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Book of Abstracts

60th Symposium on Theoretical Chemistry

Next-Generation >> Theoretical Chemistry

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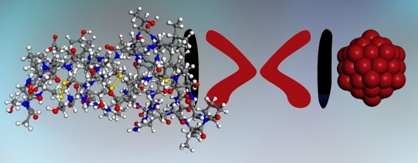

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J. Chem. Phys. **2020**, *152*, 184107
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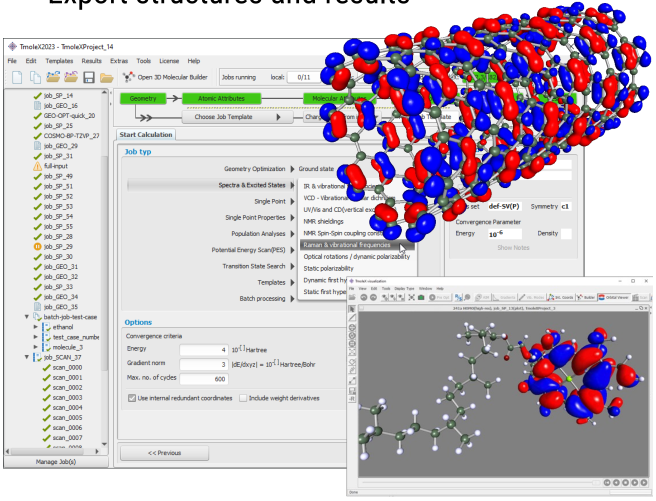

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STC >> 2024

60th Symposium on Theoretical Chemistry

Program: See reverse side

Lectures & Poster Sessions:

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🚌 Bus/Tram stations: Pockelsstraße (Bus 419, 429, 433), Mühlenpfordstraße (STR 1, 2, 10)

⇄ Postersession I: **odd** poster numbers, Postersession II: **even** poster numbers and **P217**

Conference Dinner & Party:

📅 Wednesday, 6 pm

🏠 Lokpark, Schwartzkopffstraße 3

🚌 Bus station: Bebelhof (Bus 411, 422, 431). The last bus (411) back leaves at 11.44 pm!

Activities:

📅 Wednesday afternoon

- **Bouldering:** Greifhaus, Hamburger Str. 268, 2.30 pm
- **Boat Tour:** OkerTour, John.-F.-Kennedy-Platz/Kurt-Schumacher-Str. 26 a, 2.30 pm
- **Guided City Walk:** Touristinfo Braunschweig, Kleine Burg 14, 3.00 pm

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Program STC 2024

MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
	09:00 Invited Lecture: G. Gryn’ova	**09:00** Hellmann & Peyerimhoff Award Ceremony	**09:00** Hückel Award Ceremony	**09:00** Invited Lecture: J. S. Kottmann
	09:35 Contributed Talk: S. Gugler			**09:35** Contributed Talk: A. Antalik
	09:55 Contributed Talk: P. Deglmann			**09:55** Contributed Talk: C. Zülch
	10:15 Coffee Break	**10:30** Coffee Break	**10:00** Coffee Break	**10:15** Coffee Break
			10:40 Invited Lecture: K. D. Vogiatzis	
	11:00 Invited Lecture: E. Perlt (von Domaros)	**11:15** Invited Lecture: H. J. Kulik	**11:15** Contributed Talk: C. Rickert	**11:00** Invited Lecture: V. Krewald
	11:35 Contributed Talk: A. Lieberherr	**11:50** Contributed Talk: J. P. Unsleber	**11:35** Contributed Talk: J. Tölle	**11:35** Contributed Talk: L. Bäuml
	11:55 Contributed Talk: N. Stolte	**12:10** Contributed Talk: A. Köhn	**11:55** Contributed Talk: S. Ghassemi Tabrizi	**11:55** Contributed Talk: A. Bande
	12:15 Lunch	**12:30** Lunch	**12:15** Lunch	**12:15** Closing Words & Poster Awards
	13:45 Invited Lecture: H. Bahmann	**13:30** Afternoon Activities	**13:45** Invited Lecture: J. Westermayr	
	14:20 Contributed Talk: A. Hehn		**14:20** Contributed Talk: P. Schienbein	
	14:40 Contributed Talk: E. Palacino-González		**14:40** Contributed Talk: B. Schröder	
			15:00 Contributed Talk: C. Müller	
15:30 Start Registration	**15:00** Coffee Break		**15:20** Coffee Break	
	15:45 Invited Lecture: C. J. Stein		**16:10** Invited Lecture: J. O. Richardson	
	16:20 Contributed Talk: B. de Souza		**16:45** Contributed Talk: E. Paenurk	
	16:40 Contributed Talk: M. Bensberg		**17:05** Contributed Talk: P. A. Albrecht	
17:00 Welcome to STC 2024 & Opening Lecture: S. Grimme	**17:00** AGTC General Assembly		**17:25** Invited Lecture: B. Stamm	
18:00 Welcome Reception	**18:00** Poster Session I: uneven numbers	**18:00** Conference Dinner	**18:00** Poster Session II: even numbers + P217	

Book of Abstracts

GP3-xTB: DFT accuracy at tight-binding speed

Stefan Grimme

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Recently, we optimized small (vDZP), deeply contracted AO basis sets in molecular DFT calculations using standard ECPs for all elements up to radon [1]. This strategy is furthermore applied to a minimal set of AOs which — as a totally new ingredient — is made adaptive, i.e., radially different for symmetry distinct atoms in a molecule. The ”breathing” of the AOs in the molecular environment is parameterized efficiently by on-the-fly computed effective atomic charges and coordination numbers. This so-called q-vSZP set [2] provides in typical DFT applications re- sults of about or better than DZ quality. It forms the basis of our third-generation tight-binding model GP3-xTB. This includes non-local Fock-exchange as well as other new, many-center Hamiltonian terms (e.g., atomic correction potentials and explicit local exchange). It aims at general purpose (GP) applicability in chemistry and more closely approaches DFT accuracy (actually ωB97M-V/aTZ [3]) than previous semi-empirical methods at only slightly increased computational cost (factor of 2-3 compared to GFN2-xTB). It will be consistently available for all elements Z=1-103 with f-electrons included for lanathanides/actinides. The talk describes key improvements of the underlying TB theory as well as extensive benchmarking on a wide range of standard thermochemistry sets.

Literature:

[1] M. Müller, A. Hansen, S. Grimme, J. Chem. Phys. 2023, 158, 014103. [2] M. Müller, A. Hansen, S. Grimme, J. Chem. Phys. 2023, 159, 164108. [3] N. Mardirossian and M. Head-Gordon, J. Chem. Phys. 2016, 144, 214110.

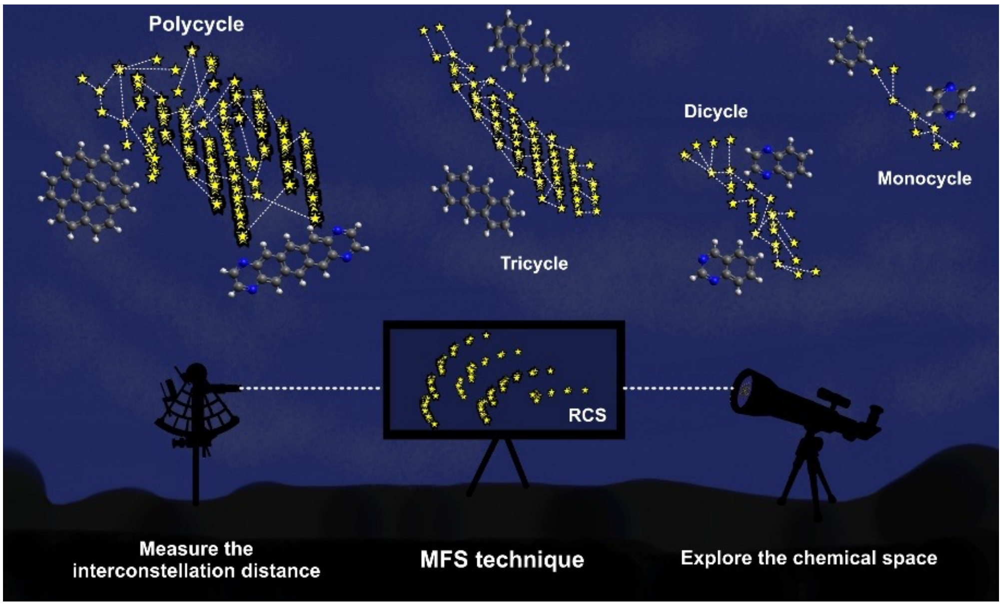
New Techniques for Quantum Machine Learning and Rational Chemical Design

G. Gryn'ova, S. Llenga

School of Chemistry, University of Birmingham, B15 2TT, UK

Rational exploration of the infinite space of hypothetical molecules and materials requires identifying the most important structural and compositional features for the target properties and applications. In this contribution, we discuss our recent efforts toward explainable machine learning for chemical design, which include new quantum-inspired representations, fragment-based fingerprints, and dimensionality reduction techniques.

For example, we will introduce the matrix of orthogonalised atomic orbital coefficients (MAOC) representation [1], uniquely able to distinguish compounds with identical compositions and geometries but distinct charges and spin multiplicities. We will also illustrate several new versions of MAOC tailored toward machine learning the properties of periodic materials, such as the band gaps of covalent-organic frameworks. To greatly facilitate machine learning tasks on large datasets and involving large molecules (or materials), we will introduce the matrix of reference similarity (MRS) technique for reducing the dimensionality and representing the chemical space most compactly. Finally, we demonstrate how new molecules and materials with optimal target properties (e.g., polycyclic hydrocarbons with low HOMO-LUMO gaps for organic electronics) can be rationally designed using the substructural filter representation (SFR), which identifies the building blocks with the highest feature importance.



Literature:

[1] S. Llenga, G. Gryn'ova, *J. Chem. Phys.*, **2023**, *158*, 214116.

Finding Molecular Minima and Transition States with Reverse Diffusion

S. Gugler, Berlin, Germany
K. Kahouli, Berlin, Germany
S. S. P. Hessmann, Berlin, Germany
K.-R. Müller, Berlin, Germany
S. Nakajima, Berlin, Germany
N. W. A. Gebauer, Berlin, Germany

Mommsenstr. 21, 10629 Berlin, Germany

Molecular relaxation and transition state finding are essential components of computational chemistry to understand reactivity. Focussing on the former, neural network force field models require large labeled datasets encompassing both equilibrium and non-equilibrium structures. As a remedy, we propose *MoreRed* [1], molecular relaxation by reverse diffusion where non-equilibrium structures are treated as “noisy” instances of their corresponding equilibrium states. We extend this framework to also denoise structures to generate transition states. Notably, MoreRed learns a simpler pseudo potential energy surface instead of the complex physical potential energy surface, thereby requiring much less and unlabelled data. We compare MoreRed to classical force fields, equivariant neural network force fields trained on a large dataset of equilibrium and non-equilibrium data, as well as a semi-empirical tight-binding model. Lastly we show the potential for elucidating chemical reaction networks by chaining a relaxation and a transition state model.

[1] K. Kahouli, S. S. P. Hessmann, K.-R. Müller, S. Nakajima, S. Gugler, N. W. A. Gebauer, *Mach. Learn.: Sci. Technol.* **2024**, accepted; arXiv:2404.10935 [physics.chem-ph]

Challenges and Progress in the Use of Quantum Chemistry for a Predictive Treatment of Chemical Reactivity Problems

P. Deglmann, Ludwigshafen/Germany

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Although Moore’s law is not valid anymore, the compute resources available for quantum chemical simulations are still significantly growing. Furthermore, the past decade has seen enormous progress in establishing methods that offer close-to-DFT-accuracy at significantly reduced computational cost while maintaining general applicability – both in the area of semiempirical tight binding methods as well as with machine learned molecular potentials. With these developments, also applications in the area of chemical reactivity become possible that were hard to tackle before, e.g. the computation of large reactive networks. A prerequisite for this, of course, represents automation of the computational workflows wherever possible: in the decision which reactions should actually be studied, in the computational treatment of these reactions and in the analysis of results.

