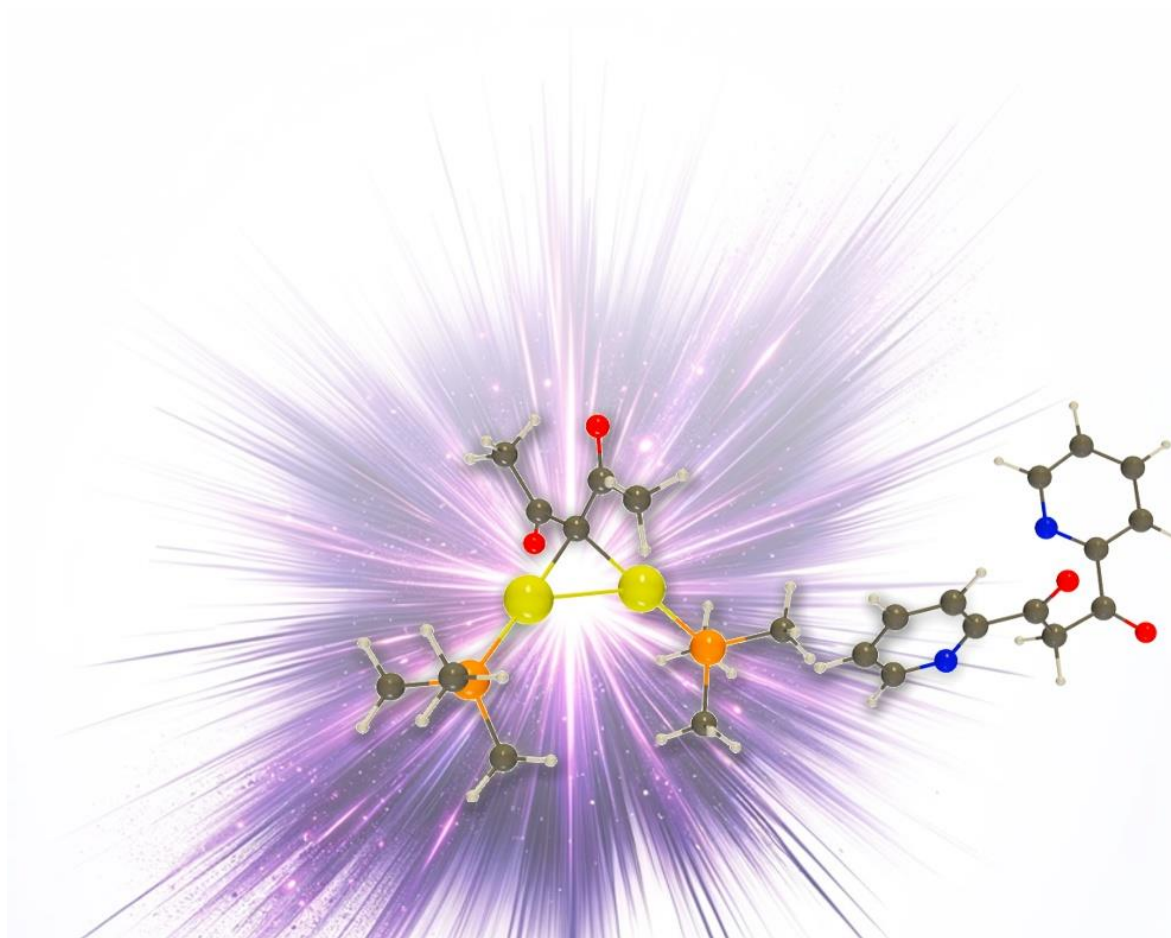# The 37th Winter School in Theoretical Chemistry 2023

Dynamic processes of molecules in electronic excited state

Poster abstracts

Poster abstracts (updated 8.12.2023)

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Interactions between pyruvic acid and aerosol surfaces

