Specifically, the free-energy profiles as a function of the pyrrole improper torsions of the porphyrin ring have been reconstructed for all the TPPS₄ aggregates allowing us to evaluate how the symmetry or the asymmetry of TPPS₄ supramolecular system can be selectively affected by increasing the aggregate dimension.

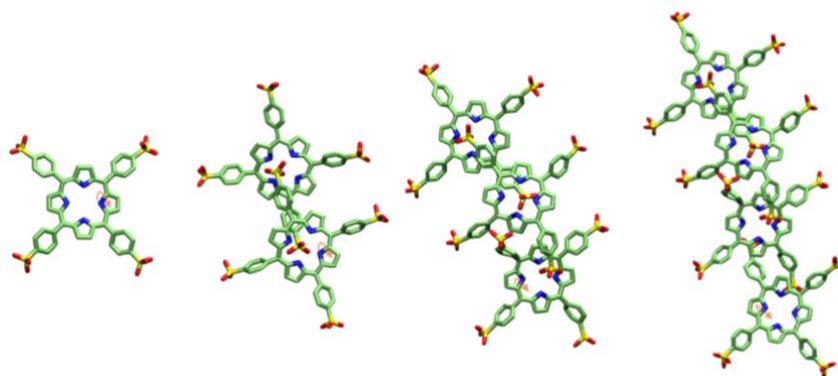


Figure 1: The monomer, dimer, trimer and tetramer of the TPPS₄ system conformations disclosed from enhanced sampling simulations.

Theoretical investigation on S(¹D) insertion reactions leading to the formation of S-bearing species in space

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The chemistry leading to interstellar sulphur-bearing organic molecules is still in need to be fully characterized. Simple S-containing species, such as OCS, CS, CH₃SH, H₂CS, have been detected in a variety of objects [1]. More complex species have been detected in the coma of the comet 67P/Churyumov-Gerasimenko [2], such as CH₄OS, C₂H₆OS, C₃H₆OS and CH₄S₂.

In this contribution we present a theoretical investigation of two reactions involving S(¹D), with two molecules, water and methanol, which are abundant in interstellar/cometary ice. S(¹D), which is metastable with a long radiative lifetime, can be produced on the ice surface by UV-induced photodissociation of precursor molecules, such as OCS, for which a secure identification in interstellar ice has been provided [3]. The reactive potential energy surfaces (PES) of the two reactions have been characterized by electronic structure calculations. All stationary points of the PES were optimized at DFT level of theory. Frequencies analysis were carried out in order to determine the nature of the stationary points. When a transition state was found, an intrinsic reaction coordinate (IRC) calculation was executed. Subsequently, single point calculations at the CCSD(T) method [4] were performed in order to refine the energy of each stationary point. Statistical RRKM calculations of the product branching fractions were also conducted in the presence of more than one open reaction channel.

The role of electronically excited metastable atoms in the ice chemistry has been recently considered in the research groups of Oberg and Herbst [5,6] for the similar case of atomic oxygen. According to those studies, the formation of O(¹D) opens up new reaction pathways which are not amenable in the case of the O(³P) reactions. Previous work from our laboratory has focused on the reactions of S(¹D) atoms with saturated and unsaturated hydrocarbons [7] confirming that S(¹D) can lead to the formation of molecules holding a novel C-S bond. In this work we have shown that species like CH₂OHSH (mercaptomethanol) are efficiently formed.

This project has received funding from the Italian MUR (PRIN 2020 “Astrochemistry beyond the second period elements”, Prot. 2020AFB3FX) and the Italian Space Agency (Life in Space project ASI N. 2019-3-U.0).

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Toward a black-box computation of accurate rate constants for barrier-less processes: new hints for a challenging problem

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The accurate characterization of barrierless reactions is crucial for gaining further insights into an array of chemical phenomena in several research areas. In this work, we present an innovative methodology that improves two cornerstone theoretical kinetics statistical approaches—variable reaction coordinate transition state theory (VRC-TST) [1] and variational transition state theory (VTST)—offering a powerful platform placed at the frontier of the most refined theoretical investigations of barrierless reactions. Our VRC-TST enhancement seamlessly integrates density functional theory (DFT) with Monte Carlo (MC) sampling, resulting in a synergistic combination that optimizes reactive fluxes with computational efficiency, flexibility, and stability. We employ a black-box strategy to identify the optimal exchange-correlation functional with respect to a reference high-level potential, effectively addressing the active-space inconsistency issue commonly encountered during reduced-active-space MC sampling. The microcanonical VTST approach is enhanced by combining the hindered rotor and harmonic oscillator models to account for the translational degrees of freedom accurately. This is achieved by applying the appropriate description based on the respective frequency values along the reaction pathway. The effective implementation of these novel approaches significantly bolsters the predictive capabilities of our method. The performance of the strategy has been assessed by two prototypical reactions, exhibiting different multireference character along the barrierless step: $\text{H}_2\text{S} + \text{Cl}$ hydrogen abstraction and $\text{CH}_3 + \text{CH}_3$ association. The former reaction plays a significant role in atmospheric chemistry due to its relationship with acid rains, visibility reduction and climate change, [2] while the latter reaction is essential in combustion chemistry and as a termination reaction. The remarkable agreement between our predictions and the available experimental data underscores the reliability and versatility of our methodology, showcasing its potential as a powerful investigative tool for a wide range of barrierless reactions. However, the obtained results, reveal the extent at which the theoretical kinetic rates obtained in the framework of the VTST are sensitive to the proper description of large amplitude motions. Our method is rooted into recent advances, developments, and trends in theoretical and computational chemistry exploiting their full potential in barrierless reaction characterization. In particular, the improvement of the available TST procedures and the implementation of the whole strategy in a black-box user-friendly platform paves the way toward systematic investigations of gas-phase reaction mechanisms involving barrierless entrance channels, which play a key role in widely different areas ranging from astrochemistry to atmospheric chemistry and combustion.

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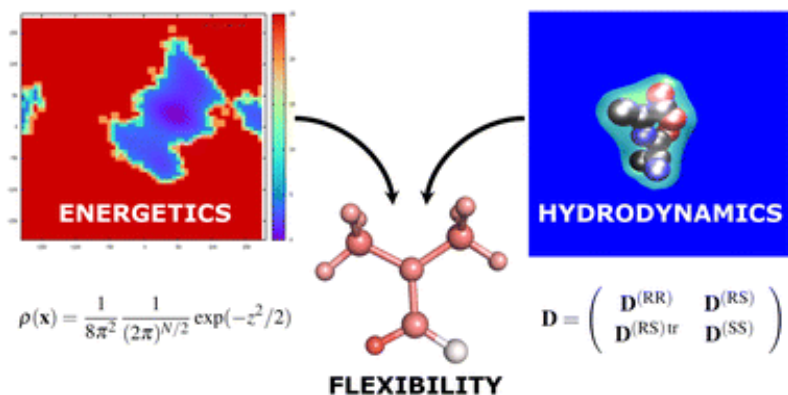
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The roto-conformational diffusion tensor as a tool to interpret molecular flexibility

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Stochastic modeling approaches can be used to rationalize complex molecular dynamical behaviours in solution, helping to interpret the coupling mechanisms among internal and external degrees of freedom, providing insight into reaction mechanisms and extracting structural and dynamical data from spectroscopic observables. However, the definition of comprehensive models is usually limited by (i) the difficulty in defining – without resorting to phenomenological assumptions – a representative reduced ensemble of molecular coordinates able to capture essential dynamical properties and (ii) the complexity of numerical or approximate treatments of the resulting equations. In this contribution, we address the first of these two issues. Building on a previously defined systematic approach to construct rigorous stochastic models of flexible molecules in solutions from basic principles, we define a manageable diffusive framework leading to a Smoluchowski equation determined by one main tensorial parameter, namely the scaled roto-conformational diffusion tensor, which accounts for the influence of both conservative and dissipative forces and describes the molecular mobility via a precise definition of internal–external and internal–internal couplings. We then show the usefulness of the roto-conformational scaled diffusion tensor as an efficient gauge of molecular flexibility through the analysis of a set of molecular systems of increasing complexity ranging from dimethylformamide to a protein domain.



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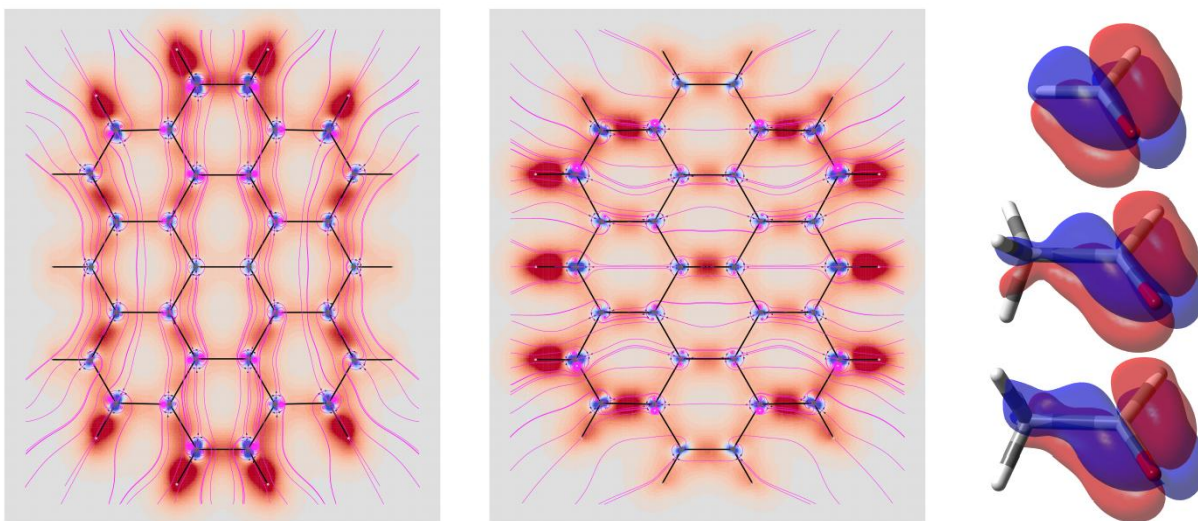
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Electronic Current Densities and Origin-Independent Property Densities Induced by Optical Fields

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The interaction of a molecule with optical fields is customarily interpreted by means of induced time-dependent electric polarizabilities, magnetizabilities and mixed electric-magnetic polarizabilities. In general, these properties can be rationalized by integrals of density functions formulated in terms of induced charge and current densities. Here, we focus on what has been done so far at theoretical level, and on what can be expected to be unveiled from the topological study of suitable density functions, endowed with the fundamental requirement of origin invariance. Densities characterized by such a property can be integrated all over the configuration space to obtain electric dipole polarizability and optical rotatory power. Corresponding maps visualize domains mainly involved in the molecular response. The diagonal components of origin-independent density tensor functions have been computed, confirming the ubiquitous presence of counter-polarization regions in the proximity of the atomic nuclei. They are associated with toroidal electron currents, induced by time derivative of the electric field of impinging radiation. Electron (de)localization in these systems is readily observed and estimated. The optical rotation density of the carbonyl chromophore is studied in detail. Its essential feature is the separation in quadrants of alternating sign of the density about the CO bond. The presence of an extrachromophoric perturbation determines asymmetry in the extension of the quadrant distribution, thus causing optical rotation.



