Computational Chemistry Modelling and Simulations of Finite Systems

Book of Abstracts

High Performance Computing Centre, University of Évora, Portugal
12-13 September 2023

HPC CHAIR & EUROCC2

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Opening Talk

New 'low-cost' electronic structure methods for large systems

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All widely used semi-empirical quantum chemical methods like PM6, DFTB, or GFN-xTB are formulated in a (almost) minimal basis set of atomic orbitals, which limits the achievable accuracy for many important chemical properties. Recently, we proposed a new special purpose tight-binding (TB) electronic Hamiltonian termed PTB[1] which is expressed in an accurate polarized valence double-zeta AO basis set (vDZP). The basis has been specially optimized in molecular DFT calculations using standard ECPs for all elements up to radon[2]. The PTB method aims primarily at reproducing the one-particle density matrix of a DFT reference calculation with the ωB97X-V range-separated hybrid density functional[3] in exactly the same AO basis. The combination of ωB97X(-V) with vDZP/ECP and an adjusted D4 dispersion correction defines a new member in our hierarchy of efficient composite electronic structure methods, termed ωB97X-3c[2] and is used as reference.

The PTB procedure is non-self-consistent employing only two matrix diagonalizations, includes new non-local potentials, as well as established parts from GFN-xTB and requires only simple overlap integrals as input. Compared to ωB97X-3c calculations, speedups of 3-4 orders of magnitude are achieved so that runs for molecules with 100-200 atoms are completed in a few seconds of computation time on standard desktop computers. The use of the PTB density in typical computational chemistry applications as well as for non-SCF-iterative DFT-GGA schemes is discussed.

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Day 1 - Session 1

Deciphering key interactions of ligand binding to proteins using high-level quantum mechanical methods (IT)

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Most of the methods used in the modelling of biomolecular systems rely on empirical parametrization and thus - at least indirectly - on some sort of training, limiting insights as well as applicability domain. A significant part of potential targets for drug design, like RNA or metalloproteins, are outside their usual applicability domain and require significant efforts of parametrization.

CCSD(T) is a generally applicable method, which is known to provide highly accurate results for all types of organic, main-group and transition metal-containing systems. The recently developed DLPNO-CCSD(T) method is an approximation to CCSD(T), providing similar accuracy at a significantly lower cost and scaling, and it is nowadays applied in routine calculations on systems with dozens to hundreds of atoms.

In this talk we present recent advances in the DLPNO-CCSD(T) method, which significantly improve its performance and accuracy, including e.g. extrapolation to the complete PNO space limit. We provide best practices for its application in real-life (bio)chemical applications. We show recent applications of the DLPNO-CCSD(T) method in biomolecular systems, including protein-ligand interactions as well RNA-ligand interactions. The computed accurate interaction energy can be decomposed into its components between different molecular fragments, and we show how this can be applied in deciphering key interactions between a ligand and its biomolecular target.

Effect of finite phonon lifetimes on the spin dynamics in a dysprosium single-molecule magnet (CT)

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The design of nanoscale information storage devices based on molecular magnets requires the preparation of materials with well-designed spin-phonon interactions such that magnetic memory persists at ambient temperatures. Understanding the fine details of spin-phonon coupling is thus crucial in designing new materials for this task. Of crucial importance for molecular spin dynamics is the phonon density of states, which directly impacts the timescale of magnetic memory, and a core part of this is the knowledge of phonon linewidths, which are inversely proportional to their lifetimes. In the past, we have assumed a fixed empirical linewidth of ca. 10 cm^{-1}, but others have suggested a strong temperature and energy dependence on the phonon linewidth [2]. However, the phonon linewidths are, in principle, accessible from first principles calculations; albeit at an extraordinary computational cost. By judiciously choosing a compact, high-symmetry molecular magnet viz [Dy(bbpen)Br] [3], we have directly obtained the ab initio linewidths. At 300 K, the linewidths vary on the order of 0.1 to 40 cm^{-1}, as a function of both energy and wavevector and have a marked temperature dependence. Subsequent ab initio calculations of the spin-phonon coupling and magnetic relaxation rates using these calculated linewidths are in good agreement with the experiment, however, there is no significant difference between rates obtained with fixed, mode-dependent or ab initio-calculated linewidths. Rather, the most important factor is the density of the q-point mesh of reciprocal space.

