



Book of abstracts

September 11th–14th, 2024
Sveti Martin na Muri, Croatia, EU

Foreword

We are pleased to welcome you to the 19th Central European Symposium on Theoretical Chemistry (CESTC) in Sveti Martin na Muri, Croatia, from September 11 to 14, 2024. The annual CESTC meetings are milestones in our ongoing efforts to advance theoretical and computational chemistry across Central Europe.

We hope this year's symposium will continue this tradition by providing opportunities to explore the latest developments in methods and applications. Young researchers, in particular, will have the chance to present their work to a community of experts. We are confident that this meeting will offer a valuable platform for discussions, collaborations, and progress toward our goals.

We wish everyone a successful and inspiring symposium.

Nađa and Tomica

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Program of the CESTC2024

Wednesday, September 11 th 2024		
ARRIVAL		
14:50–15:00	Opening	
Session 1 (Jozef Noga)		
15:00–15:40	IL01 Péter Surján	Real eigenvalues of non-hermitian operators
15:40–16:20	IL02 Aleksandra Tucholska	Duality of particle-hole and particle-particle theories for strongly correlated electronic systems
16:20–17:00	Coffee break	
Session 2 (Jiri Pittner)		
17:00–17:40	IL03 Marin Sapunar	Insight into the motion of electrons from mixed quantum-classical dynamics
17:40–18:00	OC01 Brigitta Bachmair	Roadmap to enhanced path sampling for photoreactions
18:00–18:20	OC02 Zsuzsanna É. Mihálka	Pair-function based models with an explicitly correlated extension
18:20–18:40		
18:40–20:00	Dinner	
Poster session 1		
20:00–	Posters	

Thursday, September 12 th 2024		
Session 3 (Anne-Marie Kelterer)		
9:00–9:40	IL04 Milan Ončák	(Photo)chemistry on Metal Oxide Surface
9:40–10:00	OC03 Demeter Tzeli	Accurate theoretical investigations of photophysical processes of Chemosensors
10:00–10:20	OC04 Ehsan Masumian	DFT-SAPT for a variety of intermolecular interactions
10:20–11:00	Coffee break	
Session 4 (Miroslav Medved)		
11:00–11:40	IL05 Zdeněk Mašín	Attosecond dynamics in photoionization and electron scattering from molecules: monomers vs dimers
11:40–12:20	IL06 Namrata Jaykhedkar	Theoretical modelling of energy materials: Insights from ML accelerated AIMD
12:20–12:40	OC05 Michael Gatt	MOLGA - a Julia-Based High-Performance Molecular Genetic Algorithm
12:40–14:00	Lunch	
14:00–18:20	PLEIN-AIR DISCUSSION@MAĐERKA’S BREG	
18:30–20:00	Dinner	
Poster session 2		
20:00–	Posters	

Friday, September 13 th 2024		
Session 5 (Agnes Szabados)		
9:00–9:40	IL07 Michal Malček	Potential use of graphene-based nanomaterials as hydrogen storage devices

9:40–10:00	OC06 Matej Uhliar	Theoretical proposition of potential aromatic units for optoelectronics
10:00–10:20	OC07 Szymon Śmiga	Towards the Kohn-Sham adiabatic-connection interpolation models with broader applicability
10:20–11:00	Coffee break	
Session 6 (Marko Tomislav Cvitaš)		
11:00–11:40	IL08 Ivor Lončarić	Modeling Molecular Crystals with Machine Learning Interatomic Potentials
11:40–12:00	OC08 Gabriel Schöpfer	Dissociation Kinetics in Hydrated Ions through Master Equation Modeling
12:00–12:20	OC09 Iulia Emilia Brumboiu	Core-hole delocalization effects in computational X-ray spectroscopy
12:20–12:40	OC10 Nenad Mijić	Benchmark of linear algebra for quantum chemical computations
12:40–14:00	Lunch	
Session 7 (A. Daniel Boese)		
14:00–14:40	IL09 Eva Pluhařová	Molecular Simulations of Enzymes in Various Solvents: From Domain Motion to the Active Site
14:40–15:00	OC11 Luca Grisanti	Modeling molecular assemblies in solutions to understand interaction with light
15:00–15:20	OC12 Omid Moghaddam	Molecular dynamics simulations of dynamic and static properties of cyclic polyacrylates
15:20–15:40	OC13 Piotr Michalak	Rank-reduced equation-of-motion coupled cluster triples: an accurate and affordable way of obtaining excitation energies of molecules
15:40–16:20	Coffee break	
Session 8 (Attila Tajti)		
16:20–17:00	IL10 Oldamur Hollóczki	Modeling nanoplastics and their interactions with biomolecules
17:00–17:20	OC14 Marcin Modrzejewski	Beyond-RPA description of many-body noncovalent interactions in molecular crystals
17:20–17:40	OC15 Antonio Prlj	Simulating ultrafast molecular photodynamics: from initial conditions to observables
17:40–18:00	OC16 Marcin Andrzejak	Impulsive Vibrational Spectra Modeling for Singlet Fission Studies

18:00–18:20	OC17 Rupam Gayen	Simulating a Mechanochemical Reaction: Molecular Dynamics Modelling of Mechanical Activation and Relaxation
18:30–20:00	Gala dinner	

Saturday, September 14 th 2024		
Session 9 (Danijela Barić)		
9:00–9:40	IL11 Michał Lesiuk	Approximate coupled cluster models based on tensor decomposition techniques
9:40–10:00	OC18 Tomáš Hrivnák	Investigation into photophysical properties of stacked PAHs as structured models for carbon-dot photosensitizers
10:00–10:20	OC19 András Gombás	Perturbation-adapted Perturbation Theory: Towards a Multi-Reference Approach
10:20–11:00	Coffee break	
Session 10 (Michal Przybytek)		
11:00–11:40	IL012 Tomislav Piteša	Excitonic Configuration Interaction: Theory and Early-Stage Applications
11:40–12:00	OC20 Nina Tokić	Quantum tunneling in the low-lying water hexamer isomers
12:00–12:20		
12:20–12:40		
12:40–14:00	Lunch	
DEPARTURE		

Scientific Board

Austria

- Leticia González
- Annemarie Kelterer

Croatia

- Nađa Došlić
- Tomica Hrenar

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- Petr Slavíček

Hungary

- Ágnes Szabados
- Péter Szalay

Poland

- Monika Musiał
- Michał Przybytek

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Lectures

IL 1. Real eigenvalues of non-hermitian operators

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Textbook knowledge states that Hermitian operators possess real eigenvalues. We will discuss two generalizations of this theorem.

(i) As Löwdin emphasized, this statement holds true only in a space with a positive definite metric.

(ii) Real eigenvalues of non-hermitian may also exist.

A trivial example for (ii) is operator $S H S^{-1}$, where H is hermitian, but the commutator $[S, H]$ is not zero.

Another example is provided by the Roothaan equations $F C = e S C$, where F and S (the Fockian and the overlap) are hermitian, and S is additionally positive definite. Rearranging these equations as $S^{-1} F C = e C$, one obtains a non-hermitian matrix $S^{-1} F$ (S and F do not commute in general), whose eigenvalues e are nevertheless always real.

In fact, there is a theorem in linear algebra, that a non-hermitian matrix has solely real eigenvalues if and only if it can be decomposed as a product of two (not commuting) hermitian matrix so that one of them is positive definite.

We recapitulate the proof of this theorem for matrices, and provide its generalizations to operators over a Hilbert space.

The theorem is applied for non-hermitian effective Hamiltonians (see Bloch equation, multi-reference perturbation theory).

IL 2. Duality of particle-hole and particle-particle theories for strongly correlated electronic systems

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We present a novel method for calculating the correlation energy in strongly correlated systems, which combines the particle-particle (pp) and particle-hole (ph) variants of the multireference random phase approximation (RPA) in the adiabatic connection framework. The proposed approach originates from the physical equivalence between the ph and pp descriptions of a subset of correlation energy contributions. This allows a hybrid energy expression, where ph-RPA and pp-RPA are rigorously combined into a single formula without double counting. The new approach uses only one- and two-electron reduced density matrices, but describes all physical contributions present in second-order perturbation theory, NEVPT2, which requires up to four-electron matrices. The numerical validation includes ground and excited state energies as well as singlet-triplet gaps. Possibility to extend this method to higher orders is presented.

IL 3. Insight into the motion of electrons from mixed quantum-classical dynamics

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Nonadiabatic dynamics simulations beyond the Born-Oppenheimer approximation are a necessary tool for understanding reactions involving electronically excited states of molecules. The two dominant approaches to these simulations are mixed quantum-classical approaches, most commonly trajectory surface hopping (TSH) methods, and fully quantum approaches, such as multi-configuration time-dependent Hartree. The approximation of treating the nuclei as classical particles in mixed quantum-classical approaches greatly simplifies calculations of this type and allows the treatment of systems with many degrees of freedom, limited only by the cost of evaluating the potential energy surfaces. Apart from the computational cost, simulations of this type are simpler because they can be run "on-the-fly" without pregenerating diabatic potential energy surfaces. However, results obtained from TSH simulations in terms of adiabatic states contain (without further processing) significantly less information on the changes in the electronic excited states compared to analogous results obtained in terms of diabatic states.

Particularly when the goal of a simulation is to explain the observations from a time-resolve spectroscopy experiment, the lack of focus on electronic wave functions in mixed quantum-classical approaches can severely restrict the usefulness of the simulation. Here, I will present recent attempts to create a set of tools for analysis of TSH simulations with the goal of obtaining approximate diabatic populations and similar properties without the need to generate global diabatic potentials [1]. These tools allow for easier assignment of spectra based on TSH simulations [2, 3], but also simplify comparisons between TSH and fully quantum approaches [4, 5].

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IL 4. (Photo)chemistry on Metal Oxide Surface

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Photochemistry in bulk and on surfaces plays a pivotal role in many natural and industrial processes. However, it is often somewhat disregarded by the quantum chemistry community. In my presentation, I will introduce some challenges connected to modeling of photochemical processes in complex environments.

First, I will focus on the change of color introduced by adding cobalt ions into MgO nanocubes that is connected to formally forbidden transitions that are becoming allowed through symmetry breaking and lattice vibrations.[1] Also, I will show that Path Integral Monte Carlo (PIMC) is a promising approach for treating systems that coexist in multiple electronic states at finite temperatures.[2]

In the second part, I will focus on oxygen radicals, important species in a wide range of chemical reactions and applications including cell signalling, sensing and catalysis. I will show how their spectral fingerprints and reactivity on MgO nanocubes can be modelled through quantum chemical approaches, sampling different oxygen radical positions (neat surface, defect, edge, corner...).[3]

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IL 5. Attosecond dynamics in photoionization of monomers and dimers

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Over the last few years we have developed tools for efficient description of continuum and resonant states (temporary bound states) in molecules and their applications to photoionization and electron-molecule scattering [1, 2]. The tools are based on R-matrix (Green's function) approach for solving the Schrödinger equation and are implemented within the UKRmol+ suite. We have used them to accurately calculate attosecond time-delays in monomers and to construct the first efficient models for description of photoionization of molecular dimers.