Left and center: in-plane components of electric dipole polarizability density for ovalene over the molecular plane; trajectories of the current density induced by the time derivative of the electric field are superimposed. On the right: specific rotation power density: top formaldehyde; middle acetaldehyde with achiral conformation; bottom acetaldehyde with chiral conformation. Iso-surfaces are $\pm 100 \text{ deg}[\text{dm g}/\text{cm}^3]^{-1} \text{a}_0^{-3}$ Red/blue positive/negative vales.

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Posters

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- PS2. Lorenzo Baldinelli (Università degli Studi di Perugia)
Computational Modelling of the Electrocatalytic Oxygen Evolution Reaction on Coordination Polymers
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The photochemical mechanism of the activation of Orange Carotenoid Protein

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Orange Carotenoid Protein (OCP) [1] is a photo-responsive protein found in cyanobacteria, responsible for their photoprotection. OCP activates in response to light absorption, going from the dark-adapted form (OCP⁰) to the light-adapted one (OCP^R). Once in the active conformation, OCP is able to bind the phycobilisome (PBS), the light-harvesting apparatus of cyanobacteria, and quench the excess of energy in a process known as non-photochemical quenching (NPQ).

The series of conformational changes of OCP in its activation cycle is triggered by the light-absorption and consequent excited state evolution of the chromophore bound to OCP, a ketocarotenoid named canthaxanthin (CAN). The photochemistry following the initial excitation of the carotenoid is still unclear, and there is debate on how light absorption can trigger the conformational changes of OCP. In particular, there is no clear evidence of the molecular mechanism constituting the very first step of this process [2].

In this work, QM/MM nonadiabatic dynamics were employed to simulate the excited state decay of CAN bound to OCP [3]. We found that the $S_1 \rightarrow S_0$ conversion is characterized by multiple timescales, related to the ground-state conformational heterogeneity of the ketocarotenoid, particularly regarding the puckering conformation of the β_1 ring [4]. Our simulations also revealed a hula-twist isomerization observed in a small portion of the trajectories, which could be the atomistic mechanism of the initial trigger to the photoactivation of OCP.

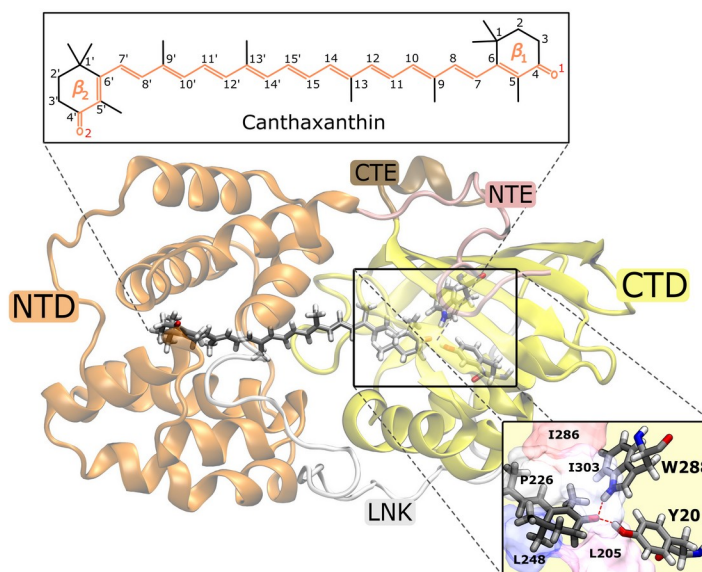


Figure 1 Representation of CAN and OCP⁰ structures.

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Computational Modelling of the Electrocatalytic Oxygen Evolution Reaction on Coordination Polymers

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One of the main pathways to produce molecular hydrogen is electrochemical water splitting.[1] To increase the efficiency of this process, the overpotential for the oxygen evolution reaction must be minimized. This can be achieved through the use of electrocatalysts.[2] Among the numerous families of catalysts studied and optimized over the years with this purpose, coordination polymers (CPs) recently gained great attention.[3] In this work, we initially defined an accurate computational protocol for the study of electrocatalytic processes on one-dimensional CPs containing first-row transition metals (Mn, Ni, Co, Fe). The protocol was experimentally validated and then used to shed light on the role of cooperativity, spin crossover effects, and metal oxidation of these systems towards water oxidation.

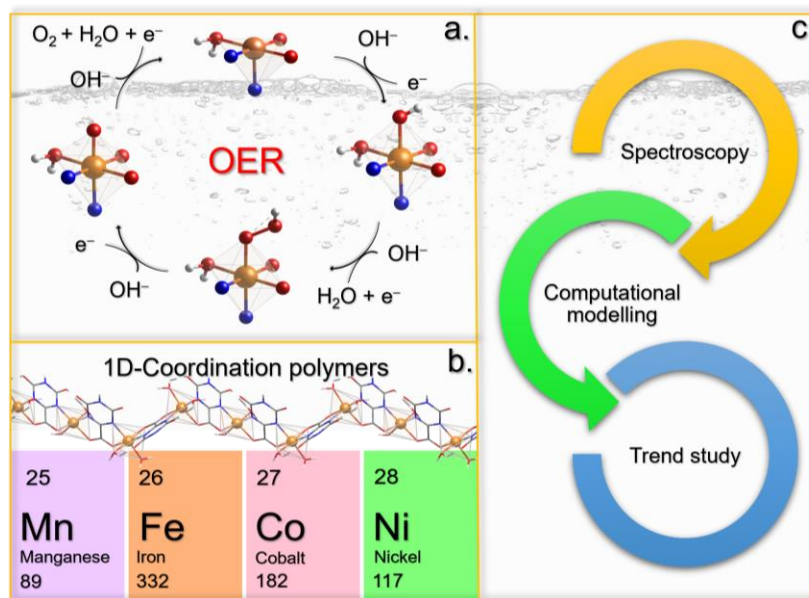


Figure 1: a) Catalytic OER mechanism in alkaline conditions. b) Schematic structure of the 1D-CPs c) Synergistic approach to explore CPs activity towards OER.

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Plasmon assisted electron dynamics in photocatalysis and circular dichroism

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Modelling complex light-driven dynamics occurring in composite systems of chemical interest, such as light-harvesting complexes or metal nanostructures (NSs) interacting with molecules, is a challenging task for theoreticians. An accurate and rigorous theoretical modelling is necessary in order to interpret and analyse the experimental data, and to suggest novel routes. Describing systems with millions of atoms at full quantum (QM) level of theory is impractical or impossible. This is the reason why a multiscale approach, based on the application of less expensive classical methods to study effectively large portions of the overall systems and of more accurate QM approaches for a small subregion, is a proper choice for this kind of systems [1]. We applied the developed methodology to plasmon-assisted photocatalysis and circular dichroism [2,3]. Light exposure at a certain wavelength in metal NSs (antenna) generates a plasmon excitation. The enhanced electromagnetic field in the vicinity of a plasmonic nanoparticle is exploited to trigger for example the generation of hot carriers in a photocatalytic system or to enhance (or quench) the signal from a chiral molecule[7,8]. The nanoparticle antenna is described classically using a time-dependent formulation of the polarisable continuum model [3], while the molecular system is characterised by a QM treatment, such as DFT and TDDFT. We investigated the H₂ generation from formic acid on Au-Pd and Au-Pt heterodimers, inspired by experimental works [4, 5] and studied the ECD spectrum of methyloxirane close to a gold nanosphere. The goal is to achieve a microscopic understanding of the factors affecting the electron dynamics of the rate determining step of the photocatalytic reaction, by looking at the charge generation and injection [6] to the formate moiety adsorbed on Pd or Pt, in presence of Au nanorod and to understand the factors which may enhance or quench the ECD spectrum.

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Computational study on light emission by NanoLuc luciferase

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Luciferases are a class of enzymes that play a crucial role in bioluminescence, a fascinating process by which certain organisms produce light through a chemical reaction. These enzymes have a wide range of applications, including food safety control, environmental monitoring, diagnostics, and drug screening [1]. The key advantage lies in the fact that light emission does not necessitate prior excitation but occurs as a result of the interaction between the reactants. Luciferases facilitate the oxidation of a substrate, converting it into a product in an excited electronic state. Subsequently, the excited state decays, emitting a photon.

One of the most promising systems tested so far is NanoLuc (NLuc), engineered from the active subunit of the *Oplophorus gracilirostris* luciferase [2]. It utilizes furimazine as its substrate and exhibits several advantageous characteristics. These include a bright luminescence, minimal background signal, compact size, and stability across various chemical environments. Although NLuc has demonstrated impressive performance and widespread use, there has been only limited analysis of the specific reaction mechanism and the characteristics of the species involved [3]. Our computational study aims to identify the crucial residues implicated in the catalytic mechanism and gain insights into the behavior of the emissive product. To achieve this goal, we conducted molecular dynamics (MD) simulations of the most relevant docking poses of furimazine with NLuc in aqueous solution. Each trajectory has been then analysed to monitor the changes of ligand's position over time and has served as an input for cluster analysis and the evaluation of secondary structure over time. Based on these initial findings, NLuc-furimamide complexes were constructed, considering various protonation states of furimamide, including neutral, zwitterionic, and anionic forms. To probe the luminescent properties, representative structures from MD clusters have been used as input for QM/MM calculations to simulate the emission wavelength. Current results, although partial, offer a picture in which the substrate in the enolic form makes for a simpler and more straightforward reaction mechanism compared to the previous studies and the zwitterionic form of the product is supposed to be the emitting species.

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Diffusion Coefficient of Lithium in Cathode Materials for Lithium Ion Batteries From DFT, Metadynamics and Post-HF

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In the roadmap towards designing new and improved materials for lithium ion batteries (LIBs), the ability to estimate the diffusion coefficient of Li ions in electrodes is key. Since it is exceptionally difficult to estimate it both computationally and experimentally, we attempted to devise a computational protocol for the determination of the Li-migration energy barrier and diffusion coefficient, focusing on a common cathode material as LiNiO_2 , that can be ported to the study of more complex and less investigated systems.[1]

We tested three different methodologies: i) sampling of the theoretical path defined by hand; ii) *ab initio* molecular dynamics (AIMD) and iii) metadynamics. We also exploited two different programs, namely CRYSTAL [2] for performing path sampling and CP2K [3] for AIMD and metadynamics simulations. From the results of our work, metadynamics emerged to be the most suitable methodology for the designation of Li migration path, which then needs to be sampled to overcome the intrinsic limitations of metadynamics and find more reliable value of the energy barrier.

We intend also to perform sampling of the identified path with post-HF methods as CCSD(T), using CRYSCOR code [4], to benchmark different DFT functionals and individuate the best performing ones for the investigation of the energy barrier of Li intercalation compounds.

Moreover, we proposed a smart and easy way to approximately calculate the effective frequency ν^* , by fitting the minimum correspondent to the initial equilibrium state of the system with a parabola and exploiting the monodimensional harmonic oscillator approximation.

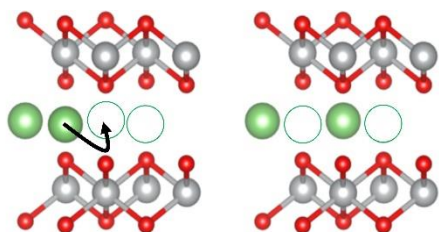


Figure 1: Schematic representation of Li migration path in LiNiO_2 .

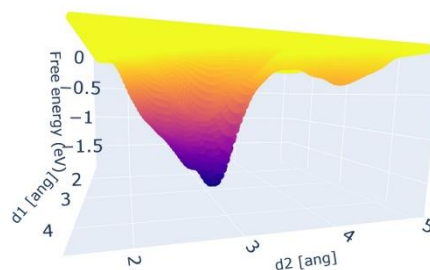


Figure 2: Computed free energy surface of LiNiO_2 .