To be useful as a predictive tool, high accuracy requirements have to be met by these high-throughput quantum chemical studies – at least finally for those reactive steps, which have a certain probability to occur. This does not only refer to the choice of DFT or post-Hartree Fock methods, but also concerns the selection of conformers of each species and computation of their entropies; furthermore, for many reactions, without an appropriate solvation treatment not even qualitatively correct results can be obtained.

Several application examples out of diverse areas of chemistry are discussed including the specific challenges encountered with these systems: stereoselective amination at a transition metal catalyst, amine induced aromatic polyimide synthesis and organocatalytic isocyanate trimerization.

Properties of amorphous materials based on quantum chemical calculations

T. Schrader, J. Khanifaev, E. Perlt, Jena/DE

Dr. Eva Perlt (von Domaros), Friedrich Schiller University Jena, Löbdergraben 32,
07743 Jena/DE

An accurate and reliable prediction of material properties from first principles is still an ongoing challenge for theoretical methods. Especially for amorphous systems, the absence of periodicity in combination with large system sizes make the application of high-level electronic structure methods infeasible. The Quantum Cluster Equilibrium (QCE) approach, which was originally proposed, implemented and applied for liquid phases, circumvents this problem of the scale gap. [1,2] Therein, the macroscopic phase is represented by a set of finite sized cluster structures, which can be characterized quantum mechanically. A statistical thermodynamics approach is then used to determine the population of the individual clusters and finally obtain macroscopic phase properties.

In this contribution, we present the extension of the QCE methodology to amorphous materials such as polymers or glasses. It will be demonstrated, how the QCE approach can predict macroscopic phase properties for non-periodic systems based on highly reliable electronic structure methods. We discuss necessary adjustments regarding the cluster construction and characterization as well as the implementation. Furthermore, model enhancements such as the inclusion of anharmonicity will be discussed. [3] First preliminary results will demonstrate the feasibility of the approach and we will discuss the potential impact and future studies in the outlook.

Literature:

[1] E. Perlt, M. von Domaros, B. Kirchner, R. Ludwig, F. Weinhold, Sci. Rep. 2017, 7, 10244.
[2] J. Blasius, J. Ingenmey, E. Perlt, M. von Domaros, O. Hollóczki, B. Kirchner, Angew. Chem. Int. Ed. 2019, 58, 3212-3216.
[3] J. Khanifaev, T. Schrader, E. Perlt, J. Chem. Phys. 2024, 160(12), 124302.

Vibrational Strong Coupling in Liquid Water from Cavity Molecular Dynamics

A. Z. Lieberherr, Oxford, UK; S. T. E. Furniss, Oxford, UK; J. E. Lawrence, Zürich, CH; D. E. Manolopoulos, Oxford, UK

Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom

We assess the cavity molecular dynamics method for the calculation of vibrational polariton spectra using liquid water as a specific example. We begin by disputing a recent suggestion that nuclear quantum effects may lead to a broadening of polariton bands, finding instead that they merely result in anharmonic red shifts in the polariton frequencies. We go on to show that our simulated cavity spectra can be reproduced to graphical accuracy with a harmonic model that uses just the cavity-free spectrum and the geometry of the cavity as input. We end by showing that this harmonic model can be combined with the experimental cavity-free spectrum to give results in good agreement with optical cavity measurements.

Since the input to our harmonic model is equivalent to the input to the transfer matrix method of applied optics, we conclude that cavity molecular dynamics cannot provide any more insight into the effect of vibrational strong coupling on the absorption spectrum than this transfer matrix method, which is already widely used by experimentalists to corroborate their cavity results.

The Impact of Active Learning on Machine Learning Potentials for Quantum Liquid Water

N. Stolte, Bochum/DE, J. Daru, Budapest/HU, H. Forbert, Bochum/DE, J. Behler, Bochum/DE, D. Marx, Bochum/DE

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Machine learning potentials (MLPs) trained on *ab initio* data allow us to perform molecular dynamics simulations of larger systems and longer time scales than accessible with *ab initio* molecular dynamics, while maintaining the level of accuracy of the *ab initio* method. However, training of MLPs requires a substantial number of expensive *ab initio* calculations. Active learning is a strategy to construct data sets used to train MLPs, often in the context of reducing the number of expensive ab initio calculations. Today, active learning is routinely used in training of machine learning potentials. However, the efficiency of active learning across different systems is not well-understood. We study active learning strategies based on committee disagreement for the training of a high-dimensional neural network potential for quantum liquid water at ambient conditions. We investigate in detail the performance of active learning, at the level of computational requirements, train and test errors, and the quality of the final potentials in simulations including nuclear quantum effects.

Electronic structure at molecule-semiconductor interfaces

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Physikalische und Theoretische Chemie,
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The interface between molecules and semiconductors plays an important role in many areas of chemistry such as heterogeneous catalysis and energy conversion. Theoretical studies of representative systems are an important tool for the development of more efficient catalysts or energy materials and provide valuable insight into the charge-transfer mechanisms at an atomistic level. The accurate description of the electronic structure in these systems, especially at the interface is challenging but crucial for a quantitative prediction of macroscopic properties.

In this work, prototypical models for the interface between organic dyes and a metal oxide semiconductors are studied using density functional theory with particular emphasis on the application of flexible hybrid functionals. For composite systems, the performance of hybrid functionals is often limited due to system-dependent parameters that controls the overall amount of exact exchange. This can be overcome by introducing a real-space dependent exact-exchange admixture, as in local hybrids, or a density-dependent range-separation function, as in exchange functionals with local range-separation (LRS).

LRS-functionals can be implemented efficiently and have been shown to be superior to their counterparts with a global RS parameter for basic chemical properties as well as band gaps in molecular systes.[1,2] They are further assessed for ionization energies, electron affinities and band gaps of small TiO_2 clusters, as well as the energy levels in representative systems with an interface between an organic dye and TiO_2.

For larger model systems with a sizable TiO_2 cluster, time-dependent DFT calculations with local hybrid functionals provide the best compromise so far for the description of the electronic states of separate systems and at the interface.[3] The most recent local hybrid functional with additional range-separation is considered as well, highlighting the influence of long-range exact exchange.[4]

Literature:

[1] S. Klawohn, H. Bahmann*, J. Chem. Theory Comput.* **16**, 953 (2020).
[2] M. Brütting, H. Bahmann, S. Kümmel, *J. Chem. Phys.* **160**, 181101 (2024)
[3] D. Gemeri, J. C. Tremblay, H. Bahmann, *Advances in Quantum Chemistry* **88**, 329-350 (2023)
[4] S. Fürst, M. Haasler, R. Grotjahn, M. Kaupp, *J. Chem. Theory Comput.* **19**, 2, 488–502 (2023)

Extending the Tool set for Excited States in Solids

A.-S. Hehn, Kiel, Germany

Computational Chemistry Group for Theoretical Spectroscopy and Heterogeneous Catalysis,
Christian-Albrechts-University Kiel, Max-Eyth-Straße 1, 24118 Kiel, Germany.

Describing excited states in extended systems, i.e. solids, surfaces, or condensed-phase systems, poses a challenge to state-of-the-art quantum chemistry: Photo-chemical processes in crystals or networks often depend crucially on the system's topology [1], highlighting the importance of implying periodic boundary conditions for theoretical simulations. However, periodicity in combination with often extended system sizes standardly restricts investigations to time-dependent density functional theory (TDDFT) ansätze, entailing inherent short-comings of the method. Motivated by the purpose to extend the applicability of TDDFT, with the aim to create a sophisticated tool set for the static and dynamic description of excited states, recent TDDFT method developments [2,3,4] will be presented including perturbative spin-orbit coupling corrections and extensions to describe semi-local core states in transition metals within the Gaussian and augmented plane wave method.

[1] D.-G. Ha *et al.*, *Nat. Mater.* 21, 1275 (**2022**).

[2] T. Kühne *et al.*, *J. Chem. Phys. 152*, 194103 (**2020**).

[3] A. Hehn, B. Sertcan, F. Belleflamme, S. K. Chulkov, M. B. Watkins, J. Hutter, *J. Chem. Theory Comput. 18*, 4186 (**2022**).

[4] B. Sertcan, J. Hutter, A. Hehn, *ChemRxiv, 10.26434/chemrxiv- 2024-3qzjg*.

Control of Ultrafast Charge-Transfer in Functional Energy Materials via Chirped-Pulses and its Time-Resolved Spectroscopic Revelation

J.H. Soh[1], X. Xu[2], R. Hildner[2], T. la Cour Jansen[1], E. Palacino-González[3]*

[1] *Theory of Condensed Matter, University of Groningen, Netherlands*
[2] *Optical Spectroscopy of Functional Systems, University of Groningen, Netherlands*
[3] *Theoretical Chemistry Institute, Heinrich-Heine Universität Düsseldorf, Germany*

The manipulation of the ultrafast quantum dynamics in a system can be achieved using tailored light fields. In our work, we demonstrate control over the nonadiabatic dynamics of a model system describing ultrafast charge-transfer in a condensed-phase dissipative environment using chirped pulses[1]. Adjusting external photo-excitation conditions, such as the chirp parameter, modifies frequency resolution, modifyung the total population of the excitonic and charge-transfer states over long times. From a time-resolved spectroscopic perspective, we introduce an excitation scheme with two delayed pump pulses: a chirped pulse and a transformed-limited pulse, and measure time-resolved double-pump fluorescence signals. This simple scheme allow to directly monitor the effect of the additional phase introduced by the chirped excitation on the electronic coherences that determine the time-resolved spectra. By altering the arrival order of the chirped pulse and adjusting the chirp parameter, signals reveal specific system information. To validate our model we directly compare our simulations with recent experimental signals from R. Hildner and coworkers[2]. Signals reveal that chirped pulses significantly enhance vibrational system dynamics, showing substantial signal intensity dependence on chirp conditions. Our investigations demonstrate that photoexcitation with pulses of time-dependent frequencies is a promising tool for steering charge-transfer properties of nanofunctional materials towards a desired target outcome.

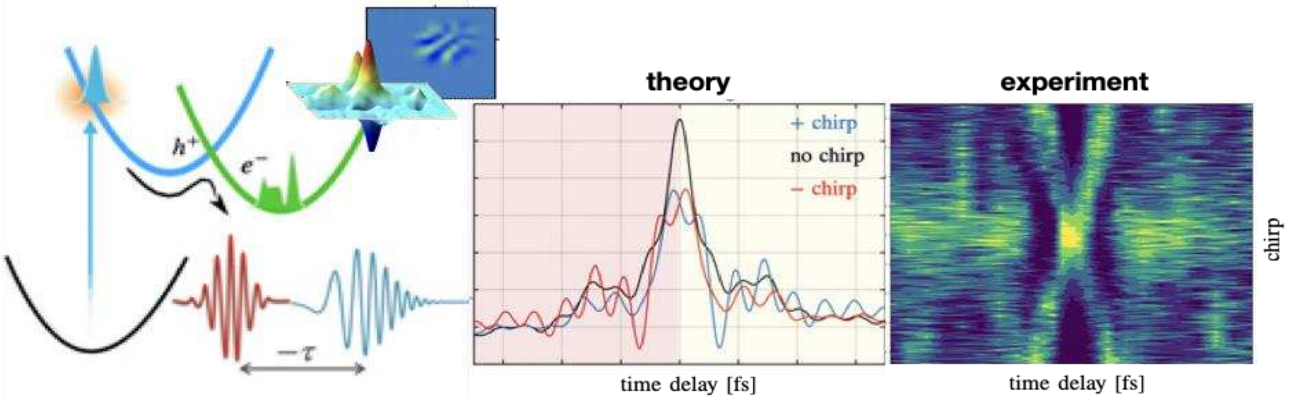

Figure 1: Sketch of photoinduced charge-transfer dynamics in a vibronic model with tailored pulse effects (left); simulated (middle) and experimental (right) double-pump time-resolved fluorescence spectra for a P3HT:PCBM thin-film. Vertical and horizontal axes of right figure represent pulse chirp parameter and inter-pulse delay time.