Attosecond time-delays have become a frequently studied observable, thanks to the development of the RABITT scheme (Reconstruction of Attosecond Beating by Interference of two-photon Transitions) which allows measuring collision time-delays in experiments combining high harmonics and the fundamental driving infrared laser field [3,4]. The commonly used approach to study such multi-photon processes is by employing explicitly time-dependent calculations, see e.g. [5]. Nevertheless, those calculations are naturally highly computationally demanding and don't allow us to use the state of art models available for single-photon ionization, see e.g. [6]. To overcome this limitation we have recently developed a new time-independent (stationary) approach, based on the R-matrix method, for direct calculation of multi-photon matrix elements for complex molecules [1]. While allowing to employ highly sophisticated multi-channel models (including hundreds of ionic states), it expands the range of tools available for analysis of various multi-photon phenomena.

Applied to RABITT, the stationary method led to the discovery of two new contributions to the RABITT delay: the electronic coupling delay and the dipole laser coupling delay [7,8]. Typically, RABITT delays are used to provide information only about the field-free scattering delay but the new contributions show the potential of the method to study laser-driven electron-molecule interactions too. In this contribution we will discuss our results for non-polar and polar molecules, including a comparison with recent experiments in methane [9], where we showed that the RABITT delays can be represented using complex β parameters, similarly to the atomic case.

The R-matrix calculations are variational which presents the usual challenge of exponential scaling of the problem with system size. To alleviate this problem we have implemented the ORMAS approach and applied it to study photoionization and resonance formation in dimers of formic acid and ammonia [10].

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IL 6. Theoretical modelling of energy materials: Insights from ML accelerated AIMD

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Lipases and closely-related cutinases are important enzymes for commercial bioprocessing applications. New lipases with unique properties are being sought by many industry sectors. Recent studies in this laboratory isolated a novel lipase (AML) with high thermal and solvent stability produced by *Amycolatopsis mediterranei*.

Modelling studies revealed an exposed active site *without* the classical lid structure seen in true lipases. The homology of AML with other polyester degrading enzymes prompted an investigation of AML for applications in plastics degradation. AML was shown to be highly active in degrading the plastics poly(caprolactone) and poly(butylene) succinate. These materials were hydrolysed at ambient temperature by 80 and 90% respectively. However, AML showed no activity towards PLA and PET. AML was examined for its ability to support catalysis in Deep Eutectic Solvents (DES). It was stable in this medium and activated two-fold in the presence of choline chloride based eutectic solvents. The presence of choline chloride alone greatly enhanced its activity and thermostability. AML was shown to catalyse the synthesis of sugar fatty acid esters in the presence of DES. Taken together these studies point to the potential for AML to be a robust, versatile industrial biocatalyst with application in the biodegradation of plastic polyesters and biocatalytic synthesis of sugar fatty acids.

IL 7. Potential use of graphene-based nanomaterials as hydrogen storage devices

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Hydrogen energy is considered to play an important role in solving the problems of energy crisis or decarbonization of environment. Hydrogen gas is an excellent energy carrier but its storage under ambient conditions remains to be an unresolved issue. Current hydrogen storage technologies ranging from energetically demanding high-pressure tanks and liquefaction to more advanced methods such as liquid organic hydrogen carriers or metal-organic frameworks. Another energetically feasible option is reversible hydrogen adsorption and desorption on the specific adsorbent. Graphene-based materials already found utilization as adsorbents of individual gas molecules. Their adsorption ability can be significantly improved by modification with heteroatoms, such as transition metals (TMs). The TM atom in such systems serve as reaction center or adsorption site, e.g. for interaction with H₂ molecule.

Hydrogen binding/adsorption performance of circumcoronene (CC) doped with first row TM atoms was studied at the DFT level of theory [1-3]. It was shown that the most promising materials for H₂ storage are CCs doped with Fe, followed by Cr and Mn. These systems are able to bind up to three H₂ molecules per one TM atom via formation of η^2 -dihydrogen bonds. Formation of these bonds was confirmed also by Quantum Theory of Atoms in Molecules and via Density of States analysis. On the other hand, CC decorated with Fe possess the ability to cleave H₂ molecule, resulting in the formation of FeH₂ residue [4].

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IL 8. Modeling Molecular Crystals with Machine Learning Interatomic Potentials

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Molecular crystals are a common and important class of crystalline materials. However, modelling molecular crystals based on first principles (eg. with density functional theory) is often difficult due to the size of a typical unit cell. Therefore, high-throughput calculations for the discovery of useful properties are rare. In this presentation, I will show how machine-learned interatomic potentials can enable accurate and fast calculations of mechanical and thermal properties of molecular crystals enabling an understanding of experimental observations as well as high-throughput search for materials with the desired properties. In principle, to train machine learning potential one would need to create a sufficiently large database of molecular crystals calculated with the desired accuracy. This is also a very challenging task and we will show how to avoid this step using transfer learning and existing databases of small systems.

IL 9. Molecular Simulations of Enzymes in Various Solvents: From Domain Motion to the Active Site

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Enzymes are extraordinary catalysts satisfying the needs of living organisms. Their natural cellular environment is aqueous, but crowded, because macromolecules occupy up to 40 % of the volume of the cells.

Perhaps more surprisingly, a wide range of enzymes do not denature and moreover retain catalytic activity in organic solvents. This opens a path for carrying out new unnatural reactions. However, proteins are frequently studied in aqueous solutions without the presence of other macromolecules or organic molecules both in vitro and in silico.

The change of the reaction medium alters protein conformational equilibria, substrate binding, enzyme kinetics and selectivity. Thus, it is highly desirable to investigate enzymes not just in aqueous buffers.

We focus on two interesting systems: *Candida antarctica* lipase B in organic solvents and Glutamate dehydrogenase in crowded environment. By means of classical molecular dynamics simulations we characterize motion of the protein domains, conformational fluctuations and behaviour of the substrates in the active site. The results shall provide deeper understating of enzymes' functioning in various media.

IL 10. Implementation and application of biocatalysis at Servier

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Through the fragmentation of plastic waste, micro- and nanoplastics (MNPs) are formed and distributed through our environment. While these particles have been observed in food, various organisms, and even in human tissues, their impact is still unclear, partly due to the variety of MNPs in composition, size, shape, compounds at their surface (i.e. corona), and partly due to the limitations of analytical techniques to observe them. Molecular modeling offers a structural insight into the interactions of MNPs with biomolecular systems, leading to a deeper understanding of the environmental and health effects of these pollutants [1].

Molecular dynamics simulations have revealed the fundamental interactions between MNPs and lipid bilayers [2]. In the passing of the MNP through a membrane, the role of the corona was shown. Depending on the composition of the corona, the thermodynamics of the sorption into the bilayer (e.g. a blood-brain barrier model) can be varied significantly. Thereby it is feasible that with the right compounds adsorbed onto the surface of the particle, the passive transmembrane transport through the blood-brain barrier can be thermodynamically and kinetically possible. In agreement, only two hours after mice are fed with food containing environmentally relevant concentration of MNPs, plastic particles appear in their brain tissue just after two hours [2].

When interacting with biomolecules, the composition of the MNP is decisive. Simulations and quantum chemical calculations showed that MNPs can alter the secondary structure of proteins [3, 4]. Depending on the plastic compound, the relative energy between α -helix and β -sheet structures of the same protein can be shifted significantly. While polyethylene was found to stabilize the helix, nylon-6,6 was prone to change the peptide into a β -sheet [2, 3]. Since neurodegenerative diseases may be related to changes in secondary structures of certain proteins, these findings show that further research in the field is essential.

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IL 11. Approximate coupled cluster models based on tensor decomposition techniques

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In this talk, recent advances in the development of approximate coupled cluster models based on tensor decomposition techniques will be outlined. In particular, we will focus on high-level methods, namely coupled-cluster method with single, double, and triple excitations (CCSDT) [1,2] and CCSDT(Q) perturbative correction [3]. For the compression of the coupled-cluster triple and quadruple amplitudes tensor we employ the Tucker format [4]. The efficiency of the method relies on the fact that the optimal size of the excitation subspace sufficient to obtain a constant relative accuracy in the correlation energy scales linearly with the size of the system. Combined with proper factorization of the coupled-cluster equations this leads to N^6 scaling of the computational costs of the compressed CCSDT method [5,6], compared with the N^8 scaling for the conventional (uncompressed) CCSDT. The (Q) correction can be evaluated with N^7 cost [7]. The method is chemically accurate and even more demanding levels of accuracy, such as 0.1 kJ/mol, can be obtained with a reasonable size of the excitation subspace.

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IL 12. Excitonic Configuration Interaction: Theory and Early-Stage Applications

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Nowadays there is a versatile variety of accurate electronic-structure methods for the excited-state calculations, ranging from single-reference (TD-DFT, MP/ADC, EOM-CC etc.) to the multi-reference (CASPT2, MRCI etc.) ones. However, all of these methods scale unfavorably with the system size, and therefore are often not applicable on large molecules, such as e.g. multichromophoric systems. An alternative to the direct treatment of the full system in these cases is to employ an excitonic model. The underlying philosophy of all excitonic models is to obtain the electronic states of individual chromophores (site states), and then construct a set of their antisymmetrized products (excitonic basis). The full-system Hamiltonian is then represented in the excitonic basis and diagonalized [1]. Many of the so-far developed models rely on the famous Frenkel excitonic model, which employs an ad hoc parametrization the Hamiltonian in the basis of only local-excitation products – ones having only one site in an excited state [2,3].

In this talk I will present the Excitonic Configuration Interaction (ECI) method – an excitonic-like approach which (i) self-consistently constructs the excitonic basis so that it minimizes the full-system ground-state energy, (ii) can account for the contributions of both local and multi-local excitations, as well as the charge-transfer configurations, to the full-system states, and (iii) builds the exciton Hamiltonian independently of the method employed in the site-state calculations. The performance of ECI, as well as its comparison with the Frenkel model, will be illustrated on an array of testing examples of multichromophoric systems.