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Inside the photophysics of a light-driven molecular rotary motor

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The light-driven molecular rotary motors are molecular machines that transform the energy content of the electromagnetic radiation in a unidirectional rotary motion. The interest in molecular machines is due to their potential use in the chemical and biological fields, such as catalysis and development of nanoscale devices [1]. In this work, we focused on a 2nd generation Feringa-type motor: the 9-(2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-fluorene. This molecule contains a double-bond axle that connects two parts, the *stator* and the *rotor*, and performs a full unidirectional rotation (360°) about this latter, in an isomerization cycle characterized by two photochemical and two rate-limiting thermal steps. We carried out a theoretically and computational study of the photoisomerization pathway and related spectroscopies, exploiting the framework of the density functional theory (DFT) and its time-dependent version (TD-DFT) [2,3] combined with ab initio molecular dynamics (AIMD) simulations [4,5,6,7,8]. In order to study the photophysics of the system, we performed ab-initio adiabatic MDs simulations in both the ground and excited electronic states, preceded by an accurate calibration of the potential with a detailed balance of the environment effects obtained by the introduction of the implicit solvent [9,10] to better reproduce the experimental conditions [11]. An accurate vibrational analysis of the Raman spectra of both isomers was performed along with the assignment of the normal modes observed in the experiments. We performed a proper number of electronic excited states MD simulations to provide a molecular interpretation of the photoisomerization pathway. Then, relying on these electronic excited state MD, we monitored some energetic and structural parameters in order to deduce common aspects in the relaxation dynamics. A clear mechanism emerges, based on a bi-phasic decay from the Franck-Condon region right after the excitation and characterized by the sequence of coupled vibrations including or related to the stretching of the carbon-carbon bridge bond. These results allowed us to clearly interpret trends of spectroscopic results experimentally observed.

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Investigation of the key role of DMF solvent in PVDF-based electrolytes

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The development of high-performance Lithium-ion batteries has long been at the forefront of energy technologies, given the urgent need for large-scale deployment of renewable energy sources, together with the electrification of transportation.

The electrolyte, which is a fundamental component of such electrochemical systems, is often the limiting factor directly affecting the performance and safety of the battery [1,2]. In this context, Poly(vinylidene difluoride)-based electrolytes have attracted huge attention due to their interesting ionic conductive properties and capability to overcome safety issues by replacing flammable organic liquid electrolytes [3]. Despite the interest in these polymer electrolytes, the mechanism of Li-ion diffusion in PVDF-based electrolyte is not well understood. Recent experimental studies [4] have argued that residual DMF solvent, which is used during the electrolytes preparation to dissolve the polymer-salt system, solvates Li⁺ and contributes to the ionic diffusion.

Here we have used Density Functional Theory (DFT) to elucidate the role of DMF in the solvation and diffusion of Li⁺. The interaction of Li⁺ with DMF molecules and PVDF chains has been computed by constructing Li⁺(DMF)_n(PVDF)_m complexes. In addition, molecular dynamics simulation has been performed in order to obtain additional insights on the diffusion of Li⁺(DMF)_n(PVDF)_m complex.

The atomic structures and formation energies of Li⁺(DMF)_n(PVDF)_m complexes, shown in Figure 1, demonstrate that Li⁺ tends to coordinate up to three DMF molecules rather than directly binding PVDF, indicating that the interaction Li⁺-DMF is stronger than the interaction of Li⁺ with PVDF. Increasing the number of ligands, *e.g.* n+m > 4, Li⁺(DMF)_n complex interacts with PVDF as the second solvation shell.

Moreover, our molecular dynamics simulations confirm that the amount of DMF molecules coordinating Li⁺ affects the mobility of Li⁺ through PVDF chains. Our results represent a step forwarding in understanding the diffusion mechanism of Li-ion in PVDF-based electrolytes and can be used for the rational design of novel electrolytes with improved performances.

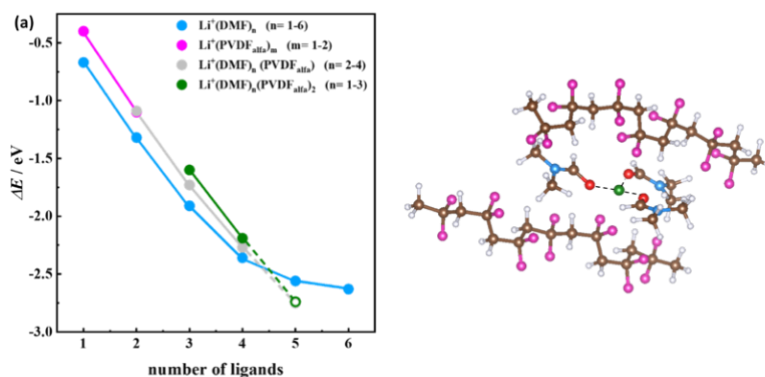


Figure 1. Formation Energy (ΔE) and a representative structure of Li⁺(DMF)_n(PVDF)_m complexes.

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Excited States from Machine Learned Effective Hamiltonians

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Machine Learning is extensively employed to bypass the huge computational cost of quantum mechanical calculations of molecules while retaining their accuracy [1], not only for ground state properties but also for the more challenging excited states [2]. Typically, one or more target properties are modeled directly with learning algorithms. A more recent and interesting approach involves learning the Hamiltonian of a system [3, 4]. This latter approach is particularly appealing, as all the properties of a system can be readily obtained from its Hamiltonian. Here we present a symmetry-adapted Machine Learning model that predicts an effective SCF Fock matrix, the central quantity in both Hartree-Fock and Density Functional Theory. We show that the model extrapolates well beyond the initial training set, and correctly describes different kinds of molecules, such as polyalkenes and aromatic compounds. We further extend the approach by coupling the learned Fock matrices with Grimme's simplified Tamm-Dancoff density functional approach (sTDA) [5], which opens a machine learning route to the system's excited states. We show that this approach provides accurate excited states at a fraction of the cost of a full quantum chemical calculation.

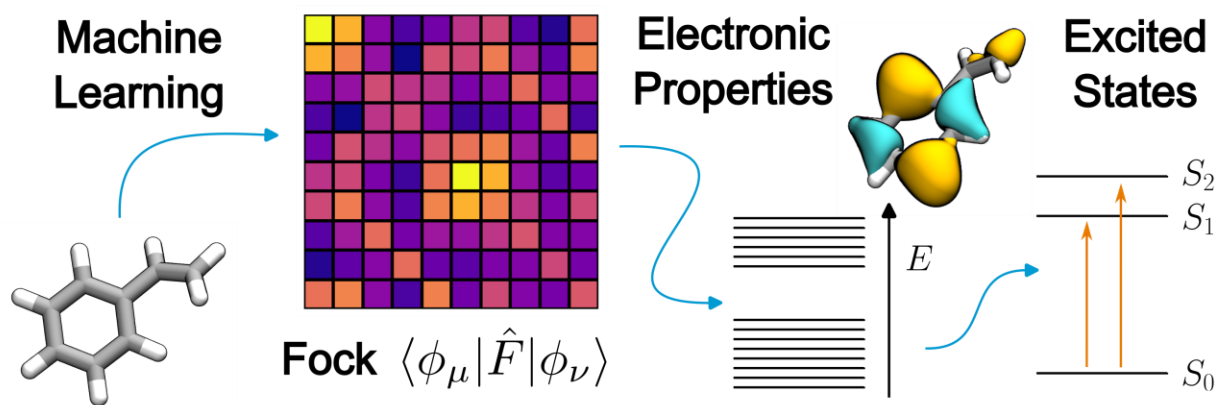


Figure 1 The Machine Learning models yields a Fock matrix from a molecular geometry. This gives direct access to the electronic properties of the system. These properties can be used to compute excited states.

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Calculation of the viscosity of Squalane from atomistic model: comparing accuracy and computational costs using both equilibrium and non equilibrium methods

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New computational power resources lead to the possibility of the calculation of physical properties of materials using detailed atomistic models.

The viscosity is the diffusive coefficients that appears in continuum equation for fluid motions.

Its measurement is difficult in high pressure or high shear rates conditions that are typical of many tribology applications. In this case molecular dynamics may be used to estimate its value [1].

The calculation of viscosity can be performed both using equilibrium methods such as Green-Kubo and non-equilibrium methods such as Sllod [2]. In this work we make a comparison and a review of these two methods performing the calculation of the viscosity of Squalane (C₃₀H₆₂) that is a small polymer molecule [3]. It has been chosen because it has already been extensively characterized, as it allows to obtain reproducible viscosity measurements thanks to its purity [4].

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Vibrational spectra of di-imidazolium ionic liquids: a computational approach.

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In this work we propose a computational study of geminal di-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids (ILs) also known as $[\text{C}_n(\text{mim})_2](\text{TFSI})_2$. We simulated infrared (IR) and Raman spectra of four ILs with n , which represents the length of the alkyl chain, ranging from 1 to 4.

Given the high complexity of these liquids, which primarily lies in the large conformational mobility of the cation [1,2], multiple conformations should be considered in order to simulate a realistic vibrational spectrum.

Using a refined version of CL&P Force field [3,4,5] we performed molecular dynamics (MD) simulations of these ionic liquids in bulk phase with the GROMACS software. For each of the four different ILs we extracted from the MD trajectory the most probable configurations, using the Gibbs’ free energy as a selection criteria.

In particular we considered triplets, each composed by one cation and two anions, which represent the smallest neutral cluster, as starting points for the simulation of vibrational spectra with density-functional-theory (DFT) methods at the B3LYP/6-311G* level of theory.

For all systems, after the simulation of Raman and IR spectra, we assigned the most significant vibrational modes and we compared our results with experimental data obtained in liquid phase by M. Falconieri’s group, exploring the differences between the four different ILs.

Our results are in a reasonable agreement with experimental data, proving the validity of our approach.

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Fine Tuning DFT-D Methods for Large-Scale Systems

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Density functional theory methods with dispersion correction (DFT-D) have demonstrated their effectiveness in accurately describing intermolecular interactions in molecular systems. However, some challenges still persist when applying these methods to large clusters and mesoscopic systems, leading to discrepancies with highly accurate reference calculations. In this study, we present a straightforward protocol to enhance the accuracy of DFT-D methods specifically for molecular clusters of growing size, with a particular focus on liquid systems. Our goal is to develop robust and computationally efficient approaches for describing large-scale systems to allow first-principle molecular dynamics (FP-MD) simulations.

In our initial study [1], we introduced the optimization method by focusing on the interaction energy of acetonitrile as a test case, leveraging Quantum Monte Carlo calculations as a reference. Remarkably, we achieved a level of accuracy comparable to this gold-standard method (statistical error of .0.1 kcal/mol per molecule), demonstrating the potential of the refined DFT-D model. Subsequently, we employed this model in first-principles molecular dynamics simulations of liquid acetonitrile, unveiling significant improvements over experimental data and surpassing the default correction.

Building upon these promising results, we further applied the optimization protocol to reproduce accurate intermolecular interactions in a series of water clusters using dispersion corrected DFT models [2]. Through careful optimization, we achieved exceptional agreement with Quantum Monte Carlo calculations, with an average absolute error per monomer of approximately 0.1 kcal/mol. These findings strongly endorse the adoption of our procedure for developing tailored DFT-D models that accurately capture the behaviour of specific molecular systems.

This research provides valuable insights into the application of DFT-D methods, enabling greater accuracy in the study of molecular clusters and large-scale systems. The outcomes contribute significantly to the advancement of reliable and efficient computational tools for conducting condensed-phase simulations and targeted molecular analysis. Ultimately, these developments pave the way for a deeper understanding of complex molecular behaviour and facilitate various scientific applications.