References

[1] J.H. Soh, T.L.C. Jansen and E. Palacino- González, 024110, **160**, *J. Chem. Phys.,* 2024

[2] X. Xu, T.L.C. Jansen, R. Hildner and E. Palacino- González - *in preparation*

A grand-canonical hybrid explicit/implicit solvation model

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The accurate calculation of solvation contributions to the free energy is key for the prediction of reaction kinetics in solution. Hence, many solvation models have been proposed ranging from an implicit to a fully explicit description of the solvent molecules. Microsolvation models, where only a small number of explicit solvent molecules are considered are reasonably successful but suffer from the fact that the commonly applied rigid rotor/harmonic oscillator approximation is inaccurate due to the many floppy degrees of freedom. A rigorous alternative can be obtained by a grand-canonical sampling of the solvent degrees of freedom in a cavity around the solute.[1] However, thermodynamic constraints are not well defined for such a small explicit system.

In this talk, I will demonstrate how we overcome these limitations by explicitly including information on the interaction Hamiltonian between the explicit subsystem and its implicit environment. Key to our derivation is a probabilistic interpretation of the thermodynamic variables in the small explicit subsystem. While several models[2,3] exist that incorporate spatially resolved information on the solvent distribution in the implicit description, they rely on *ad hoc* closure equations that strongly affect the results of a simulation. In contrast, our approach gathers the relevant information from explicit grand-canonical sampling. The explicit sampling of a small region around the solute allows us to accurately estimate the free energy of the system.

While our approach is computationally more demanding than implicit solvation models, it is much more economical than fully explicit calculations. With accurate neural network potentials[4] emerging as surrogate models with *ab initio* quality, we expect our systematically improvable model to be a strong competitor to highly parameterized state-of-the-art solvation models.

Literature:

[1] Preliminary work: M. Rahbar, C. J. Stein, J. Phys. Chem. A 2023, 127, 2176.

[2] C. N. Nguyen, T. K. Young, M. K. Gilson, J. Chem. Phys. 2012, 137, 44101.

[3] S. Gusarov, T. Ziegler, A. Kovalenko, J. Phys. Chem. A 2006, 110, 6083.

[4] I. Batatia, D. P. Kovacs, G. N. C. Simm, C. Ortner, G. Csanyi, NIPS, 2022.

On the relationship between the conformational space and chemical reactivity: presenting GOAT-REACT as a new unsupervised, automated reaction search algorithm implemented in ORCA6.

Dr. Bernardo de Souza, Cologne/Germany, Dr. Christoph Riplinger, Cologne/Germany

Bernardo de Souza, FACCTs GmbH, Rolandstrasse 67, 50677 Cologne/Germany

Although mostly neglected for a long time in Computational Chemistry, the conformational sampling of flexible molecules plays a major role in most real-life problems, including chemical reactivity. The question of whether a certain guess conformer drawn, or automatically generated from a plain 2D Lewis structure, is the minimum on its PES is of no minor importance, because different conformers can have significantly different features. The topic has gained much more attention since the development of the CREST algorithm by the group of Prof. Stefan Grimme [1] and here it will be explored further in its relationship with reactions.

We have recently implemented in ORCA6 the new Global Optimizer AlgoriThm (GOAT), inspired by the classic works of D. Wales [2] and S. Goedecker [3], which can also find global minima and ensembles. However, this is not based on metadynamics and requires fewer gradient runs to converge, thus allowing it to be used together with costlier methods such as DFT. Now here we present its extension to not only find conformers, but automatically find new “reactomers”. The so-called GOAT-REACT variant traverses the potential energy surface (PES) by breaking and making new bonds and ultimately can find topologically unique variants from the initial reference structure, which are products that can emerge from the combination of two or more entities. It does so by simply crossing barriers on the PES, without any training or previous bias. While crossing the PES, one also gathers information on the transition states, which can be later used to compute reaction rates.

A discussion on the algorithm and its details will be presented, together with demonstrations of how one can use it to improve on the study of chemical reactivity.

Literature:

[1] Prachts, P.; Bohle, F.; Grimme, S.; PCCP, 2020, 14. [2] Wales, D. J.; Doye, J. P. K., JCPA, 1997, 101. [3] Goedecker, S. JCP, 2004, 120.

Automated Exploration of Chemical Reaction Networks

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Moritz Bensberg, ETH Zürich, Dep. of Chemistry and Applied Biosc.,
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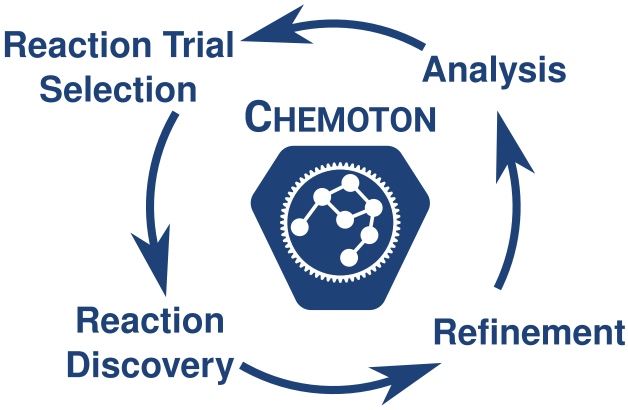
Automated exploration of reaction networks [1, 2] provides detailed models of chemical reactions, which are impossible to obtain by manual investigation. However, blindly searching for every possible chemical reaction with computationally costly electronic structure methods rarely leads to success because of the potentially infinite number of reaction paths. To address this challenge, we recently combined microkinetic modeling, sensitivity analysis, automated reaction discovery [3], and automated parameter refinement to provide a guided, efficient, and uncertainty-aware exploration strategy [4, 5].



We identify species important for the reaction kinetics by microkinetic modeling and predict uncertainties in their concentrations by local or global sensitivity analysis. Based on this information, we refine the reaction network during the exploration in a rolling fashion. Furthermore, we explicitly take the concentration uncertainties into account to arrive at an accurate reaction network.

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Using Machine Learning to Bypass Electronic Structure Method Uncertainty in Chemical Discovery

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Machine learning (ML)-accelerated discovery of materials, i.e., via surrogate models paired with efficient optimization algorithms, holds immense promise to overcome the conventional limitations of computational cost of first-principles electronic structure calculations. Nevertheless, surrogate models inherit the bias of the underlying electronic structure method. In most cases, the electronic structue method of choice is Kohn-Sham density functional theory (DFT), which suffers simultaneously from both self-interaction error or density delocalization error and static correlation error, to varying degrees depending on the density functional approximation. When novel and challenging materials, such as open shell transition metal complexes, is the target of a discovery campaign, few benchmarks are liable to be available for selecting the optimal electronic structure method or DFT functional. Furthermore, investigation of large regions of chemical space (e.g., by varying metal, coordination environment, or oxidation state in a transition metal complex) will likely lead to the conclusion that different electronic structure methods are more suitable for some compounds than others. I will first describe our analysis of the sources of error from the underlying DFT functional[1]. I will describe how we have used consensus from functionals to make more robust predictions of spin crossover behavior, as validated by experimental datasets[1], and I will describe how we have incorporated both prediction of multi-reference character and DFT consensus to find method-insensitive light harvesting chromophores[2]. Next, I will describe our development of ML-informed density functional models, including a recommender that can identify which DFT functional is most predictive to obtain accurate properties of transition metal complexes[3]. I will describe our recent efforts to extend this regress-then-classify strategy to a purely regression-based model that acts in its own right as a density functional. Finally, time permitting, I will describe our efforts in predicting, detecting, and correcting for high multireference character in transition metal complexes[4-6] as well as some of the datasets we have curated for testing electronic structure methods[7].

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Accelerating Scientific Discovery on the Azure Cloud

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In silico experiments leveraging state-of-the-art computational chemistry approaches are expediting scientific research and discovery. This acceleration has been enabled by increasingly powerful hardware and advanced machine learning and AI models. Computational chemistry applications involve compute-intensive workloads, which makes them well suited for scalable cloud architectures such as Microsoft Azure.

This talk will highlight recently added features of Azure Quantum Elements [1] that are empowering chemists to accelerate the discovery pipeline. In particular, simulations of molecular properties made possible with Accelerated Density Functional Theory (Accelerated DFT) will be discussed. [2]

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Next-generation scientific visualization in computational chemistry: Exploring interactive molecular models in augmented reality

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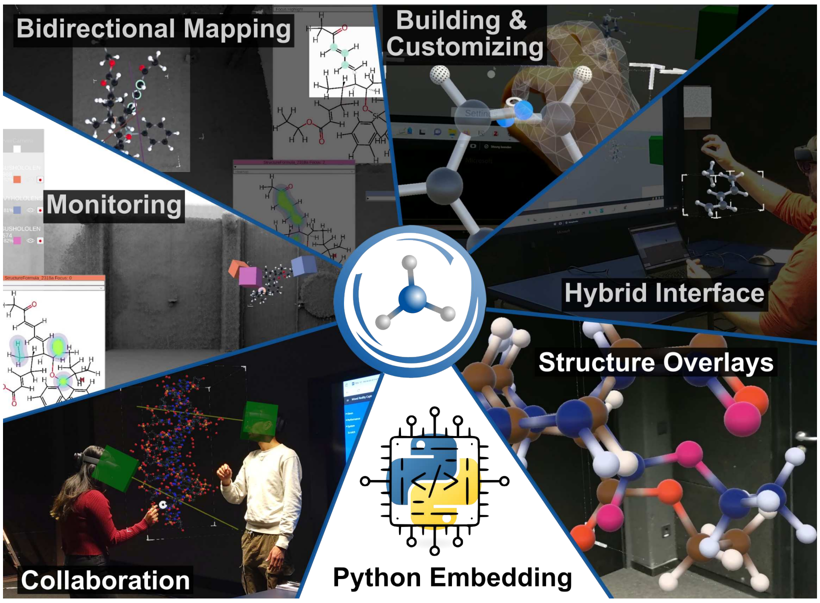
Three-dimensional geometric models of molecules, molecular assemblies or crystal structures are at the heart of chemical thinking. Thanks to great advances in computer-graphics hardware over the recent decades, tools for scientific visualization are pervasive in present-day research, but the current standard of 2D projected images puts limits to the visualization of complex 3D structures and even more so on interaction with or modification of such models. Recent progress in the development of head-mounted displays for virtual reality (VR) or augmented reality (AR) offer the potential to overcome this barrier, where in particular AR appears promising for scientific applications.

In this contribution, we present recent advances in the development of our framework chARpack ("chemistry in Augmented Reality package") [1,2]. The framework supports multiple hardware platforms including optical see-through and camera see-through devices, as well as traditional 2D displays. The various platforms can interconnect and allow for both collocated and remote collaboration in a shared, interactive 3D environment. This also facilitates a seamless transition between 3D stereoscopic views with true 3D input and traditional desktop computers with mouse-and-keyboard input, preserving established workflows in computational chemistry.