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OC 1. Roadmap to enhanced path sampling for photoreactions

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The study of photoreactions occurring on multiple coupled potential energy surfaces is crucial for understanding a wide range of phenomena including atmospheric processes. Oftentimes, these pose the additional challenge of involving rare channels, i.e. infrequent and yet relevant reactions whose timescales exceed that of a typical time step by many orders of magnitude in standard nonadiabatic dynamics simulations, e.g. in trajectory surface hopping (TSH)[1]. One example is the photodissociation of ammonia, NH₃, where machine learning potentials coupled with the SHARC program package[2] allowed us to describe the rare NH + H₂ dissociation channel ($\approx 0.58\%$ yield after 1 ps).[3]

Enhanced sampling methods, such as path sampling algorithms [4], are able to drastically reduce the cost of simulating the dynamics of rare reactions, but are currently almost exclusively limited to a single electronic state. Therefore, we recently extended the forward flux sampling technique to electronically excited states, coined Nonadiabatic Forward Flux Sampling (NAFFS).[5] The attempt to apply NAFFS to the rare photodissociation channel of ammonia pointed out the limitations of this methodology, which arise from the lack of time-reversibility of the underlying stochastic TSH. To overcome this difficulty, the Mapping Approach to Surface Hopping (MASH)[6,7], which is inherently time-reversible, holds promise to develop more efficient path sampling strategies for photochemical processes. Accordingly, we implemented MASH into the program package SHARC to be able to describe any number of electronic states including various spin multiplicities, such that intersystem crossing can be simulated as well. Additionally, this allows the use of MASH with a variety of quantum chemistry codes. To conclude, we present our recent endeavors to leverage the properties of MASH to achieve a feasible, accurate and widely applicable strategy for simulating rare photoreactions.

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OC 2. Pair-function based models with an explicitly correlated extension

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Obtaining a balanced description of static and dynamic correlation effects is often a challenge, especially if computational feasibility is of concern. Our approach to this problem relies on a pair-function (geminal) based reference which is augmented by an explicitly correlated (F12) correction.

On one hand, geminal-based frameworks are able to model static effects at polynomial cost, making them a more economical alternative to the complete active space method. Notably, pair Coupled-Cluster Doubles (pCCD) belongs to this class of wavefunctions. On the other hand, explicit inclusion of the interelectronic coordinate in the Ansatz can incorporate dynamic correlation and improves convergence with respect to the basis set size.

Motivated by a pCCD-based F12 approach [1], which could preserve all of these favourable properties, we explore different possibilities which combine geminal-based reference functions with the explicitly correlated framework. Our main focus is the family of wavefunctions built as the antisymmetrized product of strongly orthogonal geminals (termed SLG). The F12 correction is obtained as a perturbative (PT) correction to SLG, based on the existence of effective geminal Hamiltonians. The resulting scheme is an extension of the conventional SLG-based PT approach [2]. The special structure of SLG ensures that the F12 correction can also be computed efficiently.

We present illustrative numerical examples which assess the amount of dynamic correlation that can be recovered by the resulting SLG-F12 scheme. The effectiveness of the method will also be tested based on the quality of singlet-triplet energy gaps.

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OC 3. Accurate theoretical investigations of photophysical processes of Chemosensors

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The development of stand-alone luminescence-based chemosensors which exemplify selectivity, sensitivity, and applicability is hot research area¹. Up to now supramolecular luminescent sensors have solved many issues in a variety of research areas, *i.e.*, in biological imaging,[2] in medical diagnostics,[3] in national security,[4] in food and agricultural safety,[5] in environment,[6] *etc.*

Theoretically, the accurate calculation of the electronic structure, absorption, and fluorescence spectra of luminescence-based chemosensors candidate and the prediction of the most promising ones is not a routine task.

In this presentation, the photophysical properties of chemosensors of Ca^{2+} , Na^+ , Hg^{2+} , Zn^{2+} , and Sn^{2+} will be discussed and analyzed. Some of these sensors also can serve as molecular logic gates.[7–9] Additionally, key factors for the accurate prediction of the absorption and fluorescence spectra of chemosensors will be analyzed.[8–10] Finally, structural characteristics of molecules that can make them ideal molecules as sensors will be discussed.[9–10]

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OC 4. DFT-SAPT for a variety of intermolecular interactions

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We calculate DFT-SAPT (symmetry-adapted perturbation theory based on DFT) [1] interaction energies extrapolated to the complete basis set limit for 2312 different dimer potential curves [2]. The data set consists of typical and ionic hydrogen bonds, chalcogen, halogen, and pnictogen bonds, dispersion-dominant interactions, repulsive contacts, and mixed interactions. Neutral noncovalent interactions (NCIs) containing only lighter nonmetals and H are the ideal systems for DFT-SAPT. However, halogen bonds, H-bonds containing heavier atoms, ionic H-bonds, and repulsive contacts require careful consideration. For pnictogen and chalcogen bonds, accurate results can be obtained using regularized SAPT [3]. Interestingly, the analysis of dispersion energy decay rates shows that the contribution of C6 coefficient to the overall dispersion energy can be considered an indicative to predict the type of interaction. A contribution below 20% usually indicates σ -hole interactions, while a contribution above 50% is associated with dispersion-dominant interactions. Hydrogen bonds generally fall within the range between these two extremes, yielding another method to distinguish between these bonding types [4].

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OC 5. MOLGA - a Julia-Based High-Performance Molecular Genetic Algorithm

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There is a demand for comprehensive sets of molecular structures to compare theoretical results with experimental data in order to advance our understanding of fundamental chemical phenomena. Here, we present an approach that combines a genetic algorithm (GA) with local quantum-chemical optimizations and graph-based structure clustering to discover chemical structures. Utilizing the Julia programming language, we implement a distributed-memory parallelization model to enhance overall performance [1].

We generate the initial population by randomly distributing the specified atoms and molecule fragments in a cuboid box. The GA starts by employing fast quantum-chemical methods from XTB, Gaussian, or DFTB to optimize the geometries and calculate the energies of the structures.

In many practical cases, a substantial part of the chemical space needs to be explored, often resulting in a high number of possible isomers. Therefore, a large genetic diversity is needed within the GA's population. Our goal is to obtain structures from many distinct groups. Methodologically, we try to describe connectivity between the atoms by checking a set of distance rules and create an undirected, vertex-labelled graph representing the bonds. Subsequently, we use graph isomorphism to identify structures belonging to a group.

We have already successfully used our open-source implementation to find structures of C₁₂₀⁺ and explain the experimentally observed vibrational features [2]. Another application involves using our genetic algorithm to search for oligomers of halogenated molecules acetyl chloride CH₃COCl and trichloroacetic acid CCl₃COCl that were measured in the group of M. Fárnik (J. Heyrovský, Prague).

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OC 6. Theoretical proposition of potential aromatic units for optoelectronics

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Organic materials applicable in optoelectronics consist of added or linked aromatic units. However, not all aromatic structures are suitable for these purposes. Thus, the systematic theoretical study on the suitability of several monocyclic, bicyclic, tricyclic and pentacyclic molecules with their perfluorinated counterparts was conducted. Some of our group of studied molecules are already in use [1-3].

This contribution showcases some of the results of this structural analysis. Presented results are focused on the evaluation of vertical ionization potential, vertical electron affinity and electrochemical energy gap. Additionally, since aromatic molecules are involved, the evaluation of aromaticity with use of Harmonic Oscillator Models of Electron Delocalization (HOMED) index [4] and Bond Order Index (BOI) [5] was also part of the discussion.

In the light of acquired results, we have also proposed some aromatic molecules for synthesis and experimental spectro-electrochemical characterisation. These molecules, such as perfluorinated pentacyclic molecules with central five-membered ring, could be used in optoelectronics as n-type semiconductors.

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OC 7. Towards the Kohn-Sham adiabatic-connection interpolation models with broader applicability

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Adiabatic connection models (ACMs), which interpolate between the limits of weak and strong interaction, are powerful tools for building accurate exchange-correlation functional approximations within the Kohn-Sham Density Functional Theory (KS-DFT)[1].

ACMs functionals include both exact-exchange and the second-order correlation energy, as well as an interpolating function toward the strictly-correlated electron (SCE) regime. Several interpolating functions have been proposed in the last years targeting different properties, yet an accurate ACMs approach with broad applicability is still missing.

Recently, we have proposed an ACM functional that was made accurate for the three-dimensional (3D) uniform electron gas as well as for model metal clusters. In this work, we present an ACM functional (named genISI2) which is very accurate for both three-dimensional (3D) and two-dimensional (2D) uniform electron gases and for the quasi-2D infinite barrier model, where most of the exchange-correlation functionals fail badly, as well as for strongly correlated two-electrons systems.

Using the exact-exchange Kohn-Sham orbitals, we have also assessed the genISI2 for various molecular systems, showing a superior performance with respect to the other ACM methods for total energies, atomization energies, and ionization potentials. The genISI2 functional can thus find application in a broad range of systems and properties.

OC 8. Dissociation Kinetics in Hydrated Ions through Master Equation Modeling

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Climate change is one of the most pressing problems of our society. However, many molecular processes like aerosol formation and dissociation are still only poorly understood. One key challenge is the transition from describing small molecules which are approachable both theoretically and experimentally, to larger molecules like realistically sized aerosols as they appear in the atmosphere. Larger molecules involve two major problems: Firstly, quantum chemical calculations are computationally more expensive. Secondly, many isomers might be accessible at moderate temperatures. The goal of this work is to find strategies of how to best deal with the plentitude of isomers and thus make one step in the direction of being able to describe kinetics of larger molecules from a theoretical point of view.

To model the dissociation kinetics of ionic clusters, we showed that not only the lowest-lying isomer should be considered, but also higher-lying isomers play a significant role.[1] However, for example, clusters of $[\text{O}_2(\text{H}_2\text{O})_n]^-$ consist of a vastly growing number of isomers as n increases. Thus, considering all isomers in the kinetic modelling becomes more and more challenging.

Therefore, we take a subset of all isomers which describes the dissociation kinetics almost as good as the full set of isomers. With these isomers, we calculate the microscopic dissociation rates with a modified RRKM theory, where all isomers are treated on the same footing (AWATAR).[2] These rates are then used in a master equation, together with rates for absorption and emission of infrared radiation, to obtain temperature-dependent rate coefficients which can be directly compared with experimental data.

The structures for the modelling are obtained using a multi-step process where the initial set of isomers is generated using our in-house genetic algorithm [3] based on the semi-empirical xTB method. The structures are then clustered using our graph-based clustering algorithm [4] to sort out structures that are very similar. The remaining structures are then re-optimized using DFT methods.

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OC 9. Core-hole delocalization effects in computational X-ray spectroscopy

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X-ray spectroscopy calculations often require the use of an explicit core-hole to model orbital relaxation. For symmetric systems, the use of a delocalized core-hole can result in large errors, while a localized core-hole is able to suitably capture orbital relaxation even within the Hartree-Fock or Density Functional Theory (DFT) methods. The source of this delocalization-induced relaxation error (DIRE) is the incomplete description of orbital relaxation by the delocalized core-hole. Ultimately, DIRE can be traced back to electron correlation and improving the correlation treatment is shown to systematically alleviate the error.

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OC 10. Benchmark of linear algebra for quantum chemical computations

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Scientific computation in high-performance computing (HPC) relies heavily on numerical linear algebra, which forms the backbone of many computational algorithms. The Basic Linear Algebra Subprograms (BLAS) and Linear Algebra PACKage (LAPACK) provide standardized implementations of these important operations. However, the emergence of new hardware architectures makes it necessary to re-implement these routines to take full advantage of the capabilities of modern systems and thus achieve the highest possible performance.