Computational exploration of the oxygen(1D) reactivity with C_2H_x hydrocarbons: astrochemical reaction pathways (CT)

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Understanding how complex organic molecules are formed in the harsh environment of the interstellar medium has long presented a significant puzzle to scientists. In molecular clouds, irradiation of ice plays a crucial role in producing complex organic molecules. In this work, we present ab-initio molecular dynamics (AIMD) simulations to model reaction taking place on ice with astronomical compositions. Specifically, we model the reactions between oxygen(1D) and C_YH_X on the ground and excited electronic states. We observe which organic molecules are formed and find several possible pathways along the potential energy surface for their formation. To predict relevant photochemical reaction pathways, we perform non-adiabatic ab-initio molecular dynamics and demonstrate the important role of the dynamics on the excited states by identifying secondary products that form on those surfaces. Additionally, we model the effect of the ice environment on the resulting products.

Day 1 - Session 2

fromage: A library for the study of molecular crystal excited states at the aggregate scale (IT)

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The study of photoexcitations in molecular aggregates faces the twofold problem of the increased computational cost associated with excited states and the complexity of the interactions among the constituent monomers. A mechanistic investigation of these processes requires the analysis of the intermolecular interactions, the effect of the environment, and 3D arrangements or crystal packing on the excited states. A considerable number of techniques have been tailored to navigate these obstacles; however, they are usually restricted to in-house codes and thus require a disproportionate effort to adopt by researchers approaching the field. In this talk, I will present the FRamewOrk for Molecular AGgregate Excitations (fromage), which implements a collection of such techniques in a Python library complemented with ready-to-use scripts including tools for geometrical analysis, exciton characterization, and a variety of ONIOM schemes. Each is illustrated by examples of diverse organic molecules in condensed phase settings. The program is available at https://github.com/Crespo-Otero-group/fromage.

A computational insight on the effect of encapsulation and Li functionalization on $Si_{12}C_{12}$ heterofullerene for H_2 adsorption: A strategy for effective hydrogen storage (CT)

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This article presents the hydrogen storage capacity of Ar encapsulated and Li functionalized $Si_{12}C_{12}$ heterofullerene using state-of-the-art Density Functional Theory (DFT) simulations. We find that the Li atom regioselectively prefers to bind at the top of the tetragonal sites of Ar encapsulated $Si_{12}C_{12}$ heterofullerene with a maximum binding energy of 2.02 eV. Our study reveals that inert gas Ar encapsulation inside bare $Si_{12}C_{12}$ provides greater stability to the heterofullerene by reducing the distortion. Hence, it provides a steady platform for Li decoration and successive H_2 adsorption. The adsorption energies of sequentially hydrogen-adsorbed $Si_{12}C_{12}Li_6$,$Ne@Si_{12}C_{12}Li_6$, and $Ar@Si_{12}C_{12}Li_6$ are compared, and it is observed that H_2 molecules prefer to adsorb over Li decorated $Ar@Si_{12}C_{12}$ with maximum adsorption energy. Each Li atom decorated over $Ar@Si_{12}C_{12}$ adsorbs a maximum of $5H_2$ molecules with an optimum adsorption energy of 0.11−0.22eV,resulting in a gravimetric density of 9.7wt% which is well above the US-DoE target. The adsorption mechanism of H2 molecules over $Ar@Si_{12}C_{12}Li_6$ has been thoroughly investigated using the electrostatic map and topological analyses. The type of interaction involved in the adsorption of H2 molecules over the $Ar@Si_{12}C_{12}Li_6$ surface is found to be a weak noncovalent interaction. Thermodynamic study reveals that almost all the $30H_2$ molecules remain adsorbed over the system at a low temperature of 100−120 K and undergo maximum desorption at 250−400 K, maintaining the structural integrity, which infers that the $Ar@Si_{12}C_{12}Li_6$ nanocage can be considered as a potential hydrogen storage material.