Our present core application is a comprehensive virtual molecular model kit that enables intuitive creation and manipulation of molecular structures. Further features include a customizable force field, measurements and structure overlays [2], or the bidirectional mapping of 3D structures and 2D structural formulas [3]. A new interface also allows to integrate Python scripts, which gives perspective to arbitrary customization of the 3D environment.

Besides applications in chemical research and education, the chARpack framework also opens up new possibilities for exploring the field of human-computer interaction (HCI) and therefore provides a platform for interdisciplinary research.



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Exploration of the Two-electron Correlation Space with Data-driven Quantum Chemistry

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The data-driven computational methodology developed by our group combines quantum chemistry with machine learning (ML) to surpass size limitations of accurate but computationally demanding methods such as coupled-cluster (CC). We have previously demonstrated the speedup and transferability that the data-driven CCSD (DDCCSD) model can achieve. [1-3] One major limitation of the DDCC models is the size of the training sets that increases exponentially with the system size. Effect sampling of the amplitude space can resolve this issue. Five different amplitude selection techniques that reduce the amount of data used for training were evaluated, an approach that also prevents model overfitting and increases the portability of DDCCSD to more complex molecules or larger basis sets. [4] Extension to perturbative triples (T) and alternative architectures based on graph neural networks will be also discussed. We recently developed a physics-informed neural network for DDQC that achieved a ten-fold increase in accuracy than our previous models. [5] For example, in the physics-informed workflow for coupled-cluster theory (DDCCNet model), we are introducing the actual equations of the coupled-cluster theory into the ML algorithms which allow a faster and more accurate learning process and lead to more transferable models. Finally, we have extended this approach to other quantum chemical methods, such as the variational 2-RDM (v2RDM). [6]

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Tensor-Decomposed Iterative Distinguishable Cluster Triples

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Obtaining high-accuracy data for extended molecular systems is one of the big challenges in quantum chemistry. We present a technique that allows one to reach a very high methodological level – distinguishable cluster with singles, doubles and iterative triples [1] – at a substantially reduced computational cost. This is achieved by tensor decomposing the triples amplitudes [2], as is shown in Fig. 1. We refer to this method as SVD-DC-CCSDT [3].

The tensor decomposition leads to a drastic compression of the amplitude space and reduction of both the scaling and prefactor without compromising the accuracy. The energy differences calculated with the presented technique are on average within around 0.1 kcal/mol from the CCSDT(Q) results and converge quickly with respect to the decomposition tightness, as is demonstrated in Fig. 2.

The new method is applied to resolve the controversy in the coronene dimer interaction energies, demonstrating the importance of full iterative triples.

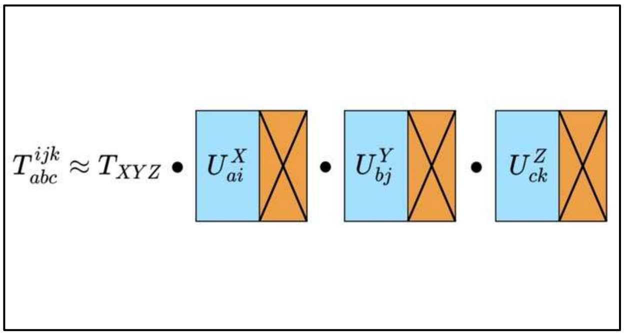

Fig 1: Tensor decomposition of the triples amplitudes.

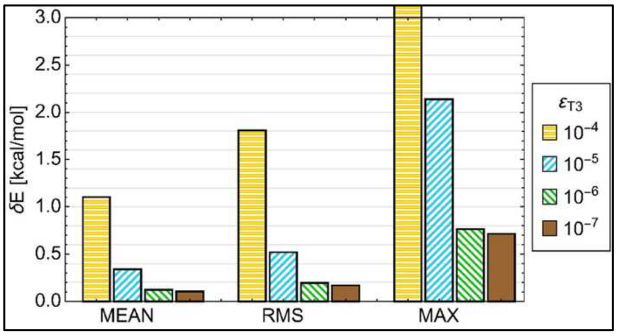

Fig 2: The error of SVD-DC-CCSDT against CCSDT(Q).

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Microscopic insights into electronic phase transitions in quantum materials using coupled cluster theory

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Gaining microscopic insights into how the interaction between electrons manifests in various electronic phases, for example in quantum materials, is essential for the fundamental understanding of phenomena such as unconventional superconductivity. Diagrammatic electronic structure theory, i.e., coupled cluster theory allows not only to accurately describe electronic phases in quantum materials [1, 2], but also enables the physical interpretation in terms of the underlying diagrammatic structure.

In this contribution, I will show explicitly how a channel decomposition of the coupled cluster singles doubles (CCSD) approximation can be leveraged to gain insights into the pairing mechanism responsible for superconductivity in the 2D Hubbard model and $CaCuO_2$. Furthermore, I will give an outlook on a reformulation of CCSD theory capable of overcoming some of the limitations of CCSD when applied to strongly interacting electrons.

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Advancements in Quantum-Chemical Methods for Heisenberg Spin Clusters: Fermionization and Symmetry Projectors

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The Heisenberg model is widely used to describe the magnetic properties of exchange-coupled clusters, which are of significant interest in molecular magnetism. Our research advances the approximation of ground states and the derivation of magnetic coupling constants for Heisenberg spin clusters using quantum-chemical methods such as Mean-Field (MF) and Symmetry-Projected Mean-Field (SPMF) theories, including Projected Hartree–Fock (PHF). We employ spin and point-group (PG) projectors to restore symmetries from broken-symmetry (BS) references, ensuring qualitatively correct representations of quantum states.

By fermionizing spin degrees of freedom, PHF can be applied to Heisenberg systems as an electronic-structure method [1]. Additionally, cluster-based PHF (cPHF) groups sites into discrete clusters, incorporating intracluster correlation at the mean-field level and capturing intercluster correlation through symmetry projection [2]. This method significantly improves the accuracy of ground state and singlet-triplet gap predictions for various spin arrangements. An alternative fermionization is provided by the Jordan-Wigner (JW) transformation, which captures substantial correlation (compared to working in the spin representation) at the mean-field level, reducing the strong-correlation character of spin systems [3,4].

We also utilize BS solutions to construct effective spin Hamiltonians, extracting a broader range of coupling parameters than the traditional BS approach by considering energies and Hamiltonian elements between different mean-field solutions [5].

Furthermore, spin and PG projectors on spin configurations facilitate efficient full diagonalization of the Heisenberg model [6]. These advancements highlight the combined potential of MF and SPMF approaches based on spin or fermionic representations as complementary methodologies for studying finite spin clusters. Similar approaches offer pathways for more accurate SPMF methods to enhance the understanding of various properties of magnetic molecules.

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Machine Learning for Photochemical Reaction Discovery

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Machine learning (ML) has made significant strides in various fields, but its integration into photochemistry, which is important for many processes relevant to nature and life as we know it, remains a challenge. In this talk, we will explore the potential of ML models developed specifically for excited states to accelerate the discovery of chemical reactions and improve the prediction of molecular electronic properties, thereby improving our understanding of photochemical processes [1]. In addition, we will address different ways of modelling excited states, including the use of new neural network architectures or the incorporation of symmetries into them [2,3]. Finally, we will discuss the integration of these predictive models with generative learning [4] and reinforcement learning [5] for advanced molecular design and efficient exploration of the vast chemical compound space.

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IR Spectroscopy and Electric Field Molecular Dynamics Simulations from Machine Learning the Atomic Polar Tensor

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Vibrational spectroscopy is a key technique to elucidate microscopic structure and dynamics. Without the aid of theoretical approaches, it is, however, often difficult to understand such spectra at a microscopic level. Ab initio molecular dynamics has repeatedly proved to be suitable for this purpose [1, 2, 3], but the computational cost can be daunting; in particular when electronic structure methods beyond GGA DFT are required. Here, a new route to calculate accurate IR spectra from machine learning molecular dynamics is presented, utilizing the atomic polar tensor [4]. The latter can be trained *a posteriori* on existing molecular dynamics simulations using the E(3)-equivariant neural network *e3nn* [5] and is a most fundamental physical observable. The introduced methodology is therefore general and transferable to a broad range of systems. Besides enabling the calculation of accurate IR spectra, the atomic polar tensor enables machine learning molecular dynamics simulations explicitly including an external electric field [6]. Applying the methodology to liquid water, a key electrolyte exposed to electric fields in electrochemical applications, we find very good to excellent agreement with available experimental data. This indicates that our approach can significantly contribute toward novel physical findings, especially where large-scale molecular dynamics simulations or expensive electronic structure calculations are required.

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From the Automated Calculation of Potential Energy Surfaces to Accurate Infrared Spectra

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With the evolution of quantum chemical methods and modern multicore computer architectures, it's now possible to simulate the infrared (IR) spectra of isolated molecules with accuracy parallel to established experimental methods which is on the order of a few cm^{-1}. Theoretical IR spectroscopy therefore provides ideal conditions for rigorous benchmarking of novel methodologies, e.g. for constructing potential energy surfaces (PESs). Although it is mainly the multi-dimensional PES that controls the accuracy of these calculations, the subsequent vibrational structure calculations also need to be carefully converged to yield accurate results [1,2].

In this contribution traditional approaches for representing a PES based on polynomial expansions will be compared to machine-learning based methods, specifically high-dimensional neural network potentials (HDNNPs) [3]. While the former approach has been automated [4], HDNNPs still require large data sets for training and a high amount of user control to achieve comparable accuracy [5]. Additionally, established methods for generating structures to be used for the data set like normal mode sampling [6] or sampling from molecular dynamics trajectories [7] will be discussed and shown to be problematic when accurate vibrational calculations are to be performed.

Drawing ideas from the traditional methods, namely the well-known *n*-mode expansion, a physically motivated iterative active-learning workflow for the construction of machine-learning based PESs is presented. Benchmark results for molecules with increasing number of atoms will be presented, showing a more consistent construction of accurate HDNNPs and a reduction in the required amount of expensive training data. The presented workflow is formulated in a general manner making it applicable also to the construction of machine-learning based PESs for other purposes such as reaction modeling or condensed phase simulations.

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From UV to Near-Infrared: Theoretical Insights into the Photochemistry of Chromophore-Extended Photoswitches

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Photoswitches are intriguing molecules capable of converting light into mechanical energy, enabling them to reversibly change their structure upon light absorption. This unique property makes them invaluable for various applications, including proton pumping, vision, and superresolution microscopy. One major challenge in this field is improving the ability to control these switches using visible light instead of damaging UV radiation. To address this, research efforts have focused on extending the chromophores of photoswitches to shift their absorption from UV to near-infrared [1,2].

Understanding photoswitches requires a detailed examination of how light-induced molecular motions are influenced by the size, flexibility, and electronic structure of their *E*- and *Z*-isomers. In this talk, I will present theoretical insights into the state-specific spectral signatures and photochemical mechanisms of a series of photoswitches. We will explore examples ranging from UV-absorbing model systems with small chromophores (6 π-electrons) to switches that absorb in the all-red and near-infrared regions.