Despite the fundamental role of BLAS and LAPACK for scientific computation, different vendors have developed their implementations to optimize performance on their specific hardware. This diversity poses a major challenge: the lack of standardization and uniform naming conventions for the different vendors' implementations makes it difficult to compile scientific tools and seamlessly switch between implementations. This problem hinders the ability to achieve optimal performance and flexibility in HPC environments. We will provide a brief overview of these implementations to provide deeper insights and a better understanding of benchmark results.

The most critical BLAS and LAPACK subroutines essential for quantum chemistry algorithms will be benchmarked and analyzed. The performance of these operations will be evaluated in both serial and parallel environments. In addition, we will benchmark various BLAS and LAPACK implementations on the largest HPC system in Croatia, Supek, provided by the University of Zagreb University Computing Centre (SRCE). By systematically evaluating these implementations, we aim to gain insights into their performance characteristics and provide recommendations for optimizing quantum chemical computations on modern HPC systems.

OC 11. Modeling molecular assemblies in solutions to understand interaction with light

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Molecular aggregates are a challenging case to model from scratch, as often there are little experimental information about the details of their structure. However, such details - involved in the intermolecular interactions, are crucial to determine their properties, and namely the response to light in term of optical properties, photophysics or photochemistry. I will present a few cases where atomistic modeling with molecular dynamics (MD) is employed to model a reliable structure for the aggregate. With the objective to decipher (chiro)-optical properties of molecular aggregate, the structural guess produced from MD can be employed to parametrize a coarse-grain electronic model useful to calculate absorption and circular dichroism spectra for the interacting assembly. The hybrid modeling scheme therefore allow a valuable interpretation of the experimental results. In another work in progress, an MD-based robust methodology is established to produce structural guesses of assemblies of biologically relevant molecules, with the objective to rationalize their photochemistry.

OC 12. Molecular dynamics simulations of dynamic and static properties of cyclic polyacrylates

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Polyacrylates, also taking polymethacrylate into account, possess unique properties that make them a crucial choice in (bio)applications. Melts of linear polyacrylates and polymethacrylates have been thoroughly investigated at both experimental and theoretical levels. Due to topological constraints, cyclic polymer chains differ from their linear counterparts. However, compared to the melt of linear polymer chains, the preparation of melts of cyclic polymer chains is much more complicated. Moreover, usually the linear extension of side chain is investigated and only little is known about the branching of the side chain substituents. In this work, atomistic molecular dynamics simulations were performed to scrutinize the static and dynamic properties of cyclic polyacrylates including poly(methyl methacrylate) (PMMAc), poly(methyl acrylate) (PMAc), poly(ethyl acrylate) (PEAc), poly(iso-propyl acrylate) (PiPAc), and poly(t-butyl acrylate) (PtBAc) below their entanglement length at three different temperatures. The main focus of the simulations was the investigation of the effect of branching and the size of the alkyl group on the static and dynamic properties of the polymer chains in their melt at the atomistic level. While the structural properties of the cyclic chains followed a trend given by the size of the alkyl group, the dynamic properties were an interplay of chain size, chain symmetry, and substituent symmetry.

OC 13. Rank-reduced equation-of-motion coupled cluster triples: an accurate and affordable way of obtaining excitation energies of molecules

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In contrast to the ground-state calculations, there is no “gold standard” in quantum chemistry for obtaining excitation energies. On the other hand, the demand for accurate calculations in this area is high, since the process of electronic excitation is utilized in many modern devices. The talk will be focused on a newly developed approximation to the equation-of-motion coupled cluster triples method (EOM-CC3) which takes advantage of the Tucker decomposition scheme to reduce the cost of computations. The decomposition is applied to the triple excitation amplitudes which results in a significant reduction of memory requirements as well as N^6 formal scaling of the method with the system size. We tested the accuracy of our method in comparison to the exact EOM-CC3 for a set of benchmark molecules. On average, the errors are below 0.01 eV, indicating the usefulness of the developed method in obtaining accurate excitation energies of large systems.

OC 14. Beyond-RPA description of many-body noncovalent interactions in molecular crystals

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The many-body expansion (MBE) of the binding energy of a molecular solid is a route toward an ab initio description of molecular crystals. The advantage of this technique is that standard wave-function codes designed for finite systems can be applied in a periodic system. However, while two-body interactions are relatively manageable in MBE at a high-level of theory, the nonadditive (many-body) component poses a challenge due to a combinatorial growth of the n-body clusters. At the same time, to avoid systematic errors and to arrive at the target accuracy of a few kJ/mol in the total energy, one needs to account for the subtle many-body dispersion effects in the interaction energy. The question arises, can this objective be achieved reliably at a cost significantly below conventional implementations of coupled-cluster theory. In this work, we propose a simple approach based on the random-phase approximation with a series of corrections derived in the expectation value coupled-cluster formalism. The test systems are solid ethane, ethylene, and acetylene, for which high-quality ab initio data exists. We examine the role of the second-order screened exchange correction as well as a series of higher-order particle-hole and particle-particle terms. We demonstrate a significant improvement in predictions of nonadditive energies over standard approaches based on DFT and direct RPA with approximate Kohn-Sham orbitals.

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OC 15. Simulating ultrafast molecular photodynamics: from initial conditions to observables

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Nonadiabatic molecular dynamics offers a powerful tool to study the excited-state dynamics of molecular systems beyond the Born-Oppenheimer approximation. The key to any nonadiabatic dynamics simulation is the definition of the initial conditions, ideally representing the initial molecular quantum state of the system of interest. We provide a detailed analysis of how initial conditions may influence the calculation of experimental observables, focusing on a range of molecular systems from small atomospheric molecules [1,2] to nucleobases in water [3]. We show how the choice of initial conditions critically affects photoabsorption cross-sections and other key observables obtained from the dynamics.

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OC 16. Impulsive Vibrational Spectra Modeling for Singlet Fission Studies

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Singlet fission (SF) has attracted increasing attention in recent years as a path toward overcoming the Shockley-Queisser thermodynamic limit for power conversion efficiency in single-junction solar cells by amplifying the number of charge carriers obtainable from a single photon. The ultimate objective of these studies is to rationalize the fundamental mechanisms of singlet fission and determine the crucial characteristics of chromophores that would be optimal for this purpose.

The singlet fission process is very rapid, taking from several to several tens of femtoseconds, so it requires ultrafast techniques of investigation. One such method is impulsive vibrational spectroscopy (IVS), in which the pumping step (10-20 fs coherent light pulse) promotes the chromophore to its first excited singlet state (S1) dressed in nonstationary vibrational wave packets, which are then smoothly transferred onto the potential energy surface of the entangled triplet pair state 1(TT), where they are detected by a second laser pulse. The assumption that the vibrational wave packets are unaffected by change in the electronic state, however, needs to be verified, especially given the claim put forth by Stearn et al. that coherent wave packets may be generated by the fission process itself [1].

A phenomenological wavefunction-based model of vibrationally coherent absorption modulation [2,3] will be presented with the results of its application to reproduce the IVS spectra of two different, pentacene-related systems [3,4], to test whether the singlet fission process in that system spontaneously generates coherent vibrational packets or if it is neutral with respect to vibrational coherences.

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OC 17. Simulating a Mechanochemical Reaction: Molecular Dynamics Modelling of Mechanical Activation and Relaxation

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Mechanochemistry deals with transformations induced and/or aided by mechanical force [1]. The most common method employed in modern mechanochemistry is ball milling (BM), but the inherent nature of it makes it difficult to experimentally investigate individual impacts [2]. Therefore, we have developed a novel methodology for molecular dynamics (MD) simulations tailored to model the milling process. Our protocol incorporates neutral, rigidly constrained balls to exert mechanical force on the reactants. Thus, non-equilibrium MD simulations were performed offering a molecular-level insight into mechanically activated events. For this, the reaction of 18-crown-6 ether (18c6) with KCl, that was used as a model system, was implemented within the GROMACS package. Distinct simulations were run to capture one milling collision event of a KCl crystal particle with increasing momentum of balls, which resulted in fracture for low/momentum impacts and complete granulation for high/momentum impacts. Consequent re-crystallization took place on the time scale of several hundreds of nanoseconds. Further simulations performed with 18c6 and KCl crystal in the system confirmed and vividly captured the conformational changes in 18c6 molecules upon complexation with potassium. Our findings complement experimental observations by PXRD analysis and Raman in situ monitoring. We also reproduce formation of the monohydrate and the dihydrate complexes, that were observed in experiments with the moisture present. Our simulations explain the conformation of these hydrates, their role in stabilizing the complex, and their impact on the coarsening of the product mixture. This protocol for MD simulations of milling procedures enables deeper understanding of mechanochemical processes especially ball milling processes, thereby providing, for the first time, a molecular-level insight of complex mechanochemical phenomena.

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OC 18. Investigation into photophysical properties of stacked PAHs as structured models for carbon-dot photosensitizers

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In recent years, carbon dots (CDs) became one of the most studied carbon-based nanomaterials due to their remarkable photophysical and chemical properties, while maintaining high degree of biocompatibility and low toxicity. Design and utilization of CDs in new applications including, e.g., photocatalysis, require understanding of the underlying physico-chemical processes as well as their chemical structure and spatial arrangement. However, the CDs are class of material with inherently high complexity and varied composition. To mimic the properties of the bulk CD structure a mixture of polyaromatic hydrocarbons (PAHs) was shown to be utilizable [1]. We follow this strategy and propose a bottom-up design approach for CDs based on stacked PAH aggregates with tuned properties founded on easy to compute monomer properties using quantum-chemical approaches. Starting from a large set of (un)substituted anthracene, pyrene and perylene molecules, including their potential nitrogen doping, we develop a protocol for identification of their ideal combinations for their application in oxidative/reductive quenching processes. Given the extent of the sampled set and modeling of larger multimer aggregates, applicability of simplified time-dependent quantum-chemical models for calculating electronic transitions is also discussed.