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Pyruvic acid and its conjugate base, the pyruvate anion, are both common compounds in the atmosphere and are present within seawater, fogs, aerosols, and clouds having both biogenic and anthropogenic origins[1,2]. Due to the environmental-specific reactivity of pyruvic acid, it has been shown to be able to alter both the chemical and optical properties of atmospheric particles[3]. This study aims to investigate the atmospheric molecular clusters comprised of (pyruvic acid)$_1$(H$_2$O)$_{0-5}$, (pyruvate)$_1$(H$_2$O)$_{0-5}$, (pyruvic acid)$_1$(Na$^+$)$_1$(H$_2$O)$_{0-5}$, (pyruvate)$_1$(Na$^+$)$_1$(H$_2$O)$_{0-5}$, (pyruvic acid)$_1$(Cl$^-$)$_1$(H$_2$O)$_{0-5}$, (pyruvic acid)$_1$(NaCl)$_1$(H$_2$O)$_{0-5}$, (pyruvate)$_1$(NaCl)$_1$(H$_2$O)$_{0-5}$, (Na$^+$)$_1$(H$_2$O)$_{0-5}$, (Cl$^-$)$_1$(H$_2$O)$_{0-5}$, (lactic acid)$_1$(H$_2$O)$_{0-5}$ as well as (propionic acid)$_1$(H$_2$O)$_{0-5}$. The aim is to probe how different structural features affect stability as well as cluster formation, and cluster growth potential of these clusters in the gas phase. Additionally, the aim is to investigate how the clustering influences the photochemistry of pyruvic acid and the pyruvate anion including transitions to electronic excited states. Benchmarking of methods was performed with Gaussian and ORCA while the subsequent modelling, configurational sampling, cluster formation free energy calculations, and hydrate distributions on the clusters were carried out by employing the software Jammy Key of Configurational Sampling (JKCS)[4]. Preliminary results show that the commonly used choice of methods is GFN1-xTB for pre-optimization, DFT/ωB97XD/6-31++G(d,p) for geometry optimization and vibrational frequency calculations, and DLPNO-CCSD(T)/aug-cc-pVTZ for electronic energy corrections when applied in the configurational sampling protocol. Preliminary results show that the cluster formation free energies of the pyruvic acid/water clusters are positive and become increasingly larger with the cluster size, which clearly indicates that aerosol particles must be present to adsorb pyruvic acid on to the surface. Current work focuses on modelling the aerosol surface composed of a bilayer of sodium chloride to probe the interactions between pyruvic acid and water with the surface. Future work would be to perform molecular dynamics simulations of the clusters with the surface and comparing IR spectra of the clusters.

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Multiconfigurational Description of the Excitonic States in Light Harvesting 2

Roberto Cacciari

The work is focused on the use of an *ab initio* theoretical procedure for the accurate study of a Light-Harvesting (LH) System and subsequent replication of its UV-Vis spectrum. Such systems are found in plants and photobacteria, in which they absorb sunlight and transfer it to a Reaction Centre (RC) in the form of excitation energy. Such transfer of energy is properly termed Excitation Energy Transfer or just Energy Transfer (ET).

In LH systems, the collection of solar energy and its transfer from one system to another, until the Reaction Centre, is particularly efficient. The efficiency is based on the interaction between the characteristic chromophores. In this work, the reference LH System comes from crystallographyc data of LH2 from *Rhodopseudomonas acidophila*, which uses bacteriochlorophyll a (BChls a) molecules as chromophores.

The study of such systems has underlined the importance of a quantum mechanical approach. Hence, the treatment of a model of the LH2 according to the Frenkel-Davydov Exciton Theory is proposed. The model consists of the complete B800 and the B850 rings, for a total of 27 monomer chromophores, and the Q_y ($S_0 \rightarrow S_1$) transition for each BChls. The Molecular Exciton approach involves the coupling of the excited states of all monomers, which mix and form excitonic states. Thus, it needs the calculation of a coupling term between the monomer states. This term is a Coulomb interaction which is usually approximated to a simple dipole-dipole. But the procedure proposed in this work implements an expression for the coupling terms which computes the interactions between molecular charge densities, thus it is not affected by any approximation bias. Regarding the newest information about the description of BChls, here a State Average - Restricted Active Space Self Consistent Field with a following Multi-State Second-order Perturbation Correction (SA-RASSCF/MS-RASPT2) is proposed.