Modelling ultrafast dynamics in graphene nanoflakes and PAHs (CT)

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In this work, we study the deactivation pathways that take place after the UV excitation to the excited state manifold of coronene and circumcoronene, small moeities used as simplified models for graphene quantum dots, nanoflakes and poliaromatic hydrocarbons (PAHs)[1-3]. We use the wavepacket method ML-MCTDH[4] to study the time evolution of the states as well as their lifetimes.

The full-dimensional non-adiabatic dynamics results show that the different absorption spectra are only due to electronic delocalisation effects that change the excited state energies, but their structural dynamics are identical. Breathing and tilting motions drive the decay dynamics of the electronic states ndependently of the size of the aromatic system. This promising result allows the use of coronene as a model system for the dynamics of larger polycyclic aromatic hydrocarbons (PAHs) such as graphene sheets or nanoflakes.[4]

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Oxygen activation through a biomimetic tungsten(IV) complex (IT)

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Biology offers a source of inspiration for transformations of special relevance namely the activation of small molecules like O_2, CO_2, N_2, etc. One such example is acetylene hydratase which contains a formally W(IV) active site containing aromatic 1,2-dithiolate ligands, a cysteine residue, and an aqua ligand. This active site is generally called metallopterin, or more appropriately in this case tungstopterin.

Recently,[1] a stoichiometric oxygen activation was reported by Mösch-Zanetti and co-workers wherein a formally W(IV) complex $\{WO(6\text{-}MePyS)_2[P(CH_3)_3]\}$ (6-MePyS = 6-methylpyridine-2-thiolate) can effect a stoichiometric di-oxygen activation and cleavage. This complex is inspired by acetylene hydratase but instead of the aromatic dithiolate coordination it contains pyridine-thiolate as a ligand.

In this talk a mechanistic proposal will be given for this reaction. A density functional protocol [DKH2-PBE0-D4/x2c-TZVP(x2c-SVP)] will be used as a quantitative tool to evaluate barrier heights and free energies of intermediates in order to put forward quantum chemically viable routes for this transformation.

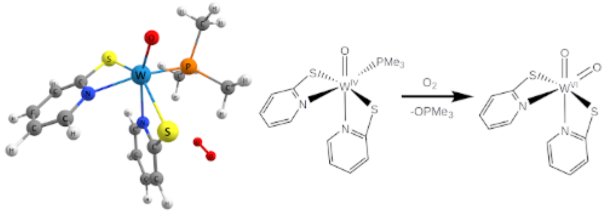

Figure 1: Tungsten complex used for oxygen capture and activation

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Day 2 - Session 1

Understanding the decisive role of global electron density transfer on reaction rates within Molecular Electron Density Theory (IT)

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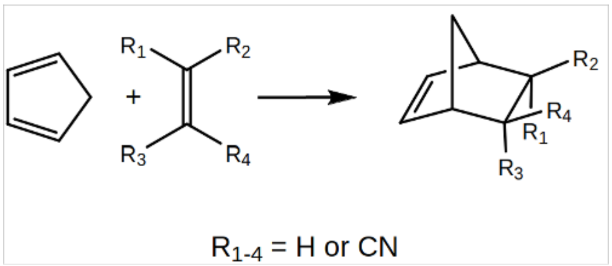
The polar Diels-Alder (P-DA) reactions between cyclopentadiene and the cyanoethylene series, experimentally studied by Sauer, have been studied[1] within the Molecular Electron Density Theory (MEDT)[2], which establishes that changes in electron density, but not molecular orbital interactions, are responsible for organic chemical reactivity. Accordingly, any study of reactivity within the framework of MEDT rules out the use of molecular orbitals to interpret reactivity and makes use, instead, of quantum chemical tools based on the analysis of density functions, such as the electron localisation function (ELF)[3] or the electron density itself through the Quantum Theory of Atoms in Molecules (QTAIM)[4] and Conceptual DFT (CDFT)[5].