Acknowledgment

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OC 19. Perturbation-adapted Perturbation Theory: Towards a Multi-Reference Approach

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In 2022, a new approach in single-reference many body perturbation theory was introduced by P. Knowles [1]. The essence of the idea is to derive the zero-order Hamiltonian of a quantum many-body system from a model by requiring that the zero-order is as close to the exact Hamiltonian as possible. The procedure was termed perturbation-adapted perturbation theory. One of the conclusions of a recent analysis [2] of the formulation of the method as proposed by Knowles, was that the efficiency of the single-reference method for weakly correlated systems encourages towards the extension of the theory to the multi-reference approach. The single-but-multi version of projected multiconfigurational perturbation theory [3] serves as the basis for the formulation of the multi-reference working formulae of perturbation-adapted perturbation theory as it requires the least alteration of the original approach introduced by Knowles. The following work entailed derivation, implementation and debugging of the extended approach in order to improve the description of strongly correlated systems by perturbation theory. Currently, the performance of the new method is still under assessment. The computational cost when optimally coded, is expected to scale in accordance with the single-reference version with the sixth power of the number of basis functions, introducing a linear increase with the number of determinants in the CI expansion of the arbitrary reference function. Preliminary results of a few tests performed with a parallelized working code indicate that the inherent pivot dependence of the projected multiconfigurational method itself is enlarged by this formulation of the perturbation-adapted approach. Nonetheless, the multi-reference adaptation of the Knowles-partitioning is observed to be able to account for a significantly greater part of the correlation than that of the Moller-Plesset partitioning in strongly correlated cases. While it maintains the advance of the original single-reference version in the weakly correlated regime. Additionally, the inherent slight size-inconsistency of the framework used for the formulation is not observed to be enlarged. Publication of the results are currently in progress. As for future research topics, it is found that the reformulation of the partitioning technique with reduced pivot-dependence might be a promising study. Further considerations to completely abandon the concept of the pivot using a suitable framework to formulate another version of the multi-reference extension is among future plans.

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OC 20. Quantum tunneling in the low-lying water hexamer isomers

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Studying water clusters is of great importance because the behavioral essence of intermolecular forces between the water molecules mimics that of the bulk. The water hexamer is a particularly interesting water cluster to investigate both experimentally and theoretically because it is the smallest one with 3D structure, often called the smallest water droplet. This cluster is an assembly of six water molecules that are weakly-bound by hydrogen bonds. In water hexamer, a number of low-energy isomeric structures have been located computationally. However, the lowest structures detected experimentally are prism, cage and book [1]. Apart from these structural isomers, the water hexamer prism also has two intriguing low-lying hydrogen bond network isomers close in energy.

At very low temperatures, molecules in the cluster can rearrange and generate new, equivalent structures. These structures are connected to one another by some symmetry operation. It is observed that the water hexamer system has a great number of possible minima, but only the ones connected by short and energetically accessible tunneling paths cause significantly observable splittings. The method used for calculating the tunneling splittings is based on instanton theory. In order to obtain the ground-state splitting, the procedure involves constructing a WKB wavefunction along the instanton path and its harmonic surroundings for each well and putting the acquired wavefunction in the Herring formula which ultimately results in tunneling splitting. The excited state splittings are generated using an analogue approach [2]. The main advantage of this method lies in its applicability to determining both ground- and excited-state splittings. Another great advantage of the presented method is its appropriateness for mid-large systems in full dimensionality and the possibility of combining it with on-the-fly methods for electronic structure calculations.

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Posters

P 1. Is High-level Calculation Necessary for Assessing the Atmospheric Reactivity of Pentachlorophenol with Hydroxyl Radical? DFT vs. Ab initio Calculations

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During the last decades, the interaction, reactivity, and properties of organic compounds related to anthropogenic activities have become an interesting topic in atmospheric chemistry. This work aims to investigate the reactivity of pentachlorophenol (PCP) with hydroxyl (OH) radical in the gas phase. The geometries of the stationary points were determined at the M06-2X/6-311++G(d,p) level and for the energetics we employed the CASPT2 and CCSD(T) methods using series of extended basis sets. This allows us to compare and analyze both the method and basis set effects, especially for the H-abstraction where the application of the CCSD(T) method is “on the edge” because of large excitation amplitudes and also the T1 diagnostic.

Further, we reported the rate constants and branching ratios for each reaction channel over the 220-400 K range. We also predicted the atmospheric lifetimes under different OH concentrations in the troposphere and at varying altitudes in the Earth's atmosphere (from 0 to 10 km), corresponding to temperatures from 298.15 to 223.29 K. Our findings indicated that PCP is a significantly persistent pollutant. Furthermore, we demonstrated how different computational methods can influence our understanding of PCP environmental fate. Finally, we advocated that, where possible, carefully chosen wave function based correlated calculations are reasonable benchmarks for assessing the quality of the thermo-kinetic data. In the case of single-reference CCSD(T) calculations, the careful analysis of excitation amplitudes is a must.

P 2. Excited state coupling between non-orthogonal fragments based on second quantized formalism

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The coupling of electronically excited molecular states is an important effect for methods using fragmentation schemes. The usual approach is to use the interaction of two transition dipoles, which approximates the full Coulomb contribution. Unfortunately, this simple scheme deteriorates as the interfragment distance decreases [1]. There are more sophisticated approaches, but as the interacting fragments get too close, the exchange, overlap, and charge transfer (CT) effects also become prominent.

This study's main goal is to describe the coupling between non-covalent chromophores, which leads to a fragment-based model [1,2]. For such complexes, the Hamiltonian of the supersystem can be partitioned into monomer ones, plus the interaction between them. The supersystem basis can be written as the product of the monomer wavefunctions, which are non-orthogonal. By applying an adequate second quantized formalism, we arrive at equations that feature both exchange and Coulomb parts and exhibit an ordered structure with respect to the overlap of the orbitals. The terms involving ionic states contributing to Charge Transfer excitations can be similarly derived and calculated.

Using this formalism, we can quantify the coupling contributions in the short-distance regime and evaluate the effect of the overlap-scaled terms, which are often neglected. The role of the charge transfer states is also found to be significant, especially for stable ionic states. Interestingly, the mixed terms, where a CT and a local excitation are coupled, affect the accuracy considerably, since they introduce eight new terms to the effective Hamiltonian matrix. These effects are demonstrated on the test dimers.

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P 3. Full Configurational Analysis of Cucurbit[7]uril Complexes by Tensor Decomposition of Molecular Dynamics Trajectory

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Cucurbit[7]uril's (CB7) most important interactions with benzene molecule were investigated by tensor decomposition of ab initio molecular dynamics trajectories and subsequent quantum chemical calculations. Simulation of molecular dynamics was performed on-the-fly using the PM7 hamiltonian implemented in MOPAC2016.¹ Molecular dynamics was propagated via the Verlet integrator in **qcc** for a total duration of 5 ns.² The trajectory was spanned by Cartesian coordinates and complete configurational analysis was performed using the 2nd-order tensor decomposition tool principal component analysis (PCA).³ PCA was used as a dimensionality reduction method and a total of 10 dimensions in the newly formed reduced space of coordinates were retained (describing >87% of the total variance). For these 10 dimensions, a probability distribution function was generated and a brute force combinatorial algorithm was applied to search for all strict local maxima of the resulting function, from which the initial guess structures were generated. All these generated structures were optimized at the B3LYP-D3BJ/6-31G(d) level of the theory using Grimme's D3 dispersion correction and Becke-Johnson damping.^{4,5} After optimizations and clustering of geometries, configurations dominated in content (>99% according to the Boltzmann distribution) were structures with bifurcated hydrogen bonds between CB7 and the π -system of the benzene molecule. Detailed analysis of the structures and standard Gibbs energies of binding will be presented.

Acknowledgment

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P 4. X-ray Constrained Wavefunction limits when handling relativistic effects (Hg, HgH₂, HgPhen₂)

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X-ray constrained wavefunction (XCW) fitting [1] is used to explore how much of relativistic effects can be transferred from a relativistic wavefunction to the non-relativistic one. XCW employs energy minimization (Schrödinger equation) with an extra condition, namely the (λ) weighted minimization of the agreement between the reference/experimental (relativistic) structure factors and the XCW (non-relativistic) structure factors.

It is found, that relativistic effects can be absorbed within the XCW wavefunction, but the XCW electron density is sensitive to data resolution, the chosen standard deviation of the data, and the actual system [2]. Despite that the agreement between the structure factors is matched (reciprocal space), the electron densities (direct space) differ.

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P 5. COMPARISON BETWEEN INITIAL CONDITIONS SAMPLED FROM ANHARMONIC AND HARMONIC WIGNER DISTRIBUTIONS

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The choice of initial conditions is an important aspect in molecular dynamics simulations based on trajectory surface hopping methods [1][2]. Sampling from the harmonic Wigner distribution is a popular choice for generating initial conditions due to its low cost, while giving a better energy distribution than thermal sampling [2]. However, this comes at the expense of information about anharmonicity and normal mode coupling. Those effects can be accounted for by sampling from an anharmonic Wigner distribution. We derived an expression for the vibrational self-consistent field (VSCF) Wigner distribution in the harmonic oscillator basis, which offers a computationally feasible way of generating a better approximation for the full anharmonic Wigner distribution.

In this work the anharmonic system studied is the cyclic formic acid dimer. First, we investigate which normal modes are particularly problematic when sampling from the harmonic Wigner distribution. Subsequently, we show the differences between initial conditions sampled from the harmonic and VSCF Wigner distributions. Finally, we show the effect of sampling on trajectory surface hopping dynamics.

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P 6. Fine-Tuning the Hydrogen Bond Strength: Enhancing the Photochromic Behaviour of Triarylhydrazone Photoswitches

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Hydrazones represent a novel and intriguing type of molecular photoswitches, based on geometric isomers, which demonstrate remarkable thermal stability of the metastable isomer owing to intramolecular hydrogen bonding (IHB). Our research group extended the hydrazone-based photoswitch repertoire by introducing novel subclass of hydrazone photoswitches, namely photochromic heterocyclic triarylhydrazones (TAHZs). In order to expand our current understanding, we aimed to further investigate the impact of intramolecular hydrogen bonding on the photochemical Z→E quantum yield. Thus, in this study, eight novel 2-(p-nitrobenzoyl)heteroaryl hydrazones are examined, each containing one of four distinctive heterocyclic rings possessing varying abilities to participate in the hydrogen bond formation. Consequently, such diversity of heterocycle motives allowed to thoroughly investigate the correlation between IHB strength and exhibited photochromic properties, focusing on efficiency and thermal stability. To rationalize the main features of examined hydrazones, we employed (TD)-DFT calculations addressing the conformational studies, optical properties of Z and E isomers, kinetic stability of meta-stable forms, and reaction mechanisms of thermal isomerizations, including the analysis of substituent effects (phenyl vs pirydine). Performed computational study (MN15/def2-TZVPP) were able to correctly predict thermal isomerization reaction energies and activation barriers ($MAE\Delta G < 2$ kcal/mol), reproduce the absorption spectra band-shapes and position of their maxima as well as justify the impact of IHB strength and substituent in hydrazine part on exhibited properties. Additionally, computations also revealed that N-inversion is the rate-determining step in a complex sequential mechanism of thermal E → Z isomerization.