These two terms, the molecular state energies and the molecular state couplings, have been used for building the Frenkel-Davydov Hamiltonian operator. Its diagonalisation gave the excitonic excitation energies and their character in terms of the monomer's excited state delocalisation. With this information, the theoretical UV-Vis spectrum has been calculated in good agreement with the experimental one. Moreover, the results give a fine description of the relationships between the ring's monomers and reports the delocalisation and properties of the most influencial excitonic states of the system.

Assessing Coulomb interactions in molecular aggregates: example applications of Frenkel's model

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The accuracy of evaluating the UV-Vis absorption of noncovalently bound molecular aggregates relies on the distances between molecules. When intermolecular distances and molecular sizes are of similar magnitude, the conventional dipole-dipole approach becomes invalid, and at least Coulomb interactions have to be properly described. Frenkel's formalism, in which the dimer is separated into two interacting monomers, has proven to be highly effective. A recent development, integrated into the OpenMolcas package [1][2], allows for the assessment of Coulomb couplings, within Frenkel's formalism, employing multireference, multiconfigurational energetics for individual monomers, such as MS-RASPT2/SA-RASSCF. The main advantage of this method is that the computational bottleneck lies in calculating the energetics of the single interacting monomers. In this poster, I will showcase the applications of this code to dimeric aggregates of molecules with extended π systems, such as Bacteriochlorophyll (BChl)-like models or azobenzene derivatives. Various properties, including H- and J-aggregate formation and absorption spectra, will be discussed and compared to those of the isolated monomers.
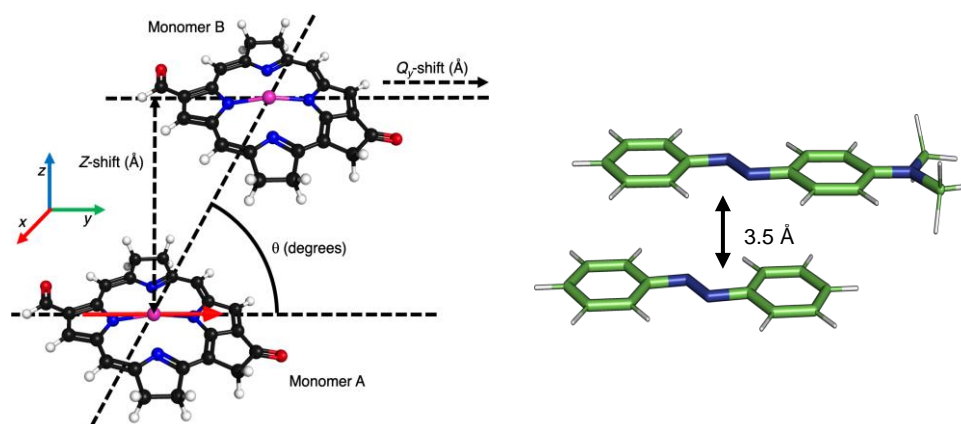
Figure 1: Homodimer model of BChl-like structures. Heterodimer model of azobenzene derivatives.

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Accuracy of One- and Two-Photon Intensities with the Extended 2 Polarizable Density Embedding Model

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The recently developed extended polarizable density embedding (PDE-X) model is evaluated for the spectroscopic properties of organic chromophores solvated in water, including both one- and two-photon absorption properties. The PDE-X embedding model systematically improves vertical excitation energies over the preceding polarizable density embedding model (PDE). PDE-X shows more modest improvements over existing embedding models for oscillator strengths and two-photon absorption cross-sections, which are more sensitive properties. We argue that the origin of these discrepancies is related to the description of polarization effects, suggesting directions for future development on the embedding model.