CDFT analysis of the global and local electrophilicity power of these series of cyanoethylenes explains the increase of reaction rates with the increase of electron-withdrawing -CN substitution, as well as the (a)synchronous nature of the single bond formation process. The quantum topological energy partitioning method known as Interacting Quantum Atoms (IQA)[6] allows establishing that the global electron density transfer (GEDT)[7] taking place at the polar TSs is the main factor responsible for the experimentally observed acceleration, by favouring the bond formation processes. The combination of IQA with the Relative Energy Gradient (REG) [8] method along the reaction path, known as REG-IQA, reveals that while the rupture of the multiple bonds is the factor most contributing to the barrier, the favourable interactions in the forming single bond regions account for the driving force of the reactions.

In this talk, besides exploring the application of some of the quantum chemical tools most frequently used in MEDT studies, the new rationalization of these relevant experimental organic reactions within MEDT will be discussed.



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Modeling complex chemical reaction system - The MreaDy approach to simulate combustion-related processes (CT)

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MReaDy (Multiprocess Reaction Dynamics program) is a program for studying reactive dynamic systems using a global potential energy surface (gPES)[1]. Potential Energy Surfaces (PES), based on ab initio calculations, is a powerful tool to study the rate of elementary reactions and their dynamics. It is useful to compute state-to-state rate constants. In a more complex mechanism, we will be in the presence of different and simultaneous elementary reactions, corresponding to all the possible reactive and non-reactive collisions between the species present and leading to the respective products. Attempting to build a traditional PES for such a system quickly becomes impossible. To circumvent this problem, a global Potential Energy Surface (gPES) can be defined by integrating various PESs, each representing an elementary reaction expected to play a role in the chemical process. MReaDy is built in such a way and performs reactive dynamic calculations based on such gPES. We present the results of this approach to hydrogen combustion, HO_2 collisional stabilization[2,3], and confined combustion reaction in CNT[4].

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Automated reaction mechanism discovery with AutoMeKin2021 (IT)

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A computational protocol is proposed in this talk for use in discovering reaction mechanisms. The method does not rely on either chemical intuition or assumed a priori mechanisms, working in a fully automated fashion. The pipeline consists of three steps:

1. Exploration of reaction mechanisms through Molecular Dynamics simulations or chemical knowledge-based algorithms.
2. Use of Graph Theory to build the reaction network.
3. Kinetics simulations.

The method has been successfully employed to study combustion chemistry, cycloaddition reactions, photodissociations, organometallic catalysis, radiation damage of biological systems, simulation of mass spectrometry experiments, and astrochemistry, and a few examples will be given in this talk. This methodology has been implemented in the open-source program AutoMeKin [1].

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Day 2 - Session 2 - Posters

Theoretical studies on the permeability of boron and nitrogen-doped graphene nanoflakes for protium and deuterium ions (Poster)

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Two-dimensional (2D) monolayer nanomaterials are the thinnest possible membranes with interesting selective permeation characteristics. Among two-dimensional materials, graphenes and hexagonal boron nitride (h-BN) are the most promising membrane materials, which can even allow the separation of proton isotopes. The current work aims at understanding the higher reported permeability of h-BN by sequential doping of B and N atoms in graphene nanoflakes. The kinetic barriers were calculated with two different models of graphenes; coronene and dodecabenzocoronene via zero-point energy calculations at the transition state for proton permeability. The lower barriers for h-BN are mainly due to boron atoms. The trends of kinetic barriers are B < BN < N-doped graphenes. The permeation selectivity of graphene models increases with doping. Our studies suggest that boron-doped graphene models show an energy barrier of 0.04 eV for the permeation of proton, much lower than that of the model graphene and h-BN sheet, while nitrogen-doped graphenes have a very high energy barrier up to 7.44 eV for permeation. Therefore, boron-doped graphene models are suitable candidates for proton permeation. Moreover, the presence of carbon atoms in the periphery of BN sheets has significant negative effects on the permeation of proton isotopes, an unexplored dimension of the remote neighboring effect in 2-D materials. This study illustrates the need for permeation study through other hetero-2D surfaces, where interesting hidden chemistry is still unexplored.