P 7. A COMPARISON OF INDUCTION ENERGY FROM FINITE-FIELD AND SAPT

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The induction energy is one of the component of interaction energy, which is tremendously difficult to calculate for molecules in their excited state (ES). When considering the interaction between an ES of one system and the ground state (GS) of another system, the multipole moments of the ES charge distribution can be different from those of the GS. [1] A purely multipolar description of the inductive effects encounters serious problems because of the divergent nature of the multipole expansion, while the bipolar expansion of the induction energy converges slowly. [2] For many years there was no methodology to use Symmetry-Adapted Perturbation Theory (SAPT) [3] for calculating induction energy of molecules in ES. Recently, such possibility became available due to work from research group of Michał Hapka from University of Warsaw and Katarzyna Pernal from Lodz University of Technology called SAPT(MC). [4][5] which can calculate induction energy in ES. However, there is possibility to calculate induction energies in ES using numerical derivatives of Energies (Finite Field Approach) given that one can obtain ES energies of a given monomer in presence of other monomer, which is the difficult part. This method allows using energies from various theories ranging from cheaper-faster to expensive-accurate theories.

We have calculated induction energies from second derivative of ES energies in presence of field from other monomer. While for the SAPT calculation we have selected SAPT(UHF) [6] with the Maximum Overlap Method (MOM), [7] and SAPT(MC). SAPT(UHF) for the ES leverages non-aufbau orbitals derived from MOM, allowing it to effectively handle cases of broken spin symmetry. Remarkably, SAPT(UHF) shows a high level of agreement with SAPT(MC), demonstrating its robustness in accurately predicting interaction energies even in cases of ES. Our study will attempt to benchmark the Induction energy of molecules in ES using Finite Field Approach to determine the best suitable method for describing the ES property, ultimately contributing to the development of method under the formalism of SAPT for ES.

P 8. Dicopper tetrakis(μ -acetato)-diaqua Quantum crystallography study

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Quantum crystallography (QC) relies on synergy of both experimental (X-ray or diffraction experiment) and theoretical (quantum chemistry) approaches. In this study the dicopper tetrakis(μ -acetato)-diaqua complex (copper(II) acetate) model case is presented. Structure of the copper(II) acetate is interesting due to the Cu²⁺-Cu²⁺ interaction and was previously studied experimentally [1] and theoretically [2].

Copper ions are in the oxidation state 2+, that means that three possible multiplicities have to be considered (1BS, 1R, 3). Broken symmetry 1BS is the energetically preferred spin state as already shown previously [2]. Here we choose the DKH2/BLYP/jorge-DZP-DKH computational protocol. The theoretical structure factors (SFs, Fourier transform of electron density that magnitude is measured in the X-ray diffraction experiment) are generated in two ways: one is based on the experimental data [1] (397256 SFs, resolution 1.294 Å⁻¹) the other on choosing a given range of hkl's (1594004 SFs, resolution 5.542 Å⁻¹). These theoretical structure factors are then used in Multipole model (MM) refinement (a technique used to refine electron density upon experimentally measured structure factors). Goal of this study is the comparison of calculated and experimental data (QTAIM analysis, d-populations, SFs) as well as of the MM flexibility. In addition, the impact of the alternation of thermal models/modes, variation of data resolution, as well as error estimation in the SFs will be critically evaluated.

Acknowledgment

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P 9. Improving the description of molecular electron transport using NEGF method in conjunction with ab initio quantum chemistry embedding

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Quantum electron transport through molecules has been of interest in both experimental and theoretical studies for decades, due to its potential applications in a range of fields, including the design of solar cells and molecular electronic systems, as well as the understanding of biochemical processes. The primary model setup for investigating these phenomena is the single-molecular junction (SMJ), in which the studied molecule is placed between nano-sized metal electrodes. The non-equilibrium Green's function (NEGF) technique represents the state-of-the-art theoretical framework for investigating these processes, allowing flexibility in the choice of methods for determining the electron structure of the system. The NEGF technique is usually coupled with density functional theory (DFT) for qualitative investigations. However, numerous studies have indicated that the limitations of DFT make this combination unsuitable for a quantitative estimation of these properties.

In this study, we coupled the NEGF method with ab initio quantum chemical methods suitable for a reliable and cost-effective estimation of electron transport properties based on our previous benchmark studies[1]. To this end, the Green's function is derived from the many-electron ionic states of the system. The majority of the SMJ model system is comprised of metal electrodes which makes the evaluation of the ionic states of the entire system practically impossible. Therefore, only the ionic states of the molecule are identified using embedding schemes to incorporate the effect of the electrodes. The projection-based embedding (PbE) method is employed, which is a formally exact embedding scheme based on orbital localization[2]. Even at the DFT level, this approach permits the selection of the DFT functional for the molecule and the electrodes separately, thus providing the most appropriate description for both. Additionally, the many-electron ionic states can be calculated for the molecule from high-level ab initio wave function models, making this method a promising candidate for a more accurate estimation of electron transport properties.

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P 10. Sensitivity analysis in photodynamics: How the electronic structure controls cis-stilbene photodynamics?

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Computational photodynamics is vital for unraveling reaction mechanisms and interpreting experiments, but inaccuracies in nonadiabatic dynamics can lead to misinterpretations. This is evident in the photochemistry of cis-stilbene, where similar experimental outcomes have been variably interpreted.

We explore cis-stilbene photochemistry using trajectory surface hopping with different electronic structures (OM3-MRCISD, SA2-CASSCF, XMS-SA2-CASPT2, and XMS-SA3-CASPT2). While excited-state lifetimes are consistent (360-295 fs), reaction quantum yields vary widely: cyclization from nearly zero to 35% and photoisomerization from over 50% to complete suppression. Interestingly, calculated photoelectron signals appear similar across different scenarios, misleadingly suggesting reliability.

Stationary points on the potential energy surface do not predict simulation outcomes or help in method selection. We propose incorporating sensitivity analyses in simulations. Although using multiple methods is impractical, nonadiabatic simulations with external bias offer a resource-efficient solution.

P 11. Combining the Hückel and PPP-Model Hamiltonians with pCCD-based methods in PyBEST

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In quantum chemistry, theoretical models are crucial for understanding electronic structures and molecular behavior. The Hückel model, introduced by Erich Hückel in 1931 [1], offers a simplified method to estimate molecular orbital energies by focusing on π -electrons in conjugated systems. The Pariser-Parr-Pople (PPP) model, developed in the early 1950s [1], extends this concept by incorporating electron-electron interactions for a more comprehensive understanding of molecular electronic structures [2].

This study provides a detailed analysis of both model Hamiltonians, utilizing advanced software tools and modern quantum chemistry methods to study the electronic structure and properties of large conjugated systems available in the PyBEST software package [3,4]. Specifically, we focus on pCCD-based methods for modeling prototypical organic molecules. [5,6].

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P 12. A Computational Model Study of the Interaction of Methylorange Dye with Doped Polypyrrole

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Polymer-based actuators have interesting applications in conducting films, drug delivery and sensors [1,2]. Actuation in conducting polymers is based on redox switching between the doped conducting and undoped insulating states and connected with large volume changes responsible for actuators bending. Zig zag conformations of polypyrrole polymers linked by small organic molecules show a significant deformation and high current density [3]. We investigated an accordion type polymer, poly(phenazine 2,3-diimino(pyrole-2-yl)) (DPP) doped with polyvinyl sulfonic acid (PVSA), upon interaction with the redox dye methyl orange, which serves as an actuator for dye sensing.

In this poster, we support the experimental data [3] with new computational model calculations on the conformational flexibility and redox properties of the doped polymer before and after adsorption of the methyl orange dye to learn more about the volume and electronic changes necessary for actuation.

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P 13. Investigating Proton-Coupled Energy Transfer Using Constrained Density Functional Theory

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Proton-Coupled Energy Transfer (PCEnT) is a mechanism where energy transfer between chromophores is coupled with a simultaneous motion of proton(s). A variant of PCEnT involving triplet states (PCTEnT) was recently discovered in systems combining porphyrin antenna and flavonol acceptor. Key point of interest in the study of PCEnT is the ability to excite a molecule using a lower energy than conventionally required. The description of this process is computationally demanding as many excited states, including those with a charge transfer character, have to be included. As an appealing alternative, the PCTEnT process can be efficiently investigated with Constrained Density Functional Theory (CDFT). This approach allows for the application of constraints to specific regions of a molecule, enabling a detailed analysis of the interactions driving PCEnT. In my poster, I demonstrate the performance of this approach on the porphyrin-flavonol system. I also discuss the design of other systems exhibiting PCEnT.

P 14. Sodium/CO₂ collisions: gas phase model of CO₂ reduction by hydrated electrons?

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The reduction of carbon dioxide with a hydrated electron is potentially a new promising way of capturing atmospheric carbon dioxide. Yet, only a few computational studies of this reaction have been conducted so far. This might be due to the computational difficulties with modelling of the hydrated electron as a hydrated electron owes its very existence to a complicated interaction of electron with many solvent molecules. Domcke and collaborators used hydronium radical as a possible model for the hydrated electron, bypassing thus the computational complexity of liquid state. Here, we take one step further. We investigate the possibility of using a carbon dioxide molecule and a sodium atom, as a simple gas phase model for the reaction. This is done through both static and dynamic simulations. For the representation of electron transfer between the sodium atom and carbon dioxide, constrained density functional theory with configuration interactions (CDFT-CI) is employed. Thus the suitability of CDFT-CI usage in molecular dynamics is explored. We also discuss possible experimental realizations of the process.

P 15. Radical Enzyme-Mediated Recycling of Glycerol

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Glycerol, a common byproduct in biofuel production, holds the potential for conversion into more valuable chemicals like 3-hydroxypropionaldehyde (3-HPA), which serves as a precursor for the synthesis of useful compounds, such as acrylamide and acrylic acid.[1–3] Enzymes facilitating the dehydration of glycerol, leading to the formation of 3-HPA, include coenzyme B12-dependent diol- and glycerol dehydratase, as well as a B12-independent glycerol dehydratase, the latter demanding a separate S-adenosyl methionine activating enzyme for catalytic activity. All these dehydratases operate through a mechanism involving the formation of radical intermediates. B12-dependent dehydratases are advantageous for biotechnological use as they tolerate aerobic conditions; however, their susceptibility to inactivation by their substrate glycerol presents a challenge. The detailed elucidation of catalysis and inactivation mechanisms enables insights that could enhance applications of these enzymes in microbial-engineered processes.

A computational study of both B12-dependent and B12-independent mechanisms of glycerol dehydration will be presented, along with the results of an investigation into the mechanism of suicidal inactivation of B12-dependent glycerol dehydratase by the substrate glycerol. The computational approach employed molecular dynamics (MD) and QM/MM methods.

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P 16. The theoretical construction of Pourbaix diagrams: Dihydroxybenzenes and phenylenediamines

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The dependence of electrochemical potential (E) on pH is described by Pourbaix diagrams [1]. These diagrams consist of three types of lines representing transfer of protons and electrons. Horizontal lines depict electron transfer, vertical lines indicate proton transfer and proton coupled electron transfer is described by diagonal lines. In principle, the density functional theory (DFT) can be used for the theoretical study of these processes. The solvent effect contribution (water) can be described by an implicit solvation model. This combination is often used for the calculation of various thermodynamic quantities due to the reduced computational time. However, the chemical accuracy of calculated pKa values for acid-basic equilibria and electrochemical potentials may be relatively low. On the other hand, the linear correlations between theoretical DFT and experimental pKa or E values can be evaluated. The corresponding Pourbaix diagram are constructed based on these linear dependencies. We present Pourbaix diagrams for dihydroxybenzenes and phenylenediamines [2-4] in this contribution. Dihydroxybenzenes and phenylenediamines have a wide range of applications in industry and biological processes, e.g., in pharmaceuticals, dyes [5] and the production of pigments [6]. The obtained results allow to identify alternative reaction pathways of radical scavenging abilities of studied molecules occurring in redox reactions and biological processes.