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Mapping Approach to Surface Hopping (MASH)

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We combine the best aspects of the two rivial nonadiabatic approaches of fewest-switches surface hopping (FSSH) and quasiclassical mapping methods to derive the Mapping Approach to Surface Hopping (MASH) [1]. Like quasiclassical mapping, MASH is rigorously derivable from the quantum-classical Liouville equation. Like surface hopping, MASH transitions between adiabatic surfaces, meaning that it recovers wavepacket branching and never moves on inverted potentials. Because of its rigorous derivation, it gives unique prescriptions for the momentum rescalings and decoherence corrections, which have proven to be controversial aspects of the standard FSSH approach. MASH trajectories evolve under fully deterministic equations of motion, which unlike FSSH, guarantees that there is always internal consistency between the active propagation surface and the time-evolved electronic state. We show that MASH exhibits improved accuracy over FSSH in various model systems and in particular can recover Marcus theory without decoherence corrections [2]. Given the current popularity of using FSSH in ab initio simulations of chemical systems, our new algorithm has the potential for offering a more accurate and rigorous dynamical method for these applications, all at a comparable computational cost [3-4].

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Nuclear-electronic orbital instanton theory for tunneling splittings

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J. O. Richardson, Zürich/Switzerland, S. Hammes-Schiffer, Princeton/USA

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The nuclear-electronic orbital (NEO) method treats selected nuclei, typically protons, on the same level as electrons in a multicomponent quantum chemistry framework.[1,2] In this way, NEO methods naturally capture the nuclear delocalization and anharmonicity of the select protons. Using multiconfigurational NEO methods, we can calculate ground state tunneling splittings in symmetric double well systems.[2-4] However, such calculations neglect the tunneling effects of the “classical nuclei” that are not treated with the NEO approach. Ring-polymer instanton (RPI) theory is an efficient approach to account for the tunneling effects of the whole molecule, but it makes a harmonic approximation for the modes orthogonal to the instanton trajectory, which is known to fail when anharmonicity is important.[5]

In this contribution, we present a method for computing tunneling splittings in molecular proton transfer systems by combining the NEO method with golden-rule RPI theory.[6] The resulting NEO-RPI method treats the transferring proton quantum mechanically with the NEO method and describes the motion of the other nuclei semiclassically with RPI theory. The application to malonaldehyde has produced promising results.

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Electron dynamics beyond the Born-Oppenheimer approximation

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Ultrafast, attosecond science is developing as a highly relevant field exploring the natural time scales of atoms and electrons. But to include the quantum nature of electrons and atoms scales enormously in effort and therefore mostly electron dynamics is treated within the fixed-nuclei approximation or nuclear dynamics are limited to few electronic states. Instead it is of great interest to bridge these two regimes and enable new perspectives, e.g. capture nuclear dynamics as a perturbation to structure and dynamics of the electronic system.

We present the description of small molecules through potential energy surfaces, dipoles and non-adiabatic couplings from ab-initio calculations to simulate coupled nuclear-electron dynamics beyond the Born-Oppenheimer picture for several hundred electronic states.

The dynamics are benchmarked with the process of High-Harmonics Generation (HHG), which necessitates accurate modeling of ionization and high sensitivity in large-amplitude electron motion/ electron dynamics. From these systems (H_2^+, H_2, LiH, H_2O), we can relate the results to standard approximations made, namely the use of Born-Oppenheimer and Harmonic Oscillator potentials.

ddX: Polarizable Continuum Solvation from Small Molecules to Proteins

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Polarizable continuum solvation models are popular in both, quantum chemistry and in biophysics, though typically with different requirements for the numerical methods. However, the recent trend of multiscale modeling can be expected to blur field-specific differences. In this regard, numerical methods based on domain decomposition (dd) have been demonstrated to be sufficiently flexible to be applied all across these levels of theory while remaining systematically accurate and efficient. In this talk, we present the numerical methods behind ddX, an open-source implementation of dd-methods for various solvation models, which features a uniform interface with classical as well as quantum descriptions of the solute, or any hybrid version thereof. We finish with numerical tests illustrating the performance of ddX and its interfaces.

Electronic Structure with Quantum Circuits

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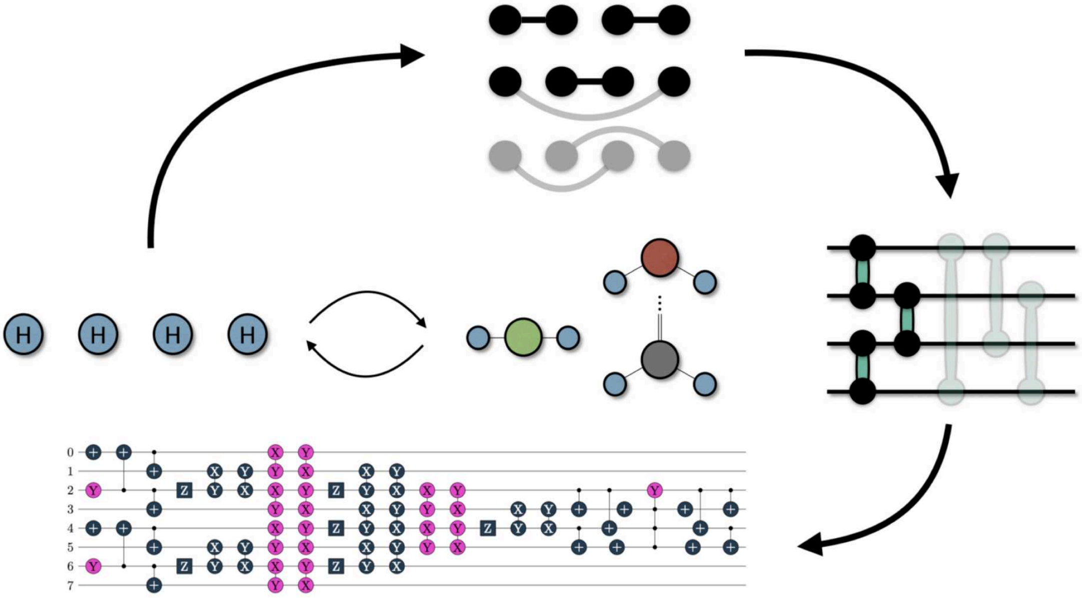
We will explore novel approaches that leverage the principles of unitary coupled cluster tailored to quantum computers. We will introduce the underlying design principles of quantum circuits that prepare approximations to electronic eigenstates and see how a differentiable framework can be realized. Along the way, we will see some explicit examples of current research and some open questions.



MiMiC: A Flexible Multiscale Simulation Framework for the Next-Generation HPC

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Nowadays, a user can choose from a wide variety of computational chemistry software packages, each coming with a set of specific features and strong suits. Many of these programs offer multiscale simulation support for modeling chemical processes in complex molecular systems, which often contain subdomains that require a higher level of theory, and/or the processes that might unfold on a considerable time scales. However, writing interfaces for such simulations involving several independent programs is always a balancing act between performance and flexibility.

Addressing this challenge, the MiMiC framework[1–3] aims to provide a general interface for different programs handling individual subsystems at varying levels of theory. It facilitates data exchange between these concurrently running programs and potentially calculates interactions that might arise between the subsystems. Notably, it implements a generalized electrostatic embedding scheme with which it has demonstrated efficient scaling for large-scale simulations using tens of thousands of cores.[4]

To minimize the implementation overhead when interfacing with various software packages, we adopted a loose-coupling paradigm combined with a multiple-program multiple-data model (MPMD). This approach offers a key advantage by not interfering with the underlying parallelization of specific programs. It thus provides significant flexibility, while maintaining high efficiency, and allows users to fully exploit modern modular high-performance computing (HPC) architectures, as present in LUMI or JUPITER, the upcoming first exa-scale supercomputer in Europe.[5]

In this contribution, we present the latest developments in MiMiC, with a particular focus on its software design, and the new and upcoming features such as polarizable embedding QM/MM as well as new external programs (CP2K, OpenMM, TinkerHP). We hope to make a case for MiMiC as a compelling choice for multiscale molecular modeling in the forthcoming era of exa-scale HPC.

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Prediction of fundamental physics and spectroscopy of small molecular ions with relativistic quantum chemistry

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In the search for physics beyond the standard model of particle physics a low-energy tabletop experiment complementary to e.g. the large hadron collider at CERN is the measurement of a hypothetical parity and time-reversal (*P,T*) violating permanent electric dipole moment (EDM) [1]. An EDM in the intrinsic frame of a polar molecule as it is computed in all common quantum chemistry packages is different than a *P,T*-odd EDM, as the former rotationally averages out for a random orientation of a diatomic molecule. A *P,T*-odd EDM on the other hand is composed of several effects such as an EDM of elementary particles like the electron or the highly exotic nuclear Schiff moment of the nucleus. The effects leading to a *P,T*-odd EDM are more enhanced in polar molecules than compared to atoms, relativistic in nature and dependent on the electronic state [2,3]. Thus, we need relativistic quantum chemistry where spin-orbit coupling is treated non-perturbatively in order find suitable systems with large enhancements and good predictions of necessary spectroscopic properties.

Molecular ions have the advantages of being sympathetically coolable, guidable by electric fields and trappable in magneto-optical traps for longer time scales [4,5]. In addition, small molecules with a high charge have the charm of a congested level structure leading to possible quasi-degenerate vibrational states. This congested level structure is favourable for a different aspect of fundamental physics, namely the search for a hypothetical change in the fine-structure constant [6]. From the perspective of stability, an increasing charge of a small molecule increases the chance of Coulomb explosion. As such, the investigation of stable highly charged molecular ions could lead to insights on chemical stability and the nature of the chemical bond influenced by such extreme conditions.

We assess the above mentioned properties on the level of two-component complex generalised Hartree–Fock and Kohn–Sham within the Zeroth Order Regular Approximation [7-10] and incorporate further correlation on the level of two-component second-order perturbation theory where necessary.

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Ab initio quantification of the nuclear dimensions for electron transfer

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Electron transfer is ubiquitous in chemistry, for instance in intermolecular redox events during catalysis, along enzymatic charge transport chains, or as intramolecular events in some mixed-valent compounds. In the Marcus–Hush model, electron transfer (ET) results in a change in diabatic potential energy surfaces, separated along an ET nuclear coordinate.[1] This coordinate accounts for all nuclear motions that promote electron transfer. It is usually assumed to be dominated by a collective asymmetric vibrational motion of the redox sites involved in the ET, but it is rarely quantitatively specified.

Herein, we describe an *ab initio* approach for quantifying the ET coordinate in mixed-valence compounds.[2] Using sampling methods at finite temperature combined with density functional theory calculations, we find that the electron transfer can be followed using the energy separation between potential energy surfaces and the extent of electron localization. The precise nuclear motion that leads to electron transfer is then obtained as a linear combination of normal modes. We demonstrate this approach for a series of dinitroradical anions falling into different Robin–Day Classes depending on the environment.

Mixed-valence compounds are often characterized by an intervalence charge-transfer (IVCT) band that is associated with intramolecular electron transfer. We will present an *ab initio* interpretation of the electronic structure of the Creutz–Taube ion,[3] whose characteristic IVCT band has received different, even diverging interpretations. Using a two-state Marcus–Hush model in combination with *ab initio* calculations, we demonstrate that both antisymmetric and symmetric vibrational motions are required to explain the shape of the IVCT band. We find that the symmetric dimension originates from geometry-dependent coupling, which in turn is a natural consequence of the well-established superexchange mechanism.