Interaction of metal nitride clusters with amino acids (Poster)

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Reliable manipulation of the interface between 2D nanomaterials and biomolecules represents a current frontier in nanoscience. The ability to resolve the molecular-level structures of these bio-interfaces would provide a fundamental data set that is needed to enable systematic and knowledge-based progress in this area. These structures are challenging to obtain via experiment alone, and molecular simulations offer a complementary approach to address this problem. Compared with graphene, the interface between hexagonal boron nitride, aluminium nitride, gallium nitride and biomolecules is relatively understudied at present. Here, we use Density functional theory (DFT) calculations were performed to investigate the electronic properties and optical absorption spectra of amino acids with metal nitride clusters. The optical absorption spectra confirm that the metal nitride clusters are active in the ultraviolet region of electromagnetic radiation.

Sticking coefficient for atoms impinging on metallic surfaces (Poster)

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We are interested in the adhesion rate that occurs through the collision process between an atom or molecule and a surface. This adsorption mechanism is of great importance in the fields of Physics and Chemistry, explaining phenomena such as catalysis and corrosion. Qualitatively, the problem can be described as an initially neutral atom approaching a metallic surface. The overlap between the orbitals of this atom and those of the surface grows, allowing for charge transfer. When an electron is transferred, the atom becomes electrically charged, and consequently, an image charge potential appears, accelerating the particle towards the surface. In the subsequent collision, the generation of phonons and electron-hole pairs in the metal steals energy from the incident atom, which can become trapped in the attractive potential. Therefore, there is a probability that this particle will be adsorbed by the surface. The theoretical challenge is to calculate this probability, which is known as the Sticking coefficient S.

The Born-Oppenheimer approximation, traditionally used to separate the nuclear part of the wave function from the electronic part, is not capable of explaining the phenomenon. Additionally, we cannot use adiabatic approximations since it is precisely the non-adiabatic effects that enable energy loss from the atom. Therefore, a complete calculation employing a precise numerical treatment of the time-dependent wave function $\Psi(z, t)$ is necessary. The modeling of this problem is simplified by the normal incidence of a neutral hydrogen atom onto the surface of a metal, which will be described by a featureless conduction band. To describe the electronic part, we will employ Anderson's model of an impurity with an additional term that represents the image charge potential.

Simplistically, the procedure to find ⊠ is based on calculating the spectrum of electronic energies using the Numerical Renormalization Group (NRG) method for each value of the distance ⊠. In the initial state, the particle is far from the surface, and its wave function is the product of the initial electronic state and a Gaussian centered at an initial position, which describes the nuclear part. The Crank-Nicolson procedure allows for the calculation of the temporal evolution of the wave function until, after the collision, the function splits into one part localized near the surface and another that moves away from it. The spatial integral of the squared modulus of the first part determines the Sticking coefficient S.

Coarse-grained model of kerogen for the modelling of thermodynamic and transport properties of confined hydrocarbon fluids (Poster)

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Shale formations are recognized as an essential source of unconventional hydrocarbons, with kerogen, the embedded carbonaceous porous material, being the dominant source of valuable organic components. The unique nanostructure of kerogen, coupled with its inherent complexity, presents a significant challenge to unraveling the behavior of confined fluids and interactions within shale formations. Molecular modelling is the only available tool to explore the properties of kerogen at the atomic level. Compared to computationally intensive fully atomistic simulations, coarse-grained (CG) simulations provide a unique way to explore large kerogen structures of up to 1 million atoms with unprecedented detail and complexity within the microsecond scale. This work presents our recent advances in utilizing CG models to simulate kerogen structures encountered in shale formations. We discuss a strategy employed to build kerogen models, focusing on their structural representation, force field, and validation against experimental data.

Chemically-accurate CG models of different types of kerogen were constructed following a two-step process by a mimetic approach that obtains a kerogen slab from cross-linking kerogen units. We postulate that kerogen structures can be represented as a combination of aliphatic and aromatic molecular units such as n-dodecane, triphenylene, benzopyrene, perylene, and coronene. By combining these molecules and adopting the SAFT force field [2] for their CG models, we generated models for four types of kerogens of different maturity including 1A, 2B, and 2D. To generate a kerogen slab, randomly chosen kerogen units were placed in a simulation box and allowed to artificially cross-link. Each of the constructed kerogen models reproduces the analytically-determined elemental composition of kerogen including H/C ratio and average aromaticity or the ratio of aromatic carbons to the total number of carbon atoms.