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P 17. Calibrating Hybrid DFT: A comprehensive evaluation of 155 hybrid DFT functionals

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The exchange-correlation (XC) potential, a vital element in the Kohn-Sham (KS) equations, is rigorously investigated across 155 hybrid functionals. Thanks to the advances in the inverse Kohn-Sham schemes, By employing the Wu-Yang inverse method, we calculate the hybrid XC potentials through the inversion of electron densities. Wavefunction theory data at the level of FCI and CCSD(T) is used as a reference to quantify errors. In addition to the XC potential, our analysis encompasses the accuracy of electron densities, total energies, and ionization potentials. We observe notable correlations between the precision of the XC potentials, the long-range Hartree-Fock coefficient, and the vertical ionization potential. Further, decomposing the total energy error as functional-driven and density-driven provides vital information on the nature of the total energy error in these hybrid DFT functionals. This study underpins the crucial factors that need to be considered in future developments of hybrid DFT functionals.

P 18. Rank-reduced tailored coupled cluster methods with up to iterative triple excitations

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Traditionally, coupled cluster calculations involving single, double, and triple excitations (CCSDT) have been prohibitively expensive. However, the recent development of rank-reduced coupled cluster theories [1,2], which scale more efficiently than their exact counterparts, has made the routine application of CCSDT methods in computational chemistry feasible. Despite this progress, both exact and rank-reduced coupled cluster methods often underperform in systems where static correlation dominates the total correlation energy. To address this challenge, tailored coupled cluster (TCC) methods have been developed, with several variants now available, such as DLPNO-TCCSD and MR-TCCSD [3,4].

In this work, we introduce rank-reduced tailored coupled cluster methods that include contributions up to the iterative triple excitations. These methods combine the TCC approach, which uses fixed internal amplitudes derived from CASCI calculations, with iterated external amplitudes, all while maintaining the advantageous computational scaling of the parental rank-reduced formalism.

Our methods recover approximately 99.9% of the exact TCCSD and TCCSDT energies when tested on a set of more than 20 small to medium-sized molecules. We also compare the TCCSDT method against TCCSD and CCSDT, demonstrating a reduction in error relative to full configuration interaction calculations.

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P 19. Investigating Emission and Triplet State Interactions in $[\text{Ru}(\text{tbbpy})_2(\text{N-HSB})]^{2+}$

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$[\text{Ru}(\text{tbbpy})_2(\text{N-HSB})]^{2+}$ is a transition metal complex with promising photochemical properties for applications such as photodynamic therapy and photoredox catalysis. It is emitting in the near- infrared region (NIR) while undergoing reactions with triplet-oxygen ($^3\text{O}_2$) to produce singlet- oxygen ($^1\text{O}_2$). Understanding its photochemical behaviour is crucial for leveraging its potential applications in photodynamic therapy and explaining the lack of emission quenching during reaction with $^3\text{O}_2$. The π -delocalized Nitrogen-HeteroSuperBenzene (N-HSB) ligand, is expected to facilitate a suitable energy separation between the metal-to-ligand-charge-transfer (3MLCT) and the metal-centered (3MC) states by stabilizing the 3MLCT state. In this study, computational chemistry methods were employed to investigate the photochemical behaviour of $[\text{Ru}(\text{tbbpy})_2(\text{N-HSB})]^{2+}$. A well calibrated level of theory, PBE0-D3BJ/def2-SVP/def2-TZVP(Ru), was identified through time-dependent density functional theory (TD-DFT) calculations, accurately reproducing the experimental absorption spectrum. TD-DFT analysis revealed two close in energy low-lying triplet states, the T1 with mixed 3MLCT and intra-ligand-charge-transfer (3IL) character and T2 with 3MLCT charge transfer character. The T1 was identified as the emissive triplet state matching experimental data. Spin-orbit coupling (SOC) calculations suggested intersystem crossing from singlets to T2 and T1 triplet state as well as to the higher lying T3. Dynamic simulations employing surface hopping and a parametrized linear vibronic coupling model (LVC) demonstrated also the existence of the two low lying triplet states, as well as an equilibrium between the low lying triplet states and the higher lying triplet manifold. The theoretical findings provide insights into the photophysical behavior of $[\text{Ru}(\text{tbbpy})_2(\text{N-HSB})]^{2+}$, enhancing its potential for photodynamic therapy and photoredox catalysis.

P 20. SARS-CoV-2 Main Protease Inhibitors Docking Score Prediction Using Conformational Flexibility-Informed Machine Learning

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This study focuses on the prediction of the docking scores of potential drug candidates targeting the SARS-CoV-2 major protease using machine learning approach. The approach combines the Kernel Ridge Regression (KRR) machine learning method with the Smooth Overlap of Atomic Positions (SOAP) descriptor. Various combinations of models and test setups were evaluated using different statistical metrics. Special attention was given to the performance of models trained on conformers generated by Molecular Dynamics simulations. By incorporating Multi-Instance Learning, a significant improvement is observed in the model's predictive capabilities.

P 21. Error analysis of SchNet neural network predictions

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Initial screening of big databases of compounds in search of molecules matching the desired quality by machine learning is well established field of study[1]. Main disadvantage is lower accuracy of the predictions in comparison to more rigorous computational methods. This accuracy is influenced by quality of the training data set, architecture and hyperparameters of the neural network[2]. Determining source of the error is nontrivial task, but it is useful in further optimization of the predictions and limits of accuracy[3].

Neural network have been constructed using SchNetPack 2.0 program package[4] and trained on docking scores towards the main protease (Mpro) of the coronavirus SARS-CoV-2 provided by AutoDock Vina 1.2.2 software[5,6]. Multiple aspects of accuracy as prediction error and generalization were considered. Prediction error have been evaluated as a mean square error and mean absolute error of the whole data set. The variance of the predictions, noise of the data set and bias of the neural network is analyzed. Generalization is described by loss-landscape analysis[7].

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P 22. Formation of Charge Transfer States in Carbon Nanostructures

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Materials capable of generating charge-separated states using light have found diverse applications including optoelectronics, photovoltaics and photocatalysis. In recent years, carbon-based nanomaterials emerged as highly promising photo-active materials featuring high modularity, accessibility, biocompatibility and low environmental impact. For example, carbon nanodots (CNDs) offer many extraordinary photophysical properties. The most explored feature is their bright photoluminescence, but there are also other de-excitation pathways occurring in irradiated CNDs that can be exploited. For instance, the formation of long-living charge-separated states in aspartic acid based CNDs enables photo-production of hydrogen peroxide from water [1]. Despite years of intensive research, a comprehensive understanding of the CND structure-activity relationships remains elusive due to the inherent diversity and structural complexity of CNDs. To gain atomistic insights into the photophysical behavior of CNDs, we analyzed the nature and transformations of excited states of functionalized and/or doped polycyclic aromatic hydrocarbons and their aggregates as models of CND fragments by means of static QM approaches as well as non-adiabatic molecular dynamics simulations.

The charge-separated states can also be formed in 2D carbonaceous nanomaterials such as graphene derivatives. Recently, we reported on the UV light induced generation of polaronic spin active states in fluorographene (FG) [2]. Interestingly, we evidenced the solvent specific nature of this phenomenon. Whereas the generation of spin-active states was robust in acetone and moderate in benzene, it was absent in cyclohexane. (Time-dependent) density functional theory (TD-)DFT calculations disclosed that charge-transfer states are plausibly formed at radical sites in FG which interact with acetone molecules in their vicinity. We also presented a scenario for multiplication of polaronic spin active species, highlighting the pivotal role of the photo-induced charge transfer from the solvent to the electrophilic radical centers in FG.

Acknowledgment

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P 23. Investigating the interaction between borophenes and different metals

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Hydrogen is a promising alternative to fossil fuels, but its' storage is a challenging task. We are searching for compounds that can adsorb hydrogen via interaction with transition metals to develop safer, more efficient, and scalable storage solutions. In our previous paper [1], we considered the circumcoronene (CC) systems decorated with transition metals (chromium and iron) and their adsorption capacity towards hydrogen molecules.

Herein, we are dealing with borophenes (a crystalline atomic monolayer of boron), which represent materials that can be used as an auxiliary medium to store hydrogen. All periodic calculations are done with the CRYSTAL software package [2] at the PBE/pob-TZVP level of theory. We are working with three surfaces: $\beta 12$, $\chi 3$, and striped borophene [3]. Interestingly, the energy per a single boron atom favors the $\beta 12$ surface. For the striped borophene, the optimization resulted in a meshed surface with hexagonal holes, which seem to be important for its stability [3]. Consequently, we decorated the $\beta 12$ and $\chi 3$ borophenes with metals (Li, Na, K, Fe, Co, Ni, Cu, and Zn), placing these above the center of the hexagonal hole on the 2D borophene surface. We are evaluating the interaction energies and the bonding patterns between borophene and metals as well as their affinity to bind hydrogen.

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P 24. Novel pCCD-based methods for designing efficient OPV materials: electronic structures and properties of BN-embedded PAHs

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Doping is a versatile strategy for enhancing the properties of organic compounds, making it attractive for the development and optimization of organic electronics. Incorporating boron and nitrogen atoms into a molecule allows for adjustable bandgap tuning, either increasing or decreasing. This tunability is crucial for designing materials with desired optical and electronic properties [1]. The boron and nitrogen atoms, forming an isoelectronic pair resembling two carbon atoms, have been utilized to replace carbon-carbon units with boron-nitrogen units in naphthalene [2]. Advanced theoretical approaches are needed to model desired properties accurately while maintaining relatively minimal computational expenses. One such example is the orbital optimized pair coupled-cluster doubles (oo-pCCD) and techniques based on it, including the IP variant of the equation-of-motion frozen-pair (fp)CC methods (IP-EOM-fpCCD and IP-EOM-fpCCSD), implemented in the PyBEST software package [3]. Some of these computationally effective models show accuracy comparable to CCSD (T) for properties such as ionization potential [4]. However, verifying their accuracy for other properties (e.g., singlet-triplet gap) is crucial to testing and establishing their reliability in modeling the excited structure of conjugated organic systems. The current study focuses on the impact of BN doping on the ionization potential, electronic affinity, and low-lying singlet and triplet excitations of all twenty-three BN-naphthalene isomers. Our results demonstrate good agreement among the fpCCD, fpCCSD, and CCSD (T) methods, which closely align with experimental values. Additionally, the comparisons among systems reveal, among other trends, that the BN-doping effect strongly correlates with whether the positioning of heteroatoms is in the same ring or not. The calculation results show higher ionization potential and singlet-triplet gap values for systems with both heteroatoms in the same ring compared to those in different rings. This study emphasizes the significance of heteroatoms (boron and nitrogen) as a donor and acceptor in electronic properties, which can guide the synthesis of organic photovoltaic (OPV) materials with desired optoelectronic properties.