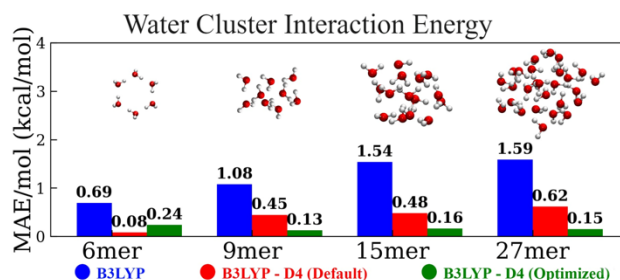


Figure 1: Mean Absolute error per molecule with respect to QMC on water cluster of growing size (i.e. from 6mer to 27mer).

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Combining CASSCF with MBE-FCI to treat large active spaces

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To this day, the *de facto* standard method to study MR systems is the Complete Active Space Self Consistent Field (CASSCF)^[1]. Unfortunately, the application of CASSCF requires to solve multiple times a Full CI (Configuration Interaction) problem, whose size grows factorially with the dimension of the active space chosen. Such limitation sets the maximum treatable size of the active space to 16 electrons to be correlated in 16 orbitals, restricting the application of CASSCF only to smaller systems. During the last few years, some approximate strategies to circumvent this prohibitive scaling have been devised, such as QMCFCI^[2], DMRG^[3] and selected CI methods, like HCI^[4].

In this work, we propose an algorithm which couples CASSCF with an approximate CI solver, namely the MBE-FCI (Many-Body Expansion)^[5] solver. The main idea of MBE-FCI is to approximate a property of the exact wavefunction, by expanding it in a series of increments arising from the correlation of any possible subset of the active orbitals. This expansion is appropriately truncated by a screening protocol that neglects the minor terms. We have exploited an implementation of MBE-FCI inside the PyMBE package, to produce the quantities required for a standard first order CASSCF orbital optimization i.e., the Reduced Density Matrices and the Generalized Fock Matrix, from which the orbital gradient is computed. To integrate the CASSCF code with the PyMBE package, an explicit interface was built.

After a first calibration of the MBE parameters, we exploited this new algorithm to perform two MBE-CASSCF calculations with a large 22 electrons in 22 orbitals active space, to evaluate the triplet-quintet gap in a Fe(II)-porphyrin, which is, by now, a classic problem where theory and experiment disagree.

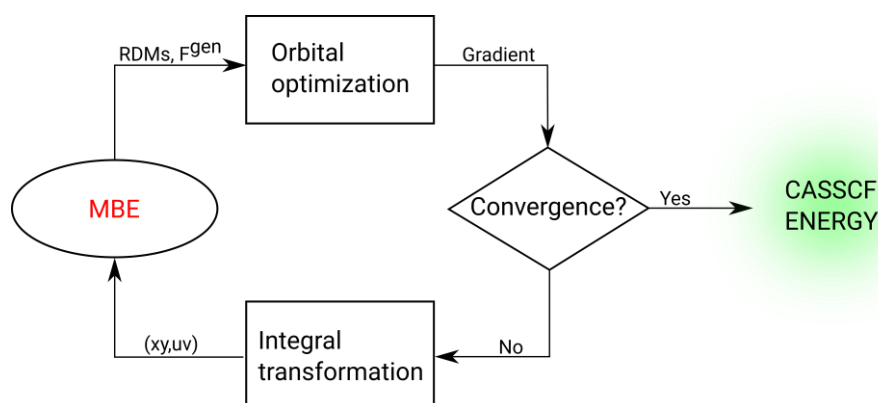


Figure 1 Scheme of the proposed MBE-CASSCF algorithm.

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Chemical Continuum: Overcoming Discrete Notions Underlying Fluctuations in Water

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Is Liquid Water really a tale of *two liquids*? Is the structure of the excess proton in water an *Eigen or Zundel* species? Can molecules dissolved in water be rigidly classified into **hydrophobic** or **hydrophilic**? Discrete or binary classifications are at the heart of the interpretation of phenomena associated with understanding the properties of aqueous solutions. In this discussion, I will share three stories that have recently emerged from our group that will attempt to challenge some of these ideas.

One of the most well studied and common interpretations of water's anomalous properties is the existence of two liquids namely the **low-density liquid (LDL)** and **high-density liquid (HDL)**. Similarly, two-state models (**Eigen** or **Zundel**) are central to acid-base chemistry which is at the heart of characterizations of proton transfer in liquid water. Here, I will illustrate some recent work leveraging unsupervised learning techniques to highlight how chemical *discreteness* limits our interpretations of fluctuations of the hydrogen-bond network in these contexts [1].

A critical first step in solvation theory is the creation of a cavity. The thermodynamics associated with this process is at the heart of hydrophobicity and its **two-length scale cross over**. I will share some recent data-driven approaches that will illustrate how shape and geometry affects the crossover in hydrophobicity.

In the final part of my talk, I will discuss some recent findings on how **oily (non-polar)** molecules can pick up **polar traits** due to subtle quantum mechanical effects. We believe that this feature is central to an ongoing raging debate in the field on the origin of the negative charge at hydrophobic surfaces which we attribute to the coupling between the hydrogen-bond network topology and charge transfer [2,3].

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From perception to computation: the new PCS-BONDS approach.

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The ever-increasing amount of data available in scientific research, in addition to the advancements in experimental techniques, allowed the application of machine learning (ML) and data-analysis tools for more effective post-processing. Moreover, computational chemistry has proven to be an effective tool for the production of valuable scientific data. The analysis of high-resolution rotational spectra provides the spectroscopic parameters for the vibrationally averaged structure of one or more vibrational states. The rotational constants are proportional to the inverse of the inertia moments in the Eckart frame. By performing measurements for a sufficient number of isotopologues (since the inertia moments depend on both masses and atomic positions) it is possible to obtain the average parameters for the corresponding vibrational states. To obtain the equilibrium geometry, vibrational contributions (computed using the VPT2 theory [1,2,3]) must be considered and the rotational constant of the equilibrium geometry must be employed in the fitting procedure. However, the computation of such Semi-Experimental (SE) equilibrium structures requires the knowledge of a sufficient number of isotopologues and experimental data is not always available [4]. To obtain high-resolution equilibrium geometries for larger molecules, two main strategies have been proposed in the literature: the Linear Regression Approach (LRA) and the Templating Molecules Approach (TMA) [5]. The first employs the known SE geometries to train a linear regression model to correlate covalent bond distances computed at lower levels of theory with the known semi-experimental values to apply refinement when new geometries are provided. The TMA approach, instead, uses the SE molecules as fragments that correct distances directly within larger molecules. The LRA approach has the disadvantage of depending on parameters that have to be custom derived, whereas the TMA approach has the disadvantage of requiring the user to manually detect the sub-fragments in the molecules. The availability of a limited number of SE fragments motivated us to develop a new composite scheme: the Pisa Composite Scheme (PCS) [6], which was proven to be effective in determining equilibrium structures whose rotational constants are close to the semi-experimental equilibrium ones. The PCS scheme requires three computations to be performed: the first is the reference structure, and two other computations are required to quantify the Core Valence (CV) correction to the geometry. The low-cost version of the method (PCS-BONDS) [7], quantifies the CV contribution to bond lengths as a fixed quantity that scales linearly with the reference bond length. The advantage of the PCS-BONDS approach is that it just relies on the principal quantum numbers of the atoms involved, instead of a larger set of parameters as it is in the case of LRA. The perception of bonds is performed employing the Proxima algorithms [8]. The PCS-BONDS tool has been developed in JavaScript and is available through a custom website where reference XYZ files can be uploaded, and the refined structure downloaded.

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Computational Study of the Charge Exchange Process Between He⁺ and CH₃CN and CH₃OH

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Computational chemistry is a powerful tool to obtain reliable information in different fields of application, ranging from the modeling of nanomaterials for energy purposes, to astrochemistry. In particular, the employment of dedicated home-made codes, free from structural errors, allows to expand the already broad range of applications. The debugging process is therefore a crucial step in developing new algorithms. In order to obtain accurate astrochemical models to match the observed abundances of interstellar complex organic molecules (iCOMs), it is pivotal to consider complete chemical networks that include reliable rate constants for the production and destructions of iCOMs. Among the plethora of possible reactions, ion-molecule processes can play a key role in the destruction of iCOMs. Helium, the second most abundant element in the Universe, can be ionized by cosmic rays to generate He⁺. Due to the larger ionization energy of He with respect to organic molecules, collisions with He⁺ represent important pathways for the decomposition of iCOMs, as demonstrated in previous works on CH₃OCH₃[1,2] and HCOOCH₃[1,3]. In the present contribution, we present a computational study on the destruction reactions of two detected iCOMs, namely methanol (CH₃OH) and acetonitrile (CH₃CN), by collision with He⁺. In the case of CH₃OH, the dissociative charge (electron) exchange mechanism was obtained by computing the entrance and exit multidimensional Potential Energy Surfaces (PESs). After an initial analysis of the accuracy of the developed codes, the non-adiabatic transitions between PESs was modeled using an improved Landau-Zener-Stückelberg approach[1], while preliminary data obtained adopting the same computational approach are presented for the He⁺ + CH₃CN reaction. In both systems, the outcomes of the computational analysis are compared with experimental results, obtained through a home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) apparatus, reporting values of absolute cross sections and product branching ratios (BRs) as a function of the collision energy in the hyperthermal energy range (i.e. from about 0.05 to ~10 eV).

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From Classical to Quantum: Investigating Halogen Bond Interactions in Ligand-Protein Complexes

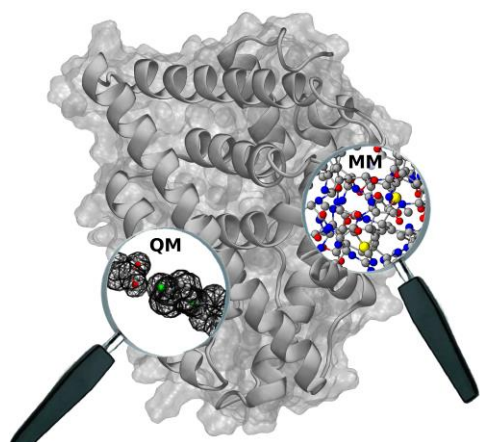
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Ligand-protein interactions play a crucial role in numerous biological processes, making their study essential for drug development and toxicity prediction. Computational methods have proven effective in interpreting ligand effects at the molecular level. Among these methods, molecular dynamics (MD) simulations based on classical mechanics (MM) or quantum mechanics (QM) have emerged as powerful tools. MM-based MD allows for faster calculations, especially for large biological systems, by describing molecules with classical potentials. On the other hand, QM-based MD accounts for electronic effects providing higher accuracy at the cost of longer computational times. An increasingly used compromise is the QM/MM hybrid approach, where a small part of the system (e.g., the ligand and/or binding site) is treated at the QM level while the rest of the protein and solvent are described using MM [1]. This approach enables efficient calculations while capturing electronic effects for a subset of the system.

One significant application that may benefit from QM or QM/MM treatment is the study of halogen bonds, which are interactions between halogen atoms and Lewis bases [2]. Halogens exhibit an accumulation of electron density around them, allowing interactions with electrophilic species, while simultaneously presenting a depletion of electrons on the atom's tip in the direction of the C-X bond, referred to as a σ -hole. This region enables interaction with nucleophiles. The anisotropy of electron density in halogen bonds necessitates a QM or QM/MM description to capture the full range of electronic contributions accurately [3]. The objective of this work was to evaluate the capabilities of MM and QM/MM methods in accurately describing halogen bond interactions in ligand-protein complexes.