The developed CG models successfully capture essential features of kerogen such as the experimental density of organic matter, compressibility, dynamic swelling, and diffusion of confined fluids. In contrast to atomistic simulations, these CG models offer a unique platform for studying the effects of different gas and oil production techniques, storage of carbon dioxide, hydrogen, and separation of organic liquids under mild and extreme conditions.

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A termolecular reaction $H + O_2 + M \rightarrow HO_2 + M$ - Studying the pressure dependence (Poster)

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To study the rate of elementary reactions and their dynamics, we use Potential Energy Surfaces, being useful to compute state-to-state rate constants. The usual approach to study such system is to make use of all the system's available rate constants and build a system of master equations. This procedure assumes that reactants are in thermal equilibrium. Studies seem to indicate that the number of non-reactive collisions can be small and the energy distribution of the intermediate species may be far from the Boltzmann distribution. MreaDy program (Multi-process Reactions Dynamics), aims to reproduce complex mechanisms, such as the hydrogen combustion, using accurate PES. We have introduced modifications on this program in order to study the pressure dependence of the reaction $H + O_2 + M \rightarrow HO_2 + M$. This reaction is one of the main sources of uncertainty when modelling hydrogen combustion chemistry, and being a termolecular reaction, it cannot be studied using normal classical trajectory programs. We start with hydrogen atoms and oxygen molecules, forming by collision excited

HO2*radicals. We can count how many of the excited HO2* radicals are stabilized by collisions at 1500, 2000, and 2500 K and pressures of 10, 20, 30 and 50 atm., and we calculate the formation rate of stable HO_2 radicals. We present preliminary results for this process showing a clear increase of the rate constant with pressure. We are also able to study the rate constants of the different reactions present in the system.

Theoretical study - Long range on LiH_2 (Poster)

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The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe1,2. The reaction LiH + H ⟶ Li + H_2 is considered to contribute to LiH depletion, while the hydrogen-exchange reaction LiH + H ⟶ LiH + H leads to the retention of LiH in this process.

In this work we report our recent studies on the long-range interactions between the reactants of those reactions. For the LiHH system, the main contribution for the long-range interactions is the dispersion interaction. To modeling the dispersion interaction, the parallel and perpendicular values of the polarizabilities, α, for the diatomics (H-H and Li-H) have been calculated and fitted.

The dispersion interaction coefficients C6 have been computed as C8 and C10 have been semiempirically estimated from C6 using a universal correlation. The total dispersion interaction was obtained as a function of Cn and inter-atomic distances3. The dynamical correlation energy has been obtained for the interaction H-LiH and Li-HH.

Experimental and theoretical studies of $O(^1D)$ + H_2O/D_2O gas-phase reactions (Poster)

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The reactions of atomic oxygen in its first electronically excited state, $O(^1D)$, play important roles in the chemistry of several planetary atmospheres, including Earth and Mars, where oxygen bearing molecules are among the major atmospheric constituents. In this work we report na experimental and theoretical study of the gas-phase reactions between $O(^1D)$ and H_2O and $O(^1D)$ and D_2O. On the experimental side, the kinetics of these reactions have been investigated over the 50–127 K range using a continuous flow Laval nozzle apparatus, coupled with pulsed laser photolysis and pulsed laser induced fluorescence for the production and detection of $O(^1D)$ atoms respectively. On the theoretical side, the existing full-dimensional ground X^1A potential energy surface for the H_2O_2 system involved in this process has been reinvestigated and enhanced to provide a better description of the barrierless H-atom abstraction pathway[2]. Based on this enhanced potential energy surface, quasiclassical trajectory calculations and ring polymer molecular dynamics simulations have been performed to obtain low temperature rate constants. The measured and calculated rate constants display similar behaviour above 100 K, showing little or no variation as a function of temperature. Below 100 K, the experimental rate constants increase dramatically, in contrast to the essentially temperature independent theoretical values. The possible origins of the divergence between experiment and theory at low temperatures are discussed.