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Coupled Quantum Dynamics of Chlorophyll B-Bands and XMS-CASPT2 X-ray Absorption Spectra

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One of the few experimental possibilities to resolve ultrafast nuclear and electron dynamics are time-resolved X-ray absorption spectra (XAS). The computational simulation of XAS is becoming increasingly important when it comes to assigning complex spectral features. This requires the development of workflows to simulate XAS at a higher level of theory for a wider range of molecules than currently available in order to offer guidance and stimulation of new experiments. Building on a previously published workflow [1], we extended it to simulate time-resolved XAS for the magnesium and nitrogen K-edge of chlorophyll. Despite numerous studies the excited state dynamics of this molecule is still not fully understood. We applied grid-based wavepacket quantum dynamics on representative XMS-CASPT2 potential energy surfaces and could thereby show that the first two excited states Qy and Qx, as well as the higher lying excited states Bx and By are strongly coupled. We investigate the possibility to follow the ultrafast intra-band population transfer within B- and Q-band, as well as the inter-band transfer from B to Q with time-resolved XAS. The transient XAS are obtained by combination of static XAS with coupled nuclear and electron dynamics. In this way we can not only describe the nuclear wavepacket dynamics, but also account for the electronic coherence and predict its influence on the XAS.

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Spectra Prediction and Peak Assignment using Graph Neural Networks

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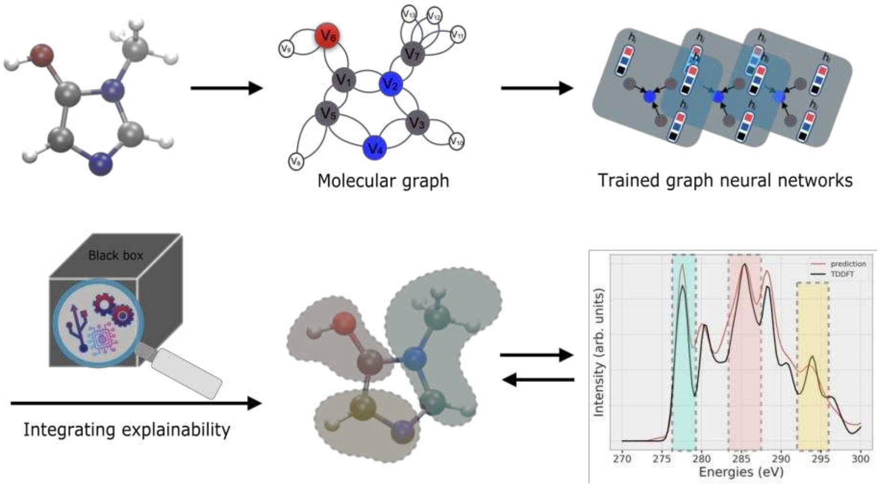
The use of sophisticated machine learning (ML) models, such as graph neural networks (GNNs) to predict complex molecular properties or all kinds of spectra has grown rapidly [1,2]. However, other than known from quantum chemistry calculations of spectra, the peak assignment is no integral part of black-box ML models. Explainable artificial intelligence offers tools to open the box: Feature attribution serves to determine the contributions of various atoms in the molecules (nodes in the GNN) to the peaks observed in the spectrum (see figure). By numerically comparing this peak assignment to the core and virtual orbitals from the quantum-chemical calculations underlying the exemplary X-ray absorption spectra data set of small organic molecules, we demonstrate how the atomic contributions deliver spectra interpretation [3]. Robustness tests further demonstrate the reliability of the predictions.



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Toward an Automated Calculation of Anharmonic Vibrational Frequencies in Arbitrary Internal Coordinates

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The calculation of anharmonic vibrational frequencies in arbitrary internal coordinates requires the computation of the kinetic energy as well as the evaluation of a multidimensional potential energy surface. Due to the myriad definitions of internal coordinates, writing an automated algorithm for this purpose is a challenging task. The various properties of the coordinates require a high degree of flexibility in the calculation of the potential energy surface to handle the key elements as choosing fitting functions, positioning of grid points, exploitation of symmetry, or the elongation of the surface. Also for the subsequent frequency calculation, which consists of high dimensional integrals due to the coupling within the kinetic energy, constraints like a *n*-mode expansion of the Wilson G matrix need to be used to allow for a general implementation of the Podolsky operator.

To proof the concepts of the implemented algorithms, the HOPO molecule is used as a benchmark system, to highlight the benefits of the internal coordinate with respect to large amplitude motions.

Understanding Reactivity Complexity in Iron-PDI-Catalyzed [2 + 2] Cycloaddition of Alkenes: Beyond DFT with SA-CASSCF/NEVPT2

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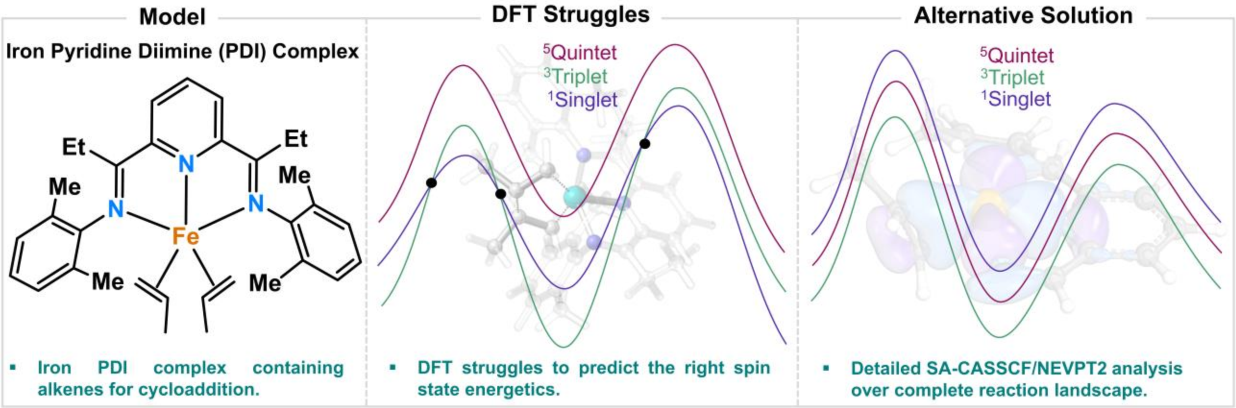
Non-innocent pyridine diimine (PDI) complexes with first-row transition metals have emerged as effective catalysts in organometallic transformations. However, understanding their reactivity is challenging due to the multi-spin feasibility of 3d metals and the presence of non-innocent ligands. While density functional theory (DFT) has been widely used to unravel mechanistic insights, its limitations as a single-reference method can potentially misrepresent spin-state energetics, compromising our understanding of these intricate systems.

In this study, we investigate an iron-PDI-catalyzed [2 + 2] cycloaddition of alkenes[1] using state-averaged complete active space self-consistent field/N-electron valence state perturbation theory (SA-CASSCF/NEVPT2) alongside DFT calculations. Contrary to DFT(TPSSh) predictions of two-state reactivity (TSR), SA-CASSCF/NEVPT2 calculations reveal a highly multiconfigurational nature and identify a different rate-limiting step with a single-state scenario. Insights into electronic ground states and spin distribution elucidate intriguing metal-ligand interactions and depict metal-ligand cooperativity throughout the catalytic cycle. Comparative analysis with DFT functionals highlights their limitations in predicting accurate results across all reaction aspects. Our comprehensive evaluation indicates that single-point energy calculations using the modern density functional MN15 on TPSSh geometries offer the most reliable density functional methodology in scenarios where computational cost is a concern.[2]



- Iron PDI complex containing alkenes for cycloaddition.
- DFT struggles to predict the right spin state energetics.
- Detailed SA-CASSCF/NEVPT2 analysis over complete reaction landscape.

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Unidentical Twins: Geometrically Similar yet Chemically Distinct Metal-Free Sites in Boron Oxide for Methane Oxidation to HCHO, CO and CO_2

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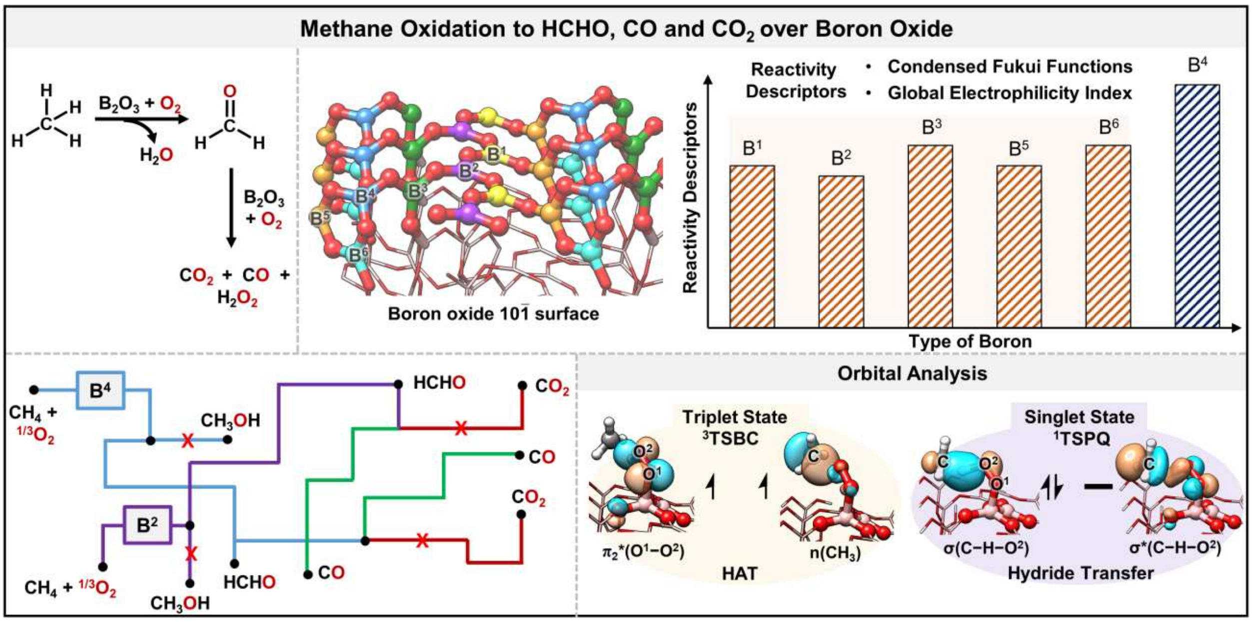
Boron-based catalysts such as boron oxide (B_2O_3) and hexagonal boron nitride (*h*-BN) that perform alkane oxidation have attracted significant interest in recent years.[1,2] Wang et al. carried out methane oxidation through an intriguing reaction where O_2, despite its stable triplet state, reacts with B_2O_3 to produce HCHO, CO and CO_2.[3] In the present works, we computationally examined the reactivity of B_2O_3 towards O_2 for methane oxidation.[4,5] We took the actual structure of B_2O_3 derived from its crystal structure and conducted periodic DFT calculations in combination with orbital analysis.[4] The B_2O_3 catalyst contains various probable sites that may be responsible for methane oxidation. We utilized DFT to compare two relevant geometrically identical B^2 and B^4 sites for their reactivities. We employed descriptors such as condensed Fukui functions and global electrophilicity index to chemically distinct these sites. The two sites are explored in-detail for the CH_4 to HCHO, CO and CO_2 conversion. Orbitals reveal that at singlet and triplet states, methane activation proceeds via a hydride transfer and a hydrogen atom transfer mechanism, respectively.