Internal conversion induced by external electric and magnetic fields in the approximation of accepting X-H (X=C, N, O) stretching vibrations

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The influence of the external electric and magnetic fields on the internal conversion process (IC) is considered. The methodology based on the assumption that electronic excitation energy during IC process is converted mainly into the stretching vibrations of the X-H (X=C, N, O) bonds and the impact of others vibrations can be neglected [1, 2]. For investigation, seven molecules with an energy gap S_1-S_0 varying from 8000 to 30000 cm^{-1}, were selected.

The calculation results show that for isophlorin, azaoxa[8]circulene, and pyromitene 567 the value of IC rate constant (k_{IC-E}) induced by electric field with strength 10^9 V/m is comparable to the value of k_{IC} in the absence of external field. These electric field strengths, for instance, are encountered in plasmonic studies [3] and strong laser-field experiments [4]. Therefore, the induced effect on the k_{IC} rate constant should be taken into consideration in the calculations of the photophysical properties of molecules participating in such experiments.

The induced effect of an external magnetic field on k_{IC} can be neglected in experiments on Earth because the magnetic contribution to the value k_{IC} becomes significant only at very strong magnetic fields of 10^4-10^7 T that cannot be achieved on Earth. However, the magnetic effect on the rate constant of internal conversion can be important in astrophysical studies, where extremely strong magnetic fields occur near neutron stars and white dwarfs.

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The magnetic induced current density pathway in lemniscular molecules

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Abstract: The number of electrons in the conjugated orbitals determines whether the ring-shaped molecules are aromatic or antiaromatic. But things become difficult in the nonplanar and twisted molecular structures. Also, the magnetically induced current density MICD originally developed for understanding the ^{1}H NMR shifts might not be applicable to lemniscular structures because the ring current pathway is not obvious and more than one current-density pathway is possible. In that case, using the Runge-Kutta method to split the current density diatropic and paratropic contributions separately, gives a clear clue about the properties of the molecule.

Horizontal proton transfer in respiratory complex I studied by hybrid QM/MM approach

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The molecular mechanism of respiratory complex I (NADH:ubiquinone oxidoreductase) has remained one of the biggest mysteries in bioenergetics. Being the largest enzyme in the respiratory chain, it couples the electron transfer process to proton pumping across the inner mitochondrial membrane, spatially separated by ~200 Å from one another. This phenomenon raises an enigmatic question: how does the energy released from the redox reaction can be transmitted for such long distances? In our work, we advocate the hypothesis that it can be accomplished by the translocation of protons along the central hydrophilic axis of the enzyme - a highly hydrated region revealed by the structural data [1-4]. We utilise state-of-the-art quantum mechanical/molecular mechanical (QM/MM) simulations to study the dynamics of horizontal proton pathways in the high-resolution structure of respiratory complex I from *Yarrowia lipolytica* [4]. We apply QM/MM free energy umbrella sampling simulations to various proton routes bridging highly-conserved protein residues of the ND2 subunit of the enzyme. Our results show low free energy barriers and favourable thermodynamics for the proton pathway laterally spanning the entire ND2 subunit. For the first time, we emphasize the critical role of tyrosine residues in coordinating the transmission, and show reasonable energetics for the proton transfer in interfacial regions of the ND2 subunit with the adjacent ND4L and ND4 subunits. Our results elucidate the long-range energy translocation processes in the membrane part of the enzyme [5], casting doubts on the canonically admitted proton pumping models in respiratory complex I.