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Day 2 - Session 3

Computer simulations of multiphoton absorption: Past, present and future (IT)

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Given the technological needs for molecular systems with tailored photophysical properties there are on-going efforts to develop cost-effective but reliable computational protocols supporting the design of efficient multiphoton absorbers. For example, it was demonstrated that two-photon absorption exhibits large application potential, including: photodynamic therapy, 3D microfabrication, or bioimaging based on two-photon microscopy.

The aim of the talk is to present theoretical frameworks for description of multiphoton absorption phenomena and a palette of computational methods - with emphasis put on their accuracy and limitations - that can be used in modeling of multiphoton absorbers. During the talk several aspect of computer simulations will be discussed: theory-experiment comparisons, simplistic models used in “structure-property” analyses, electron-vibration coupling, software availability, etc.

Computational description of light emission processes in organic TADF blue emitters (CT)

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Organic light emitting diodes (OLEDs) are among the optoelectronic devices for which research is employed intensively to enhance their performance. Blue OLEDs suffer from relatively short lifetimes and comparatively low lighting efficiency. One of the approaches to improve their characteristics is the development of luminophores with potential for thermally activated delayed fluorescence (TADF). These are compounds with high-energy excited triplet states and closely separated excited singlets. Therein, reverse intersystem crossing via thermal fluctuations might increase the overall luminescence quantum yield. In the current study, computational design is applied to estimate the characteristics of the light emission processes in a series of new organic compounds, which may emit blue light and have feasible TADF.

The structure and optical properties of a set of donor-spacer-acceptor molecules are computed with (TD)DFT [2]. The geometry of the ground and all relevant excited states is optimized. Energy and oscillator strength of the fluorescence and energy separation of the singlet and triplet excited states are used to assess the capacity for blue TADF-assisted emission. The rate constants of the various excited state deactivation processes are evaluated. The relative importance of several molecular factors for accomplishing the desired luminescence characteristics is tracked. Meta-binding to the spacer is found essential for a high-energy triplet excited state. To ensure non-zero oscillator strength of the fluorescence transition, the donor and the acceptor should close an angle lower than 75o in S1 and their frontier orbitals should overlap partially on the spacer. The pi-conjugation length of the chromophore should not exceed three rings for blue fluorescence to take place.

Following the derived molecular guidelines, several compounds are put forward as promising blue emitters for organic light-emitting diodes. Characteristic times for delayed fluorescence in the microsecond to millisecond time range are predicted for them. This research is funded by the Bulgarian National Scientific Fund, Project № KP-06-N49/3 from 26. 11. 2020.

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Unique features of hydrogen and halogen bonding (IT)

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Hydrogen bonds are omnipresent in biological and supramolecular chemistry. Nevertheless, they are still mostly represented in an oversimplified manner (positively charged hydrogen attracts close-by negatively charged heteroatom) which is easy to use but often fails to explain or even qualitatively reproduce experimental findings. In my lecture, I present a state-of-the art physical model, based on quantitative molecular orbital theory, which enables a quantum-mechanically sound, yet intuitive approach to the interesting complexity of the hydrogen bond. The latter can be dissected into understandable contributions such as covalent bonding and Pauli repulsion between occupied orbitals. Complex and seemingly exotic phenomena are unraveled and explained in a unified manner. Furthermore, the similarities between hydrogen and halogen bonding are addressed.

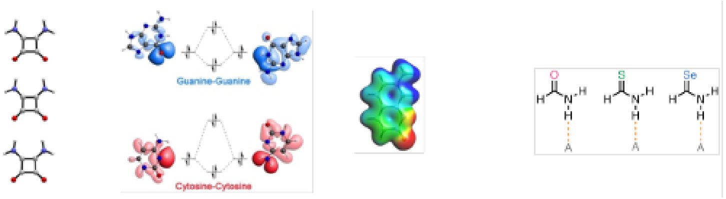

Figure 2: Different aspects of the nature of hydrogen-bonded systems.

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