The estrogen receptor (ER) was selected as a study-case for its relevance as pharmaceutical and toxicological target, and the availability of diverse structural depictions. MM-MD simulations using both single-point and extra-point parametrization of the halogen atoms electrostatics [4] were performed, obtaining an improvement in the description of the interaction with nucleophiles. However, some components of the interaction are not described at this level, such as polarization and charge transfer. To evaluate the effects of these components, model systems were constructed including the ligand and the interacting residue, and the interaction energy profiles were calculated for various orientations. QM/MM MD simulations were also conducted to study the stability of the interaction in the complexes. The simulations revealed that

when the target interaction occurred at the QM-MM interface, it was not accurately described. To achieve a proper description of the halogen bond, additional amino acid residues had to be included within the QM region. In conclusion, this study investigated the accuracy of various levels of theory in describing halogen bond interactions and provides valuable methodological insights for their treatment.

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Can Fullerene be described with Coupled Cluster theory?

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In the last few years, rank-reducing techniques have emerged in quantum chemistry as a mathematical tool able to speed up calculations, and thus being able to extend the range of application of quantum chemical methods to larger molecular systems. In this context, we exploit the Cholesky decomposition (CD) of the electron repulsion integrals (ERI) matrix [1-3]. Such a technique can compress the information stored in the ERI matrix by decomposing it in lower dimensionality tensors, therefore reducing the overall computational cost. The decomposition may be truncated in such a way that the error is always bound to be lower than a chosen threshold, thus providing robust control over the accuracy.

We exploited the CD in the coupled cluster with singles and doubles excitations (CCSD) method [4,5]. The most expensive contraction is treated using the well-known symmetric/anti-symmetric algorithm [6] and has been implemented in two different flavors. One that fully exploits the potential of BLAS routines requiring however V^3 memory of storage (V being the number of virtual orbitals), and a less performing one that requires only V^2 of memory. The code is driven towards the best option depending on the computational resources available to the user. Furthermore, we propose an implementation that in addition to CD can also exploit point-group symmetry, thus offering the possibility to study larger (symmetric) molecules. The joint effort given by the CD, the exploitation of point-group symmetry, and the parallelization of the code allowed us to perform a (frozen-core) calculation on fullerene (C_{60}) with 1800 basis functions.

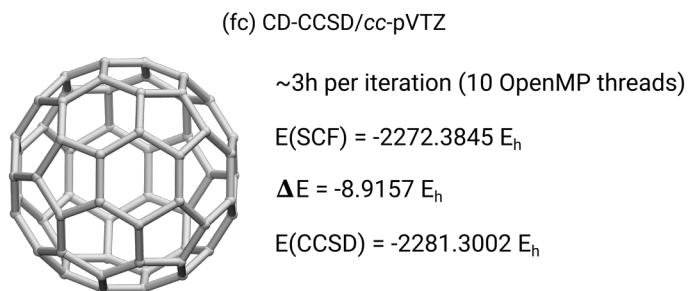


Figure 1 The frozen-core (fc) CCSD calculation on fullerene (C_{60}) of D_{2h} symmetry.

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A machine learning approach for the prediction of atomic charges of metal-organic frameworks

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Metal-organic frameworks (MOFs) are very versatile materials because of their modular structure since the framework is composed by the combination of two secondary building units (SBU): an inorganic unit (metal ion or cluster) and an organic ligand. Therefore, a plethora of combinations are available, thus allowing MOFs to cover a huge chemical space. High-throughput computational screenings are then useful to explore all the chemical and physical properties of such materials but low-cost computational methods such as tailored force-fields are required to speed up the calculation [1]. To that purpose, accurate atomic charges are crucial to correctly predict long-range electrostatic interactions. They can be derived either from quantum-mechanical calculations or generated on the fly through simplified geometrical schemes or, more recently, through Machine Learning (ML) predictive models. The latter requires suitable databases of structure and properties to be used to train the ML model. Different databases of MOFs and their properties are now available such as CoReMOF [2], QMOF [3] and ARC-MOF [4].

In this work, we present the results of the prediction of atomic charges derived from (i) a new database and (ii) the QMOF database.

On the one hand, we built a dataset of 237 structures, with up to 3000 atoms in the unit cell, for which Hirshfeld-type charges (>80000) were computed with the low-cost hybrid HF/DFT composite method PBEsol-3c [5] on the fully relaxed structures. The CRYSTAL program [6] has been used to exploit the space group symmetry and use the efficient parallelization of the code. Then, we trained a ML model by using XGBoost with atomic and environmental descriptors. The work was carried out in collaboration with Aethia srl and NetSurf srl within the ATTRACTOR project. The so-built ML model has been made available through the ATTRACTOR web site [7] where it is possible to predict the Hirshfeld-type charges by processing the CIF file of a generic MOF.

On the other hand, the QMOF database that contains more than 20000 cleaned up experimental structures (< 300 atoms in the unit cell) for which DDEC charges are available, was analysed to understand how the size and composition (i.e. metal ion types) of the training dataset affects the prediction of the atomic charges. Accurate predictions can be obtained by referring to a smaller dataset of 500 structures. Based on this result, the ATTRACTOR dataset has then been extended to have a more balanced composition in terms of different metal ions, by including some of the QMOF structures, for a better prediction of the Hirshfeld-type charges.

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How the pH controls photoprotection in the light-harvesting complex of mosses

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In response to varying light conditions, light-harvesting complexes (LHCs) switch from a light-harvesting state to a quenched state to protect the photosynthetic organism from excessive light irradiation in a strategy known as nonphotochemical quenching (NPQ). NPQ is activated by an acidification of the thylakoid lumen, which is sensed directly or indirectly by the LHC, resulting in a conformational change of the complex that leads to the quenched state. The conformational changes responsible for NPQ activation and their connection to specific quenching mechanisms are still unknown. In this talk, I will present a multistep computational protocol to investigate the pH-triggered conformational changes in the light-harvesting complex stress-related (LHCSR) of mosses[1,2]. By combining constant-pH molecular dynamics[3] and enhanced sampling[4] simulations of the LHCSR1 protein in membrane, we find that the pH sensitivity of the complex is driven by the coupled protonation of three key residues (i.e., E114, E227 and E233) modulating the conformation of the short amphipathic helix D placed at the lumen side of the embedding membrane. Combining these results with quantum mechanics/molecular mechanics calculations, we show that the quenching mechanism sensitive to the pH goes through a charge-transfer (CT) between a carotenoid (L1-Lut) and an excited chlorophyll (*a*Chl 612), which is controlled by the protein conformation (Figure 1).

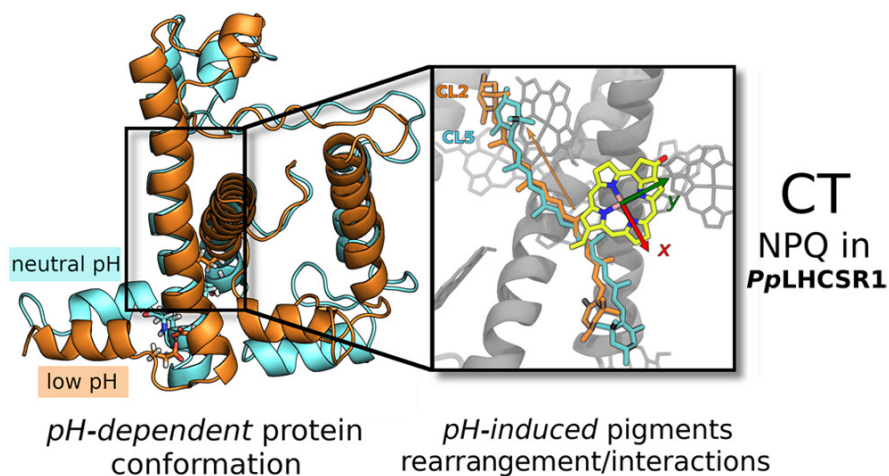


Figure 1. pH-dependent “soft switch” for increasing/decreasing the amount of quenching in LHCSR1.

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A DFT based methodology for *in silico* pKa determination of phenols

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Scientific and applicative interest in natural or synthetic phenols is mounting because of their countless applications, ranging from antimicrobials/cancer-treatments to antioxidants [1]. Further, the growth in antibiotic resistance spots a new light in tailoring natural compounds to defeat the so called “superbugs” [1]. Computational chemistry plays a pivotal role in foreseeing compounds behaviour, offering the possibility to re-draw molecules and to predict their physicochemical properties [2]. It prevents time and cost consuming experiments, suggesting easily screenable sets of data. Noteworthy, *in silico* calculation of the acid-base dissociation constants (pKa) is arduous, due to the recurrent discrepancy between the calculated and the experimental value [3]. Considering the numerous models proposed in the literature, the aim of this work is to offer a practical, accurate and ready-to-use protocol for the computational pKa determination of phenol derivatives, through a direct approach that does not requires correction factors nor mathematical fitting [4]. A screening of different functionals and solvation models is thus proposed, to identify the most performing conditions for computing pKa accurately. Four DFT functionals and three solvation models have been compared. Moreover, from zero to two explicit water molecules have been considered. Among the others, for all the analysed phenols, 2H₂O/CAM-B3LYP/SMD with 6-311G+dp basis set led to very accurate results, showing a mean absolute error of 0.37, that is an acceptable value for theoretical pKa determinations. In addition, this methodology offers reliable results with -nitro and -cyano substituents, that are usually associated with very large difference between calculated and experimental pKa value.

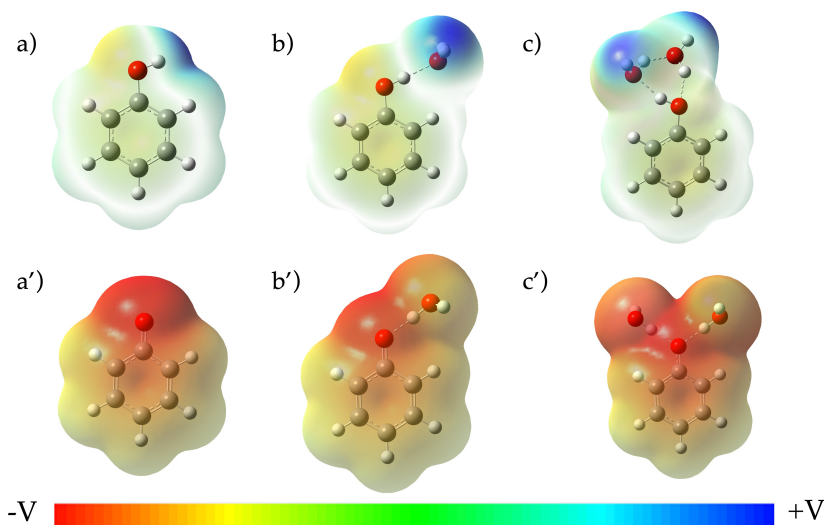


Figure 1 Surface electrostatic potential of phenol with a) 0, b) 1 and c) 2 explicit water molecules, and phenate (a'), b') and c')). Electron density obtained by calculations at CAM-B3LYP/6-311G+dp/SMD level of theory.