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Molecular mechanism and kinetics of the process of evaporation at the liquid-vapor interface of aqueous solutions

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The vapor-liquid mass transfer phenomena are interesting in many areas of science and engineering since the kinetics and mechanism of mass transfer from the liquid to vapor phase strongly influence the rate of reaction, aerosol formation, and drying materials as well as in nature plays a vital role in balancing atmospheric temperature and cloud formation. The process of evaporation has proven challenging to study experimentally, and because it is infrequent on molecular time scales, it presents a challenge for computer simulations as well. [1,2] We explore the effects of ionic solutes (NaCl) on the rate and mechanism of water evaporation with varying concentrations. The mechanism, kinetics, and potential of mean force (PMF) of evaporation of water from aqueous NaCl solutions are investigated by both unbiased molecular dynamics simulations and biased simulations using the umbrella sampling method. [3] The rate of evaporation is found to decrease in the presence of ions. The evaporation of a surface water molecule from ionic solutions can be triggered through its collision with another water or chloride ion and water combined. Thus, the mechanism of the evaporation process of ionic solutions can be more complex than that of pure water. We also present a detailed mechanism of water evaporation from the surface of graphene and graphene oxide by reducing the thickness of the pure water layer. Noticeably, water evaporation is more frequent in reducing the thickness of the water layer on graphene sheets. In contrast, it shows the opposite behavior in reducing water thickness on graphene oxide sheets. We use the umbrella sampling method to calculate the PMF across water evaporation. In the case of an ion-water system, the free energy changes (ΔF) are found to increase with increasing concentration of NaCl. The ΔF calculations of water evaporation from the graphene sheets are found to decrease with decreasing thickness of water, while a reversed trend is observed in the case of water evaporation from the surface of graphene oxide.

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ORCA 6: next-generation software for real-world applications

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In this work, we will showcase the newest algorithms and improvements implemented in the latest version of the ORCA software (Version 6.0, released 26. June 2024). With this update, it has become more feasible to compute larger and more flexible structures than before.
Thereby one of our focus points in the development of the newest ORCA software was to improve the robustness and efficiency of the SCF solver. It was completely rewritten from scratch, making sure that it uses the least possible amount of memory, and now allows calculations with more than 5.000 atoms and 50.000 basis functions.
Further development in the chemical application area of the software improves upon the use of sophisticated solvation models. On the one hand, we demonstrate how the newly implemented implicit solvation model DRACO [1] improves calculated solvation energies by automatically adapting CPCM radii to charges. On the other hand, our advanced explicit SOLVATOR algorithm [2] uses swarm intelligence to automatically place explicit solvent molecules onto any given solute, independent of the solvent used. Using this swarm intelligence procedure for our recently developed DOCKER method [3], we show how all users of ORCA 6 are now able to combine any two arbitrary structures to routinely find the optimal binding position of the structures in question.
Besides this, ORCA is now able to compute conformer ensembles for any input structure using the global optimizer algorithm (GOAT) [4], which can be used together with any method implemented in ORCA, including hybrid and non-hybrid DFT, excited states, broken symmetry, QM/MM, etc.

Overall, we present how the new and improved ORCA 6 program package enables the computation of large, flexible, real-world and chemically relevant structures faster and more accurately than ever before.

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Schrödinger cat state representing two enantiomers of $H_3O_2^-$

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The vibronic ground state of $HO\text{-}H\text{-}OH^-$ represents axial R_a and S_a enantiomers, with equal probabilities. If the chirality is measured to be R_a, then this induces periodic quantum stereo-mutation from R_a to S_a to R_a to S_a and so on. Likewise, the observation of S_a induces chirality flips from S_a to R_a to S_a to R_a and so on. The period of stereo-mutation is $\tau = 2.266$ ps. The phenomenon is supported by the light masses of the hydrogen atoms which interchange positions during stereo-mutation. Interchanges of heavier atoms would suppress the phenomenon. This heavy-atom-blockade of quantum stereo-mutation is demonstrated for SiC_4H_4. The results are obtained by means of quantum chemical calculations and by quantum dynamics simulations.

Cavity-Born-Oppenheimer Hartree-Fock: Optimizing Molecules under Vibrational-Strong-Coupling

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Polaritonic chemistry is a rapidly growing multi-disciplinary research field. The strong coupling of molecules and light within optical cavities offers a novel way to not only alter and design chemical and physical properties of molecules, but to also shape the (quantum) properties of light in various ways. When molecules are placed in such a non-classical photonic environment, it is possible to form strong light-matter-coupled hybrid states called polaritons. Recent experiments show that this strong coupling between light and matter offer a possible novel approach to control chemical reactions.
The situation in which the quantized cavity modes are coupled via their characteristic frequency to vibrational degrees of freedom of molecules is called vibrational strong coupling. In this regime, the chemistry of a single electronic state (mostly the ground state) and its vibrational spectroscopy are influenced by the cavity interaction. However, despite a plethora of suggested applications and observed novel effects, the current theoretical description is limited and far from complete.

In this contribution we investigate how the molecular structure changes under vibrational strong coupling using an ab-initio method based on the cavity Born-Oppenheimer Hartree-Fock ansatz [1,2]. By optimizing small molecules resonantly coupled to cavity photon modes, we underscore the critical significance of reorientation and geometric relaxation. Both effects are currently neglected in most computational studies. Therefore, the interpretation of computational studies based on fixed molecular structures and fixed orientation should be treated with caution. Applying the recently introduced vibro-polaritonic normal mode analysis [3], we are not only able to determine vibro-polaritonic IR spectra but also are able for a comprehensive analysis of these hybrid states. On the basis of our findings, we present a intriguingly simple concept to estimate the impact of cavity interaction on molecular geometry using molecular polarizability and dipole moments.

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External Electric Fields Facilitate Metal-free Dinitrogen Activation

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Dr. Shailja Jain: Present Address: Alexander von Humboldt Postdoc Fellow

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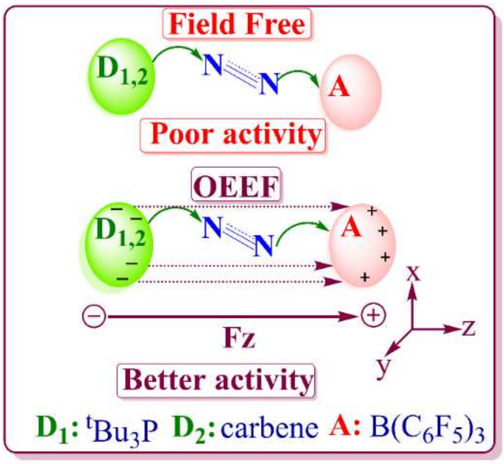
This study employs computational methods to explore the feasibility of N_2 cleavage by frustrated Lewis pairs (FLPs). We investigate two FLP systems: phosphane/borane (**1**) and carbene/borane (**2**). Previous research indicates that while these systems react with H_2 and CO_2, they do not activate N_2. Our findings demonstrate that N_2 is indeed inert under standard conditions and requires augmentation by an external tool for activation. Specifically, we show that FLP-mediated N_2 activation can be achieved using an external electric field oriented along the reaction axis of the FLP.

Remarkably, we further demonstrate that the effect of the OEEF can be replicated by introducing ionic additives such as Li^+ and Cl^-. In conclusion, our study highlights the effectiveness of FLPs in conjunction with oriented external electric fields (OEEF) in activating N_2, suggesting that this FLP/OEEF combination could serve as a general strategy for activating inert molecules.



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Flexible Polarizable Water Model Parameterized via Gaussian Process Regression

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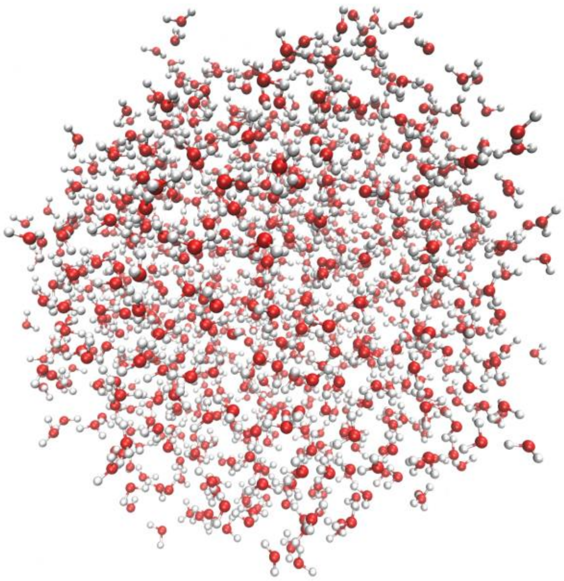
Water is often a crucial component of many molecular simulations. To be able to accurately model chemical reactions near/at water interfaces using classical force fields, it is essential to employ a water model that is both polarizable and flexible.

SWM4/Fw, our recently developed flexible polarizable water model [1], will be presented. It was optimized using Gaussian process regression, which is a machine-learning method and can predict a model's properties without requiring further simulation whenever the force field parameters are changed. SWM4/Fw reproduces many reference water properties and adds flexibility that is important for modeling chemical reactions involving bond stretching or breaking and for calculating vibrational spectra. The model is also computationally efficient thanks to the use of extended Lagrangian with Drude oscillators to represent explicit electronic polarization. The approach used to parameterize the water model based on Gaussian process regression should also be useful for developing other force fields.



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Implementation of Girsanov reweighting in OpenMM and Deeptime

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Molecular dynamics (MD) simulations provide temporal insights into chemical systems at the atomic resolution. However, slow dynamical processes are difficult to model as they go beyond the time scales that can be captured by an unbiased MD simulation.
Enhanced sampling techniques artificially increase the occurrence of rare events during the MD simulation. A dynamical reweighting technique, like Girsanov path reweighting, can be used to recover the unbiased dynamics from simulations performed at a biased potential. The combination of both methods offers a strategy to solve the sampling problem arising form processes auch as chemical reactions, complex formations or slow conformational changes.[1-5]

We present a comprehensive guide for implementing Girsanov reweighting into MD simulation and dynamical analysis programs to make this approach widely available.

Using OpenMM with opennmmtools we show how to extend Langevin integrators so that reweighting factors are calculated on-the-fly and can be recorded at regular intervals in a trajectory file. Deeptime provides estimators for dynamic models to which we have added a Markov state model estimator considering reweighted transition counts. We provide the extended software as well as the instructions for its application to low-dimensional and molecular systems. [6-9]

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Inducing Spin-Selective Transport in Nitrogen-Doped Zigzag Graphene Nanoribbons by Engineering Ground State Properties

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Spin filtering nanodevices are currently a research field of great interest.[1] Due to their inherent edge spin polarisation, slim zigzag graphene nanoribbons (ZGNRs) are promising materials for such applications.[2] Despite recent advances, the production of longer slim ZGNRs has remained a challenge.[3] One recent breakthrough came from doping the edges with nitrogen in a particular pattern, while maintaining the characteristic edge polarisation.[4] A similar doping pattern on one edge with phosphorus was investigated for spin-selective transport.[5] In our contribution, we investigate a nanojunction based on this nitrogen doping pattern. Through addition of negative charges or protonation, the energetic ordering of the two lowest-lying states with differing spin density distributions can be changed and the device turned into an effective spin filter. The electron transport is simulated using the non-equilibrium Green's function (NEGF) formalism. Global transport properties are accessed through the Fisher-Lee relation and the Landauer formula, while local current densities can be calculated through spatial maps of the lesser Green's function.[6] A combination of spatial and spectral filters enable these to be computed efficiently for larger systems.[7,8] This presents a novel way of tailoring the spin-selective transport properties of ZGNRs and therefore may pave the way for a new family of spintronic devices.

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Theoretical Treatment of Molecular Auger Decay with Non-Hermitian Quantum Chemistry

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Due to recent advances in experimental techniques, Auger electron spectroscopy is gaining renewed traction as a method to probe the electronic structure of molecules. Meanwhile, the development of modern and efficient theories for simulation of Auger spectra is not trivial due to the properties of the decay processes.

Because of their metastability, core-vacant states represent electronic resonances [1] that can be tackled with standard quantum-chemical methods only if they are approximated as bound states, meaning that their decay is neglected. The simulation of Auger decay requires to extend quantum chemistry to include a continuum description and to take into account the multitude of configurations arising from all open decay channels. In the work presented here [1–4], we make use of non-Hermitian ab initio quantum chemistry, where the molecular electronic Hamiltonian is analytically continued into the complex plane. This approach gives access to total decay widths or, respectively, lifetimes, with L^2 methods. Partial widths are evaluated using energy decomposition analysis [1,3,4] and a generalized core-valence separation [2,3].