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P 25. Finite temperature effects in the adsorption of benzene on graphene studied using ab initio molecular dynamics and machine learning force fields

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Introduction

Computational benchmark studies are often conducted using static calculations without considering the thermal motion of the particles constituting the simulated system, which can nonetheless affect the calculated structural properties of the materials [1] and compromise conclusions about, inter alia, the performance of various electronic structure methods. Therefore, systematic computational studies under relevant thermodynamic conditions are of great importance. In this work, static calculations (accounting for thermal effects via a semiclassical harmonic approximation) and ab initio molecular dynamics (AIMD) simulations (in the NVT ensemble) were carried out to investigate the effect of temperature-induced structural changes on the thermodynamics of benzene adsorption on graphene. Three semilocal density functionals (PBE [2], SCAN [3], HSE06 [4]) with dispersion interactions described by means of the DFT-D2 [5], DFT-D3 [6], DFT-D4 [7] and many-body dispersion energy method [8] were explored in addition to the nonlocal vdW-DF correlation functional with optB86b exchange component (vdW-optB86b [9]). Popular machine learning-based acceleration was used to reduce the high computational complexity of AIMD simulations. In particular, machine learned force fields recently introduced in VASP [10] were used to speed up the simulations and increase the simulation time. In addition, machine learning thermodynamic perturbation theory [11] was used to estimate the systematic errors and determine the effect of the number of k -points on ensemble averages.

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P 26. Conformational changes of SARS-CoV-2 spike activation

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Spike glycoprotein of SARS-CoV-2 virus can naturally occur in active (open) and inactive (close) conformations. Interaction with ACE2 receptors on the host cell membrane occurs only for the open conformation, thus initiating virion entry into the cell [1]. An allosteric path correlating the motion of the RBD with the motion of the junction between subdomains S1 and S2 has been proposed in the literature [2].

The conformational changes from a closed to an open structure of SARS-CoV-2 spike glycoprotein has been studied for a single unit, as well as for its complexes with selected biologically active substances, modeling allosteric inhibition at the boundary of S1 and S2 subunits. All-atom molecular dynamics simulations of selected trimeric systems have been performed under isothermal-isobaric conditions using GROMACS 2023.2 [3]. Initial protein-ligand complex geometries have been computed using molecular docking approaches in AutoDock 4.2.6 [4]. The ability of selected substances to effectively inhibit spike glycoprotein function was evaluated by the ligand-protein complex stability, differences in RBD opening trajectories resulting from the presence of the active agent, analysis of the present hydrogen bonds, and changes in work done. Free energy landscapes have been constructed with an aim of verifying existence and shape of minimum energy pathway [2], and its changes due to presence of potentially active ligand.

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P 27. Toward reliable dipole moments without single excitation and a Python-based GPU acceleration.

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The dipole moment is a crucial molecular property linked to a molecular system's bond polarity and overall electronic structure. To that end, the electronic dipole moment is often used to assess the accuracy and reliability of new electronic structure methods. This work analyses electronic dipole moments computed with the pair coupled cluster doubles (pCCD) type methods [1] available in the PyBEST software package [2,3]. The accuracy of pCCD-based dipole moments is assessed against experimental and CCSD(T) reference values using relaxed and unrelaxed density matrices and different basis set sizes. Our work indicates the importance of orbital relaxation in the pCCD model and demonstrates that dipole moments can be reliably predicted without the inclusion of single excitations [4]. In addition, to cope with reliable large-scale calculation demands for quantum chemistry, we discuss the possibility of Python-based GPU acceleration [5].

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P 28. A cross-platform tool toward theoretical modeling of organic electronics

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This study presents a dual-focused approach to advancing electronic structure calculations and their applications in photovoltaics. Firstly, we developed a graphical user interface (GUI) for PyBEST [1,2], a modern electronic-structure software package, using Electron.js. This GUI enhances PyBEST's accessibility, enabling non-programmers to utilize its capabilities effectively. Secondly, we employed PyBEST to investigate eight carbazole-based dyes for dye-sensitized solar cell (DSSC) applications. Using paired Coupled Cluster Doubles (pCCD) [3] and Equation-of-Motion (EOM) [4,5] methods, we analyzed the electronic properties crucial for DSSC performance. Our findings reveal significant bridge-to-acceptor charge transfer and dominant local bridge excitations across all dyes. We also calculated key electronic properties including ionization potentials, electron affinities, and exciton binding energies. This research demonstrates the potential of computational approaches in guiding the development of new materials for photovoltaic applications. By combining an accessible software interface with advanced quantum chemical methods, we provide a promising pathway for accelerating the design and optimization of organic dyes for DSSCs.

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P 29. Top-down projection-based embedding with projected atomic orbitals virtual space

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Embedding techniques allow the treatment of the chemically relevant part of a system at a high level of theory while the remainder is treated at a lower level and the interaction of the subsystems is approximated. A top-down projection-based embedding (PbE) calculation starts with a supersystem SCF calculation. In its original formulation this was followed by the localisation and partitioning of the occupied space into an active subsystem and its environment. A second SCF run is then called for the active subsystem using a modified Fockian that contains the interaction with the environment in the form of the embedding potential, and a projection scheme is employed to ensure orthogonality between the two subsystems. The orbitals obtained this way can then serve as the starting point of higher level calculations on the active subsystem. This treatment leaves the virtual space of the supersystem intact making high level correlation calculations expensive. A truncation of the virtual space to that of the active subsystem can be used reduce the cost of such calculations. We have found conventional MO-based localisation methods to be unreliable for virtual orbitals leading to unphysical repulsive potential energy surfaces, especially when diffuse basis functions are present. Projected atomic orbitals (PAOs) are proposed as an alternative means to generate the virtual orbital space of the active subsystem using two parameters. The PAOs of the active subsystem are constructed after the first SCF run and their complementary virtual space, the virtual space of the environment, is included in the projector used in the second SCF calculation. The performance of the PAO virtuals is demonstrated on excited states of chromophore dimers. Furthermore, a detailed investigation into the roles of the two parameters used in the construction of the PAOs is given.

P 30. Photostability of Glycine in Astrochemical Environments

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Over the past decade, astronomical observations and space missions have detected glycine, the simplest amino acid, in the atmospheres of comets and within cometary ice. More recently, the presence of glycolamide, an isomer of glycine, has been confirmed in interstellar matter. These molecules must withstand the extreme conditions of space, including exposure to high-intensity photons. Photochemical decomposition of amino acids is also considered a key process that may contribute to the origin of biomolecular homochirality. Despite its significance, the photostability of glycine in interstellar environments remains underexplored. This study investigates the photostability of glycine by simulating its exposure to cosmic radiation, focusing on its behavior in solution. To capture the effects of both the solvent and electronic excited states, we employed QM/MM (Quantum Mechanics/Molecular Mechanics) non-adiabatic molecular dynamics simulations using the CASSCF method. Our simulations specifically examine the chemistry of zwitterionic glycine within a water cluster of 500 molecules under excited-state conditions. The results reveal several reaction pathways for the decay of zwitterionic glycine. Furthermore, we compare the photostability of glycine in both solvated and non-solvated forms, elucidating the role of the solvent in this process. Our findings offer new insights into the chemistry of glycine in space, contributing to a deeper understanding of astrochemical processes and the potential origins of life.

P 31. Docking power approximations - can molecular docking reproduce experiment?

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Years following the outbreak of coronavirus SARS-CoV-2 have been marked with an unprecedented response of scientific community, with the number of researchers studying coronaviruses increasing by almost 500 % on year-to-year basis [1]. The increase in the number of publications was mostly driven by in silico research, with approximately 16,500 scientific articles focused on utilizing molecular docking approaches in fight against SARS-CoV-2 by the end of 2020 alone [2]. This interest begs the question of the extent in which the molecular docking can be used to describe studied systems.

The 671 3-dimensional crystal structures of SARS-CoV-2 main protease Mpro have been downloaded from RCSB database and served as a starting point for creation of benchmarking set. Unliganded structures and structures containing unparametrized atoms were omitted from the consideration. Remaining 508 crystal structures were then stripped of disordered atoms, artefacts of crystallization, water molecules, and split into monomeric structures. Ligands were manually inspected and corrected for wrong bond orders, incorrect isomerism, and/or missing larger fragments. Successfully corrected structures (424) were split into categories based on the type of interaction with target protein (covalent vs. noncovalent) and on the position of the ligand with respect to Mpro catalytic dyad (cavity vs. surface bound). Performance of AutoDock [3], AutoDock Vina [4, 5], and PLANTS [6, 7], in molecular docking protocols have been evaluated with a focus on their docking and screening power, utilizing newly defined parameters such as geometrically and/or energetically approximated docking power.

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P 32. Towards a credible description of excited states of a Cu(I) complex

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Photocatalytic reduction of CO₂ is a topic that has been gaining more and more interest in recent years. A photosensitizer is a key element to the whole process. Amongst the known and effective compounds that may be utilized in such a manner are metalloorganic noble metal complexes, such as iridium, rhenium, or ruthenium. However, due to their low abundance and high exploitation costs, their use in an up-scaled process is not feasible. Heteroleptic copper(I) complexes Cu(I)(N[^]N)(P[^]P) have emerged as promising alternatives to noble metal-based photosensitizers of CO₂ reduction reaction. Such compounds have in fact been synthesized, and their photocatalytic properties have been confirmed. An in-depth understanding of the photosensitizer's excited states' character and their time evolution is crucial to elucidate the molecular mechanism of the photoreduction reaction. For that purpose, one must employ computational chemistry methods alongside the experimental studies. Cu(I)(N[^]N)(P[^]P) complexes used as photosensitizers are rather bulky molecules, so the choice of computational methods is nearly limited to the DFT-based (Density Functional Theory) approaches. However, the very same structural and physicochemical properties that make the complexes good photosensitizers (large regions of π -electron delocalization and significant charge transfer (CT) character of the excited states) constitute the well-known challenges for DFT.

The aim of my research was to develop a computational approach that on the one hand will allow one to reliably describe the excited states of the Cu(I)-based complexes in terms of energetics and structural changes upon excitation, and which on the other hand will be computationally cost-effective to enable extensive studies of such large systems. For that purpose, I have compared the way different DFT-based methods, such as ROKS, Δ SCF, TDDFT, and qsGW-BSE (in combination with a range of exchange-correlation functionals) describe both the ground state and lowest excited states of a model Cu(I)-containing photosensitiser, and verified the results against the available experimental data.

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