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A mechanistic and kinetic evaluation on the reaction between OH(²Π) and halogenated organics

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Gas-phase chemistry of organic species has received considerable attention over the last decades in both atmospheric and astrochemical environments. Because of its great importance in the atmosphere, the gas-phase reaction of one of the major oxidizing agents, the hydroxyl radical, OH, with organic compounds (especially atmospheric pollutants like halogenated species) deserves particular consideration [1]. Moreover, since OH has been found in significant amounts also in the interstellar medium, these reactions may well be important in the gas-phase chemistry of interstellar clouds. For example, the reaction of OH with unsaturated hydrocarbons has been shown to have a negative temperature dependence, thus leading to a significant increase of rate coefficients at the low temperatures of the interstellar medium [2].

To shed more light on these open questions, an extensive investigation on the mechanism and kinetics of the OH abstraction/addition pathways to four different types of organic species, namely ethylene (ETH, CH₂=CH₂), trifluoroethylene (HFO-1123, CF₂=CHF), trichloroethylene (TCE, CCl₂=CHCl) and 1,2-dichloro-1,1-difluoroethane (HCFC-132b, CF₂Cl-CH₂Cl), was performed by means of state-of-the-art quantum chemical methods. The potential energy surface (PES) of their reaction with OH was theoretically characterized by evaluating structural and zero-point vibrational energy contributions at different levels of density functional theory, while electronic energies were further refined using the “jun-cheap” composite scheme (jChS) [3,4]. Kinetic calculations were carried out by employing transition state theory with its variational and variable reaction coordinate extensions [5,6], to calculate the microscopic rate coefficients [7], while phenomenological rate constants as a function of temperature and pressure were determined within the master equation framework [8].

Product distributions and temperature- and pressure-dependent rate coefficients for the reaction of ETH, HFO-1123 and TCE with OH, as well as the rate constant for the OH- and Cl-initiated H-abstraction reaction of HCFC- 132b are presented, showing an excellent agreement of the predicted rate constants with the available experimental data and providing useful knowledge for assisting atmospheric modeling [9].

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Adsorption of molecular magnets on metal surfaces

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The advancement of information technology requires the development of ever smaller and faster devices for data storage and processing. Active research in this area focuses on molecular magnets (MM), which are considered among the best candidates for application in quantum computing and quantum data storage. These applications require the ability to access and control the single molecule, so adsorption on solid surfaces is mandatory.

The adsorption and organization of these molecules occurs on the nanoscale, therefore simulations of these systems can be computationally expensive or even unfeasible depending on the level of theory employed. To address this challenge, a strategy based on semi-empirical or classical approaches is needed. These have the downside of being limited in their applicability to systems similar to those used for their parameterization. To effectively simulate MMs adsorbed on metal surfaces, it is mandatory the development of new force fields.

In this study, we assess the effectiveness of the extended tight binding method (xTB), compared to density functional theory (DFT) for simulating the adsorption of copper phthalocyanine (CuPc) on metal surfaces [1,2]. To accomplish this, a series of geometry optimization calculations have been carried out for one and two CuPc molecules on the (100), (110), and (111) copper, gold, and silver surfaces.

All the calculations were conducted with the CP2K suite of software [3] using xTB and DFT calculations [4]. The preliminary results indicate that the xTB method is able to reproduce the results obtained with DFT calculations. These results allow us to use xTB calculations to obtain the necessary data to develop a new FF for molecular dynamics simulations of some MMs adsorbed on metal surfaces.

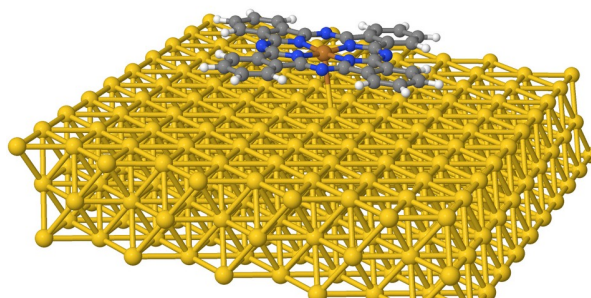


Figure 1: Copper phthalocyanine adsorbed on a gold slab (111).

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Water environment influence on the interaction between L-ascorbic acid and Anatase (101): DFT calculations and Ab Initio Molecular Dynamics (AIMD) simulations

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In this work, we provided a detailed study at atomistic level of the interaction between ascorbic acid (L-asc), at "low and high coverage", and stoichiometric anatase TiO₂ (ATiO₂) (101) surface in gas phase and water environment by using density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations (Figure 1). In gas phase, L-asc adsorbs stably on ATiO₂ (101) as dianion (L-asc²⁻) [1] adopting a bridging bidentate coordination mode (BB), with the two acid protons transferred to surface 2-fold bridging oxygens (O2c) forming OH groups (O2c-H). The presence of ascorbic acid causes a decrease of the system bandgap and a charge transfer from the organic ligand to the surface (Ligand-to-Metal Charge Transfer, LMCT), improving the photocatalytic performance of ATiO₂ (101) surface towards the air and water pollutants degradation. As the coverage of ascorbic acid increases, the superficial concentration of O2c-H groups on anatase surface increases.

AIMD simulations performed for 15 picoseconds (ps) at T=350, 450 K on both "low and high L-asc²⁻ coverage" systems show that the interaction between the organic ligand and the anatase surface is stable in the time and comparable with that obtained in vacuum despite the polarization effects of the solvent. In addition, the hydroxylation phenomena, that during the AIMD simulations lead to the formation of transient H₃O⁺ ions at the solid-liquid interface [2], suggest an extremely hydrophilic character of ATiO₂ (101) in presence of ascorbic acid.

Therefore, for the first time, our results provide insight into the role of the ascorbic acid on the structural and electronic properties of ATiO₂ (101) surface, the influence of the water environment on the ligand-surface interaction and the nature of the solid-liquid interface.

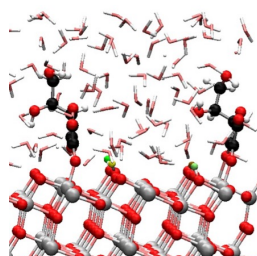


Figure 1. Interaction of two L-asc²⁻ in Bridging Bidentate (BB) configuration on ATiO₂ (101) in contact with water.

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Preliminary DFT investigation on microdiamonds formation from COH fluids in the Earth upper mantle

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Microdiamonds, discovered in metamorphic rocks under ultra-high pressure (UHPM) within continental metasedimentary rocks, have the same chemical structure as classic kimberlitic diamonds but much smaller average sizes, on the order of a few tens of μm [1]. Recently, they have also been observed in a low-temperature subduction complex of oceanic origin ($T = 600\text{ }^\circ\text{C}$; $P > 3.2\text{ GPa}$) at Lake Cignana in the Western Alps, within fluid inclusions trapped in the host rock [2,3]. Furthermore, in a unique case so far, these microdiamonds exhibit carboxylic groups on their surface. It has been proposed that carboxylic acids dissolved in the fluid medium may act as precursors for the formation of microdiamonds through a reaction in which Fe^{2+} , as a component of the host rock mineral, would act as a reducing agent for carbon [4]. The mechanisms for the formation of microdiamonds, from nucleation to subsequent growth, are still debated, and a clear understanding of them would also help to shed light on some unresolved aspects of Earth's geodynamics and the deep carbon cycle.

We employed computational chemistry approaches to investigate the possible mechanism of microdiamonds formation from organic acids in an aqueous environment. Firstly, we have developed a novel method to get a broken symmetry wave function, in the context of Density Functional Theory, to model an antiferromagnetic cluster representative of a mineral surface containing high spin Fe^{2+} . Our method overcomes some limitations encountered with standard approaches. Secondly, we have studied the adsorption of various carbon species, dissolved in the upper mantle COH fluids, onto the surface of a model mineral containing iron. Lastly, we have explored the potential energy surface of a process leading to an activated carbon species suitable for diamond nucleation and growth.

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Theoretical investigation into the activation of the N₂ molecule by means of low-valence complexes of calcium and magnesium

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Dinitrogen (N₂), the most abundant gas in Earth's atmosphere, is a highly unreactive molecule. Nevertheless, it can be converted into ammonia by nitrogenase enzymes at ambient pressure and temperature while current NH₃ industrial production relies on the energy-intensive and CO₂-producing Haber-Bosh process. As a result, a considerable amount of research is currently directed towards a more sustainable activation of N₂ under mild conditions. A recent study reported the serendipity discovery that compounds containing low-valence Ca(I) ions have the ability to coordinate and reduce N₂ [1]. The exploration of low-valence alkaline earth complexes is a new and exciting area of research in inorganic chemistry, showcasing remarkable reactivity. For example, complexes of the [BDI]₂Mg₂ type are used as selective reducing agents in both organic and inorganic synthesis reactions. However, no activity of Mg(I) complexes in activating the nitrogen molecule has been observed so far. Therefore, we conducted DFT calculations to investigate the coordination, activation, and protonation of N₂ by low-valence Ca(I) and Mg(I) complexes [2]. Our theoretical analysis demonstrates that the ability of alkaline earth metals to utilize atomic d orbitals or not is reflected in variations in N₂ binding energy and coordination mode (end-on vs side-on), as well as the resulting adduct's spin state (singlet vs triplet). These differences ultimately influence the subsequent protonation reaction, which is found to be hindered in the presence of Mg.

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Polarizable Simulations: a study of ions interaction in Amino Acids Ionic Liquids

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Polarizable molecular dynamics is a powerful tool to understand the mechanics of the interaction inside the bulk of ionic liquids (ILs). A huge research effort has been employed on ILs due to their “greener” nature compared to traditional solvents. Even if many technological applications are being introduced [1,2] there are many evidences of their toxicity towards humans and environment [3]. The very recent implementation of ionic liquids based on choline and amino acids (AAILs) is particularly relevant for their intrinsic bio compatibility. Despite their growing use in many technological setups, the physico-chemical mechanism in which AAILs interact with biological matter is still largely unknown [3] and molecular dynamics simulations can give interesting insights.

One of the crucial ingredients of the interaction energy in ionic liquids is polarization, the simulations of dynamical processes in ionic liquids has long been recognized by the community to need an electrostatic model as accurate as possible. These effects are particularly important and will affect dynamic quantities like fluidity, ionic mobility or conductivities which are all heavily underestimated by non-polarizable models [4].

New parameters based on AMOEBA polarizable force field have been determined to describe the nanoscopic behavior of AAILs. The parameters have been parametrized with high quality ab-initio data and it is able to accurately reproduce the structure and the interaction energies.

This new force field can show how the polarization is essential to accurately describe the dynamical properties of these AAILs as well as the network of interactions inside the bulk structure of the liquid.

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Modeling energy-transfer processes in the light-harvesting complex CP29: first principles simulation of transient absorption spectroscopy

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In photosynthetic organisms, light is absorbed by specialized molecular aggregates called light harvesting complexes (LHCs), protein scaffolds that host multiple pigments such as chlorophylls. The excitation energy is then funnelled by the pigment network towards reaction centres, where it is converted to chemical energy. These processes, called light harvesting, can be studied using transient absorption (TA) spectroscopy, as time-resolved spectral features are fingerprints of the LHC excited-state dynamics. However, the complexity of the signals arising from different processes prevents a complete interpretation of spectra. Atomistic simulations are a powerful tool to map all excited-state processes that occur during TA experiments. However, LHCs are challenging systems for computational chemists: LHCs are large systems in which each chromophore experiences a specific and dynamic interaction with the protein environment. In addition, simulating the TA experiments requires strategies to model excitation energy transfer (EET) processes and the relative spectroscopic fingerprints in a multichromophoric aggregate.