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Reaction mechanisms and electron flow: HAT vs cPCET case studies

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Hydrogen Atom Transfer (HAT) and Proton-Coupled Electron Transfer (PCET) are two important mechanisms in photochemistry, in electrochemistry[1], in biological processes like photosynthesis and in scavenging of harmful radicals[2]. HAT is a single-step mechanism involving the transfer of an hydrogen atom. Conversely, PCET is a general mechanism involving the transfer of a proton and an electron which can occur in sequential steps. The terminology PCET is often used to describe the concerted mechanism which, more properly, should be called concerted PCET (cPCET). Thus, both in HAT and in cPCET the same reactants lead to the same products. Actually, the definitions of the two mechanism are ambiguous in the literature and, sometimes, chemically imprecise[3], but we can state that when the electron and the proton are transferred together at any point of the reaction coordinate, the mechanism is HAT. Conversely, cPCET occurs when the proton and the electron are transferred as different entities, usually starting or arriving in different moieties of the molecule. Thus, the orbital associated to the transferred electron is not located on the transferred proton in the reagents or in the products. Looking at the structure of the transition state is not sufficient to discriminate between HAT and cPCET since it requires to follow the electron flow along the reaction path; thus, the intrinsic bond orbital[4,5] (IBO) approach can be used. We analyze different case-studies focusing on radical scavenging reactions and using IBOs to understand the mechanistic features.
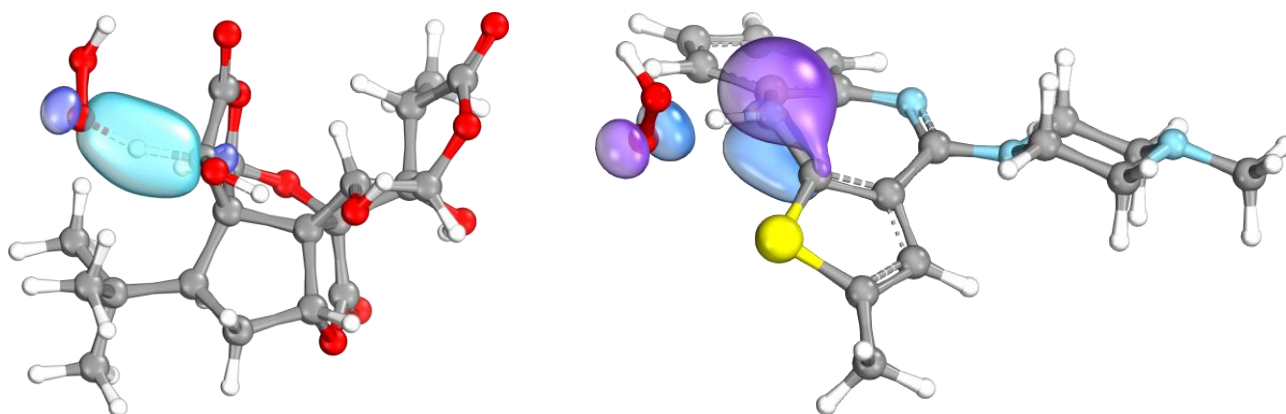
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Numerical methods in quantum chemistry

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1 Numerical basis sets

Gaussian type orbital (GTO) basis sets suffer from several drawbacks. First, tweaking the basis in one region of the domain changes the basis set as a whole since they are globally defined. Second, in calculations where the asymptotic behaviour of the wavefunction is different from that of Gaussian functions, the wavefunction is not well described by the basis set. Finally, the basis sets found in the literature are optimized for calculations without external interactions (say strong magnetic fields) present in the Hamiltonian and basis set truncation errors start to occur due to symmetry breakings. These problems are not present when using numerical basis sets, due to their flexibility and robustness. Can we use this property of numerical basis sets to develop GTO basis sets for extereme environments?

2 Reusable libraries

There is a zoo of different quantum chemistry codes, which all rely on the same mathematical procedures, e.g. quadrature and SCF. Instead of monolithic software, reusable libraries should be the future of quantum chemistry. The density functional library Libxc [S. Lehtola, C. Steigemann, M. J. T. Oliveira, and M. A. L. Marques (2018)] enables reproducable DFT calculations. What other topics could be the target for reusable software?