Combining molecular dynamics simulations with *ab-initio* multiscale methods has proven effective in modelling the excitation properties of such dynamic systems [1]. Here, we present a first-principles simulation of the TA spectra of the chlorophylls network in the CP29 minor LHC from plants. EET processes are modelled using Redfield-Förster (RF) theory [2] within the exciton framework, and the optical spectra are simulated with a Markovian lineshape theory. As reported in the **Figure**, the simulations can reproduce correctly the experimental [3] transient absorption spectra in terms of bands position, lineshape and dynamics. This promising result suggests that RF theory can effectively model EET, which is induced by nuclear vibrations and by the protein environment under partial delocalization of the excited states.

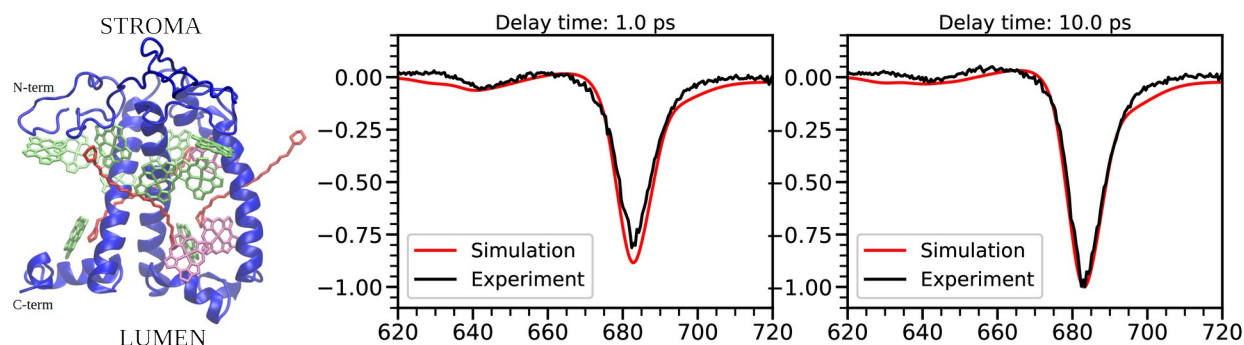


Figure: Simulated and experimental TA spectra at different delay times.

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Modelling structural, dynamic and spectral properties of proteins adsorbed on plasmonic materials

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At present, sensors that utilise engineered plasmonic materials have become the preferred choice for detecting different kinds of chemical and biological agents, ranging from small drugs to viruses and bacteria [1]. In particular, the detection and identification of the characteristic signals of proteins greatly benefit from the peculiar optical properties of metallic and/or graphene nanostructures [2,3]. As a matter of fact, the understanding of the adsorption process of (bio)molecules, especially proteins, on plasmonic surfaces and how their spectral properties are influenced by the presence of the plasmonic material can be pivotal in designing and optimising biosensing devices based on these materials.

In this context, we propose a general computational strategy for modelling plasmonic biosensors, drawing inspiration from a computational protocol widely employed to investigate spectroscopic properties of molecules in aqueous environments [4]. We adapt this protocol to suit the specific characteristics of nano-biointerfaces. Initially, we investigate the protein adsorption on the plasmonic surface, by using conformational sampling techniques that can also capture the effects of solvation [5]. Representative structures obtained from classical molecular dynamics (MD) simulations are selected and utilised to predict both electronic and vibrational spectroscopic properties of the protein adsorbed on the plasmonic surface. This prediction is accomplished through multiscale quantum mechanical/molecular mechanics (QM/MM) methods [6,7]. Specifically, the regions of the protein that are directly involved in the adsorption event are treated at the QM level, while the plasmonic nanomaterial is described with cost-effective fully atomistic classical models such as ω FQ and ω FQF μ [8,9]. The procedure permits the modelling of realistic complex systems, by accurately describing structural and spectral properties of each of their components at a reasonable computational cost.

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Chiral metal clusters: computational studies on their optical properties

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We have employed Time-Dependent Density Functional Theory (TDDFT) simulations using the polTDDFT implementation [1] within the AMS program, to assess various optical properties of chiral metal clusters. We start with a series of chiral gold nanowires to explore whether an enhancement of circular dichroism at the plasmon resonance is possible and identify its quantum mechanical origin [2]. Moreover, the effects of the conformational dynamics of 2-PET protective ligands on the electronic circular dichroism (ECD) of the chiral $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ cluster are investigated [3]. We adopt a computational protocol in which ECD spectra are calculated at the TDDFT level on a series of conformations extracted from MD simulations by using the Essential Dynamics (ED) analysis, and then properly weighted to predict the final spectrum. This result unambiguously demonstrates the need to account for the conformational effects in the ECD modeling of chiral protected nanoclusters. Finally, the role of the explicit solvent molecules to assess the optical properties of $[\text{Au}_{25}(\text{GSH})_{18}]^{-1}$ are considered [4].

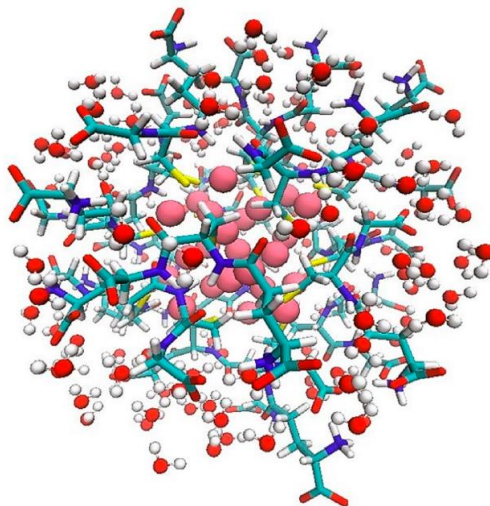


Figure 1 $[\text{Au}_{25}(\text{GSH})_{18}]^{-1}-(\text{H}_2\text{O})_{126}$ cluster conformation [4]

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Probing Heteromolecular H-bonding Interaction in Cyanuric Acid/Melamine Networks 2D with NEXAFS and XPS Core-Electron Spectroscopies

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The preparation of complex molecular architectures routinely exploits the directionality and cooperative strength of hydrogen bonding interaction, which can be used for a reversible control of molecular self-assembly [1,2] of simple organic molecules. Besides the fundamental interest of hydrogen-bonded structures, there is also technological relevance due to widespread applications of these supramolecular structures such as surface coating, molecular sensors, heterogeneous catalysis and organic electronics. Cyanuric acid (CA) and Melamine (M) are two such examples of simple organic molecules which can assemble in well-ordered two-dimensional networks on solid surfaces [3-4]. Their CA*M adduct is a prototypical molecular system exhibiting three complementary NH \cdots O and NH \cdots N hydrogen bonds which arranges in a symmetric two-dimensional array as in Figure 1.

In this work we exploit the initial state locality of K-shell core-electron excitation/ionization process to get a detailed information on the electronic structure modification which characterizes the long range order of the heteromolecular H-bonding motif of the CA*M adduct as compared to the homonuclear CA and M extended structures. Both of N K-shell Near Edge X-Ray Absorption Fine-Structure (NEXAFS [5]) spectroscopy and N 1s X-Ray Photoelectron spectroscopy (XPS) are used to get complementary information on the prototypical CA*M heteromolecular system and to characterize the H-donor/acceptor nature of the molecular constituents.

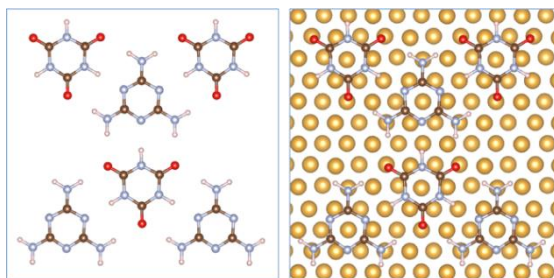


Figure 1 (Left) Unsupported and (Right) Au(111)-supported models for the CA*M H-bonding system.

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DFT Meets Wave-Function Methods for Accurate Structures and Rotational Constants of Histidine, Tryptophan and Proline

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Accurate geometrical determinations are required in the field of molecular spectroscopy to predict, support, and guide experimental measurements. However, high accuracy means high computational cost or even impossible calculations. In order to deal with these issues, several computational methodologies have been developed that can give very accurate equilibrium structures: Composite Schemes (CS), Semi-Experimental (SE), Template Molecule (TM), and Linear Regression (LR) approaches [1]. CS, rooted in the coupled-cluster model, provides structural parameters with an accuracy of 0.001 Å for bond lengths and 0.1° for angles, but it is still expensive to obtain the equilibrium structure of large molecular systems, even employing cheap variants [2]. In the SE approach, equilibrium structures are obtained by a least-squares fit of experimental rotational constants for the ground vibrational state of different isotopologues corrected by computed vibrational and (possibly) electronic contributions, but this approach requires a large number of experimental data for a complete structural characterization of large systems such as peptides, aminoacids, and nucleobases [3]. The size of molecular systems can be expanded using the TM and LR frameworks. The TM strategy is based on the fact that if an accurate equilibrium geometry is available (both experimental or computationally) for a comparable or a smaller molecule of the system under study, it can be used as a template for freezing some parameters in the fitting process. On the other hand, the LR approach provides accurate geometries adjusted by a term previously acquired by linear regression fit of semi-experimental values in comparison with their computed counterparts [4,5]. Recently, a new methodology has been developed, called PCS (Pisa Composite Scheme), which requires the contribution of three separate optimizations (MP2/cc-pwCVTZ for frozen core and all-electron, and rev-DSD-PBEP86-D3BJ/cc-pVTZ-F12). This CS procedure approaches the so-called spectroscopy accuracy without any empirical parameter at a reasonable cost [6]. In this work we applied the PCS approach, to the conformational and spectroscopic properties in the gas phase of amino acids with very distinctive features ranging from different tautomeric forms (histidine) to ring puckering (proline), and heteroaromatic structures with non-equivalent rings (tryptophan). The integration of modern double-hybrid functionals and wave-function composite methods has allowed us to obtain accurate results for a large panel of conformers with reasonable computer times [7].

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A computational insight on Au-based nanoalloys

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The growing interest in gold-based nanoalloys arises from the possibility of combining the optical features of gold with the catalytic capabilities of other transition metals, leading to a new generation of highly-effective photocatalysts.[1] Among the many alloys, nanosystems where gold is mixed with other transition metals such as Pt, Pd or Rh are extremely promising since they can successfully catalyse several essential reactions such as hydrogen generation from water, oxygen evolution, and hydrogenation of double bonds.[2] Notwithstanding their relevance, to date only a few studies focused on the characterization of these nanoalloys and only a few focus on their synthetic processes.[3]

Our study provides a systematic investigation on how the synthesis kinetics is affected by the seeds morphology, the nature of the other metal and by environmental conditions. The aim of our numerical study is to show how the formation process of nanoalloys can affect the catalytic properties of the nanoalloy itself. Indeed, in the hypothesis that the adsorption properties of molecules depend on the chemical ordering and local atomic environments at the surface, we analyse the life of first hundreds of nanoseconds after nanoalloys sintering and characterise the dynamics of coalescence.

By means of classical molecular dynamics simulation employing the software LoDiS[4], we focus on the coalescence of Au-icosahedra and cuboctahedra against another metallic M-seed (with M=Pt, Pd, and Rh), colliding with a kinetic energy comparable with a metallic vapor, in an inert or interacting environment. In the case of an interacting environment, we model its effect following the Huerto-Cortes formalism[5]. Metal-metal interaction follows the second-moment approximation of the tight-binding.

Our calculations and further analysis with the Sapphire package[6], show that in all cases there is a strong tendency Au diffuse above the M-seed. However, we observe the kinematics of the sintering process i.e., the time requested to get an almost spherical versus oblate shapes and the stabilization of one morphology versus another strongly depends on the metal M and on the interaction with the environment.

Although, there is room for a significant improvement in the description of metal-metal and metal-environment interactions, our work suggests that the environment and the temperature are the have a key-role in determining the distribution of the chemical species at the surface, hence implying a different structural conformation and thus hot-spots where (photo)chemical reactions may take place. Furthermore, we observe that the shape of the Au-seeds might be remarkable in tuning the kinematics of the sintering process (i.e. the time requested to get an almost spherical versus oblate nanoshapes) and can drive the stabilization of one nanoalloys morphology versus another.

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Quantum chemical investigation of multi-redox states in organic conjugated redox ladder polymers for electrochemical energy storage systems

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Electrochemical energy storage (EES) devices, such as batteries and supercapacitors, play a vital role in our modern society.[1] The request of materials able to store and release the electrical energy at demand is continuously growing, challenging the actual state of the art of EES technologies. Lithium ion batteries (LIB), as composed by inorganic electrode materials (e.g., cobalt-based alloys), have been largely investigated and used, however they present limits related to their environmental sustainability and low charge capacity.

Organic conjugated redox polymers (**OCRPs**) can be considered an effective alternative to inorganic based EES materials, being environmental friendly, easy to design and fabricate. However little is known about their fundamental *structure vs. redox-property* relationships.

In this contribution, we investigate via quantum-chemical calculations the structural and electronic properties of a special class of **OCRPs**, namely ladder polymers.[2] They are characterized by a rigid and highly conjugated backbone, leading to semi-crystalline solid state morphologies featuring high charge and ion mobilities. The ladder **OCRPs** we considered are polyquinoxalines (**PQL**) and **SBBL**, which is a simplified derivative of benzobisimidazobenzophenanthroline (**BBL**), a well known polymer with high charge, thermal and ion mobility.[3,4]

By combining density functional theory (DFT), broken-symmetry DFT (BS-DFT) and fragment orbital density analysis (FOD) we revealed the poly-radicaloid character of the electronic structure of neutral and multi-redox states.[5] We found that negative (electron) and positive (hole) charges, here defined polarons, relax on localized states of the polymer chain, thus featuring different structural and electron-phonon coupling properties. Multi-charged species, revealed complex electronic structures, as characterized by quasi-degenerate multiplet states showing various spin multiplicities (e.g., doublet, triplet, quartet, quintet, etc.) and response properties.

Our computational study provides insights towards the understanding of multi-redox processes for the last generation of **OCRPs**, active materials for EES and biomimetic applications.

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Origins of the pH-Responsive Photoluminescence of Peptide-Functionalized Au Nanoclusters

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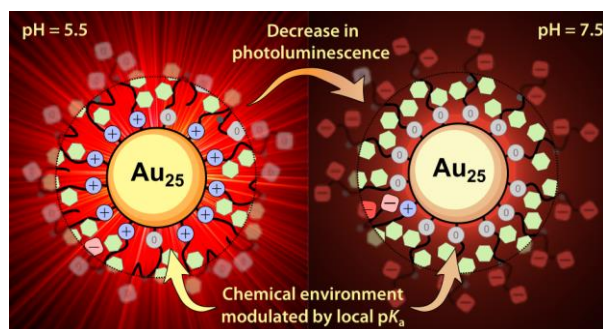
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Ultrasmall peptide-protected gold nanoclusters (AuNCs) are an emerging class of materials with distinct and tunable physicochemical properties exhibiting pH-sensitive photoluminescence (PL). As such, the photophysical properties of AuNCs are attracting intense interest for applications that range from antimicrobial devices to biomedical theranostics and industrial photocatalysts.

Through the systematic calculation of local environment-dependent deprotonation free energies, we provide insight into how the PL emission intensity of peptide-coated Au₂₅ is inversely related to solution pH, in line with previous experimental observations [2]. Utilizing a hybrid quantum/classical computational methodology, the Perturbed Matrix Method [3] (MD-PMM), we deliver a simplified computational description of the multifaceted, complex, and nontrivial coupling that a large number of ionizable groups impose on the interdependent protonation/deprotonation equilibria of Au₂₅(Peptide)₁₈ nanoclusters. We find that the pH-sensitive nature of Au₂₅'s PL emission can be explained via pH-tunable electrostatic interactions occurring between titratable N-terminal amine and C-terminal aspartate moieties [4]. Our findings provide an insight into how the deprotonation equilibrium of N-terminal amine and side chain carboxyl groups cooperatively respond to solution pH changes, explaining the experimentally observed, yet elusive, pH-responsive fluorescence of peptide-functionalized Au₂₅ clusters.



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Awarded Communications

- A1. Filippo Lipparini (Università di Pisa) – Roetti Medal
New Algorithms and Numerical Strategies from Classical Models to Quantum Chemistry

- A2. Silvia Alessandrini (Università di Bologna) – Del Re Prize
Modelling weak interactions in the gas phase: from non-covalent bond to reactions rates

- A3. Matteo Capone (Università degli Studi dell'Aquila) – Scrocco Prize
Illuminating PhotosystemII Catalysis: Molecular Insights from QM/MM Simulations

New Algorithms and Numerical Strategies from Classical Models to Quantum Chemistry

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The development of new models in theoretical and computational chemistry must always be associated to the parallel development of their computational realizations. Computational chemists are among the largest users of computational resources, and the development of efficient, scalable codes in the community is intrinsically linked with the theoretical advances that have been produced in the last several decades. However, applying theoretical models to larger and more complex systems can become challenging, as even the most efficient and scalable implementation hit the limits of available computational resources. For this reason, the design of new algorithms and the development of new numerical techniques has become a more and more prominent field of research. In this contribution, I will present three examples of algorithmic improvements that have been used to accelerate existing models. First, I will illustrate the use of Schwarz's domain decomposition to recast the Conductor-like Screening Model (COSMO, or C-PCM) equations into a set of sparsely coupled equations that can be solved at linear scaling computational cost [1,2]. Second, I will present an application of differential geometry to the computation of an accurate density matrix as a guess for self-consistent field calculations in ab-initio molecular dynamics [3]. Finally, I will discuss the use of the Cholesky decomposition of the two-electron integrals matrix as a tool to accelerate post-Hartree Fock calculations of energy and properties [4,5].

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Modelling weak interactions in the gas phase: from non-covalent bond to reactions rates

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Non-covalent interactions (NCIs) are fundamental in several aspects of life (e.g., the folding of proteins or structure of DNA) and have also a key role in reaction pathways, where they can affect the structure of reactive intermediates and transition states. Modeling such interactions is a key aspect for quantum-chemistry, which should be able to describe prototypical NCIs occurring in the gas phase, from both the structural and energetic point of view. To this aim, two recent works [1,2] have developed accurate composite schemes based on the coupled-cluster ansatz including single and double excitations and a perturbative treatment of triples (CCSD(T)) or its the explicitly correlated counterpart of such method, i.e., the CCSD(T)-F12 method. Both these methods are used in conjunction with a triple zeta basis set as starting point of the composite schemes, that include also (i) the extrapolation to the complete basis set (CBS) limit and (ii) the core-valence (CV) correlation effects. These terms are computed either using the MP2 method or the MP2-F12 one when explicitly correlated coupled cluster is employed. The development of these composite schemes is illustrated using as reference the interaction energies of fourteen non-covalent complexes (A14 dataset) [3,4] and discussing the balance of diffuse functions in the basis set.

In a second part, the determination of equilibrium structures for the complexes of the A14 dataset is considered. In this case, the best composite schemes for the energy determination are used to derive the equilibrium structures of the non-covalent complexes and these are compared with the results of a double-hybrid density functional and with those of the literature [2].

The performance of these new composite schemes is discussed with few examples. A comparison with experimental results obtained via rotational spectroscopy is used to understand the accuracy of the computed structures. Then, the use of such composite schemes in the determination of reaction rates for models of astrochemical interest is outlined, with a look to future steps.

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illuminating PhotosystemII Catalysis: Molecular Insights from QM/MM Simulations

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Light-induced reactions play a vital role in various chemical processes, including organic synthesis and natural phenomena such as photosynthesis. In the latter, photosystem-II (PSII), an essential enzyme, utilizes light energy to perform water oxidation, making possible the storage of sunlight in energy-rich biomolecules, and therefore PSII is one of the main molecular actors that allows the existence of life on earth as we know it. Even if our awareness of the photosynthesis process goes back a long way, several chemical aspects have remained substantially unclear. Far from being a mere intellectual challenge, their comprehension is crucial to laying the theoretical foundation for transferring this knowledge to artificial photosynthesis devices. Among the mechanisms that have drawn particular attention is the charge separation (CS) process, which occurs at PSII's reaction center (RC) comprising both chlorophylls (Chl) and pheophytins (Pheo), and leads to the production of oxidation equivalents stored the close by Mn/Ca cluster . This cluster, upon absorbing four photons, is able to convert two water molecules into molecular oxygen, protons, and electrons. Since 2015 I have been exploring such topic through the utilization of multi-scale quantum mechanics/molecular mechanics (QM/MM) molecular dynamics simulations, and allowed me to contribute to significant advancements in the understanding of two extensively debated aspects of PSII catalysis. On one hand, I had the chance to contribute to the identification of the molecular intricacies involved in the most energy-demanding step of the water oxidation cycle [2,3,4]. On the other, I played a role in confirming the nature of the primary electron donor in the CS process and ruled out alternative proposed pathways [5]. Leveraging QM/MM-MD and minimum energy path calculations, it was possible to elucidate all the molecular events and enthalpic barriers from the last photon absorption to the complete regeneration of the Mn/Ca cluster catalyst as: O-O bond formation, oxygen release and cluster regeneration. Furthermore, our studies allowed to propose a rationale for the large entropic barrier observed in the rate-limiting step. Additionally, employing classical MD simulations in conjunction with the Perturbed Matrix Method, our work has produced pioneering direct calculations of the charge separation kinetics in the RC of PSII [5]. Furthermore, we have computed the reduction potentials of the key components in the RC, thereby eliminating one of the proposed pathways due to its unfavorable free energy cost. Our findings highlight two distinct charge separation channels in the RC with considerably different time constants. Ultimately, we have determined that the Chl_{DI}-Pheo_{DI} couple serves as the primary and dominant radical pair formed upon light absorption. Although the transfer of this knowledge to artificial devices is not trivial, these findings might hopefully contribute to progress towards this ambitious goal, starting from the very comprehension of the natural mechanisms we aim to reproduce. Also, it is possible that the robustness and flexibility of the methodologies used in these endeavors can inspire and serve other scientist in the study of similarly complex molecular mechanisms in biological systems.

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Sponsor Communication

S1. Federico Ferrari (E4 Computer Engineering)

Deployment of "ready to run" HPC infrastructures for molecular sciences

Deployment of “ready to run” HPC infrastructure for molecular sciences

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In this presentation we're going to talk about how the company E4 Computer engineering deploys ready to run HPC infrastructures built on the customer needs, without being vendor dependent, using the more suitable technologies and how these infrastructure can serve and help also molecular sciences to achieve their goals efficiently with few specialized internal IT staff. Specifically, in this talk we're going to illustrate who is E4 computer engineering and his sister E4 Analytics, what we do, with who we work with, the structure of two our solutions: Medooza 2.0 and Gaia, why the parallel storage is important and which ones we use, and we're also going to explain some of our success cases in this 2023 like the cluster Armida, Dompé and others with the helping of some benchmarks.

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