We present results for different core-ionized states of several systems with up to 12 atoms, among which Ne, $C_2H_{2,4,6}$, and C_6H_6, as well as a selection of heterocyclic organic systems. The total and partial decay widths are calculated using coupled-cluster theory with single and double substitutions (CCSD) and equation of motion (EOM)-CCSD, while Auger electron energies can be computed making use of EOM-double ionization potential-CCSD. Our results agree well with previous theoretical and experimental work. We also report recent advances to reduce the computational cost making use of many-body perturbation theory and a different wave function expansion (configuration interaction singles) which exhibit promising accuracy. Partial widths are used to generate Auger spectra and allow to predict population of electronic states and fragmentation pathways following Auger decay.

Further interest lies in systems with third-row elements. These exhibit core-holes and Auger electrons in a wide energy range, depending on the shells that are involved in the decay process. Our methods reproduce the shell selectivity of Auger decay in Ar and H_2S, including the very high efficiency of Coster-Kronig (intrashell Auger) decay. Ultimately, our method has also been extended to resonant Auger decay which happens in core-excited states and results and trends for different states of Ne and H_2O will be reported.

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Fourth-Generation High-Dimensional Neural Network Potentials for Atomistic Simulations in Solution

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Machine learning has found many applications in the fields of chemistry and materials science, and high-dimensional neural network potentials (HDNNPs) have become an accurate tool to represent the multi-dimensional potential energy surface in atomistic simulations. Here, we compare the performance of two types of HDNNPs which are 2G-HDNNPs and 4G-HDNNPs, in the description of organic molecules in aqueous solution. While it has been shown for many systems that 2G-HDNNPs are well suited to represent local bonding as a function of the atomic environments, they are not applicable to systems in which long-range charge-transfer is important. The 2G-HDNNPs effectively capture important local interactions by focusing on the vicinity of atoms inside the cutoff sphere, providing a highly accurate description of short-range interactions. However, their limitation arises when dealing with systems where interactions extend beyond the local environment, necessitating the consideration of the influence of atoms outside the cutoff sphere. Such systems can be addressed by 4G-HDNNPs, in which the atomic charges depend on structural or electronic changes even very far away in the system. The 4G-HDNNPs overcomes the limitations of 2G-HDNNPs by including long-range electrostatic effects and non-local charge-transfer, making them particularly useful for accurately modeling complex systems where long-range interactions play a critical role.

On the Role of Singles Amplitudes in ADC(2) and CC2 for Low-Lying Electronically Excited States

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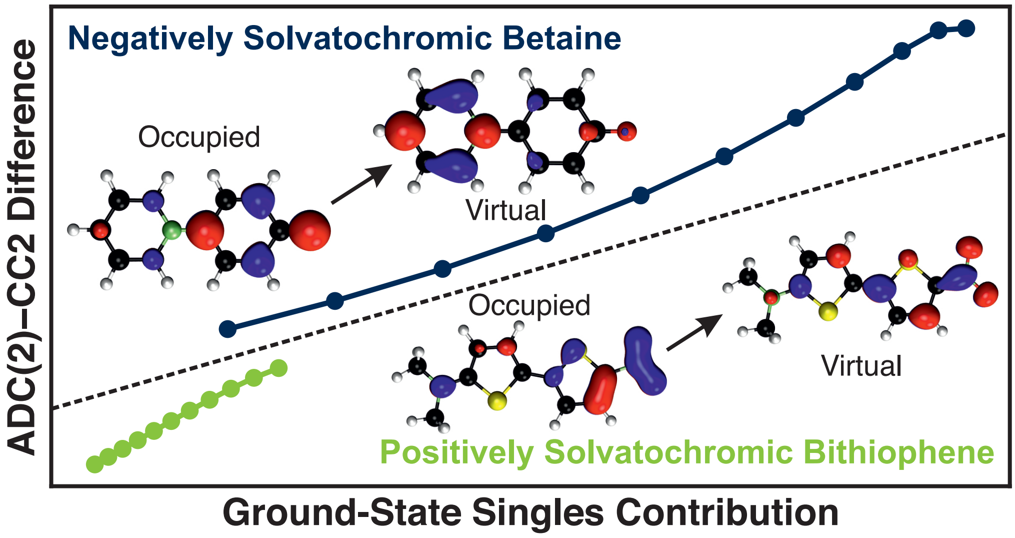
The popular second-order methods CC2 and ADC(2) typically perform very similarly for single excitations of organic molecules. However, as rationalized in this work, significant deviations between these two can occur if the ground state and a low-lying singly excited state arise from a strong coupling between their leading configurations [1]. Such a configuration mixing is partially accounted for in CC2 through the ground-state singles amplitudes, but is missing in ADC(2), permitting unusual deviations between the results obtained with these methods. Here, we investigate how severe this effect can become at the example of two solvatochromic dyes: a negatively solvatochromic betaine dye and a positively solvatochromic bithiophene. These two dyes allow to study the limits of both small and somewhat larger excitation energies and configuration mixing by tuning the $S_0 \rightarrow S_1$ energy gap through the polarity of the environment, e.g., described by the continuum solvation model COSMO. Higher-level calculations at the CC3 level provide information on the accuracy of ADC(2) and CC2 in the vacuum case. The most extreme deviation between ADC(2) and CC2 is found for the betaine dye in vacuum, where the ADC(2) result is 0.45 eV below that of CC2. In this case, the methodical error of CC2 with respect to CC3 is only 0.05 eV. With increasing excitation energy in polar solvents, the CC2–ADC(2) deviation decreases to a value of only 0.15 eV. For the bithiophene, which has larger excitation energies, these effects are reversed due to the opposite solvatochromism, but also smaller in magnitude: the deviation increases from 0.08 eV in vacuum to 0.16 eV in the conductor limit of COSMO. Although for these two dyes larger deviations are observed for smaller excitation energies, the extent of configuration mixing does not generally correlate with only the size of excitation energy.



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Grand canonical ensemble approaches for modeling electrochemistry in CP2K

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We present the implementation of two grand canonical ensemble approaches in the open-source computational chemistry software CP2K that go beyond the existing canonical ensemble paradigm (Chai, Z.; Luber, S. Under Review). The first approach is based on implicit solvent models and explicit atomistic solute (electrode with/without adsorbed species) models and includes two recent developments: The grand canonical self-consistent field (GC-SCF) method (J. Chem. Phys. 146, 114104 (2017)) allowing the electron number of the system to fluctuate naturally and accordingly with the experimental electrode potential and the planar counter charge (PCC) (J. Chem. Phys. 150, 041722 (2019), Phy. Rev. B 68, 245416 (2003)) salt model completely screening the net charge of the electrode model. In contrast with previous studies, in our implementation, the work function (absolute electrode potential if the potential drop at the electrolyte-vacuum interface is omitted) is the constrained quantity during an SCF optimization instead of the Fermi energy. The second approach (referred to as the two-surface method and the numerical titration method) (Phys. Rev. Lett. 88, 213002 (2002), J. Chem. Phys. 122, 234505 (2005), J. Am. Chem. Soc. 126(12), 3928–3938 (2004)) is based on fully explicit modeling of solvent molecules and ions. It is used to calculate the electron chemical potential corresponding to an equilibrium electrochemical half-reaction (M^(n+m)+ + n e^(-) ⇌ M^m+) which involves DFT molecular dynamics. This opens the way for forefront electrochemical calculations in CP2K for a broad range of systems.

Moreover, we present a new and efficient self-consistent continuum solvation SCCS implementation based on the solvent-aware interface (J. Chem. Theory Comput. 15, 3, 1996–2009 (2019)) which utilizes a solute-solvent interface function based on convolution of electron density in the CP2K software package relying on the mixed Gaussian and plane waves approach (Chai, Z.; Luber, S. To Be Submitted). Our implementation has been tested to successfully eliminate non-physical implicit solvent regions within the solute and achieve good SCF convergence, as demonstrated by test results for both bulk and surface models such as liquid H_2O, titanium dioxide, and platinum.

Understanding the Photodissociation of Molecular Solar–Thermal (MOST) Compounds Using (XMS)–CASPT2: (Fulvalene)$M_2(CO)_4$ (M = Ru, Fe)

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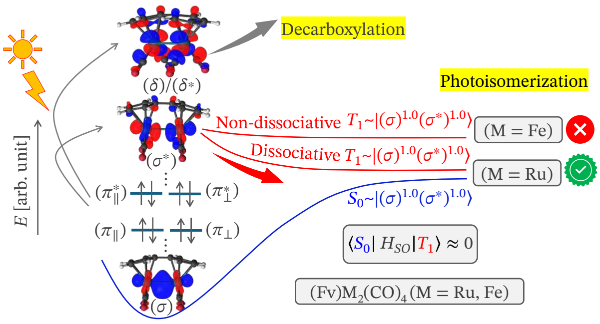
Molecular Solar–Thermal (MOST) fuels are promising sustainable energy solutions, storing solar energy in chemical bonds and releasing it as heat on demand, similar to rechargeable heat batteries.[1] The (Fv)$M_2(CO)_4$ (Fv = fulvalene, M = Ru) system is a pioneering MOST storage candidate with intriguing wavelength–dependent photochemistry.[2] Irradiation > 350 nm drives a unique *syn*–to–*anti* photoisomerization *via* an enduring triplet intermediate, while < 300 nm causes deleterious decarboxylation. Transitioning to abundant metals, such as Fe, is desired for large–scale applications, but the Fe analogue resists photoisomerization > 350 nm and still induces decarboxylation.[3] The excited–state mechanisms of both photo–reactions remain unexplored, crucial for designing new MOST molecules. Using time–dependent density functional theory (TDDFT) and relativistic extended–multistate complete active space second-order perturbation theory (XMS–CASPT2) with spin–orbit (SO) coupling, we uncover the relevant involved excited–states in (Fv)$M_2(CO)_4$ (M = Ru, Fe) and elucidate the mechanisms behind decarboxylation and photoisomerization. All low–lying excited–states in these systems are metal–centered, with Fe states red–shifted compared to Ru. Excitations to M_δ orbitals, interacting with CO_σ orbitals, trigger decarboxylation, showing strong multiconfigurational behavior. In Ru, these states appear < 300 nm, while in Fe, > 350 nm. We identified a "dissociative" metal–centered $^3[(\sigma)^1(\sigma^*)^1]$ triplet–state stabilized by 0.44 eV following (Ru—Ru)σ bond scission, originating from a $^1[(\pi^*)^1(\sigma^*)^1]$ state *via* intersystem crossing (ISC), aided by strong SO- coupling in a barrierless Marcus "boundary" region. This $^3[(\sigma)^1(\sigma^*)^1]$ state prevents nonradiative decay, ensuring a long lifetime. In Fe, the ground state's multiconfigurational nature leads to low–lying triplet states, indicating a Marcus "inverted" region with high ISC barriers and weaker SO–coupling. This results in a slower rate of populating the $^3[(\sigma)^1(\sigma^*)^1]$ state, which is non-dissociative along the (Fe—Fe)σ bond, preventing photoisomerization. This study provides insights into the excited–state relaxation mechanisms of (Fv)$M_2(CO)_4$ (M = Ru, Fe), crucial for advancing MOST technologies.



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Effect of Anchoring Dynamics on Proton-Coupled Electron Transfer in the Ru(bda) Coordination Oligomer on a Graphitic Surface

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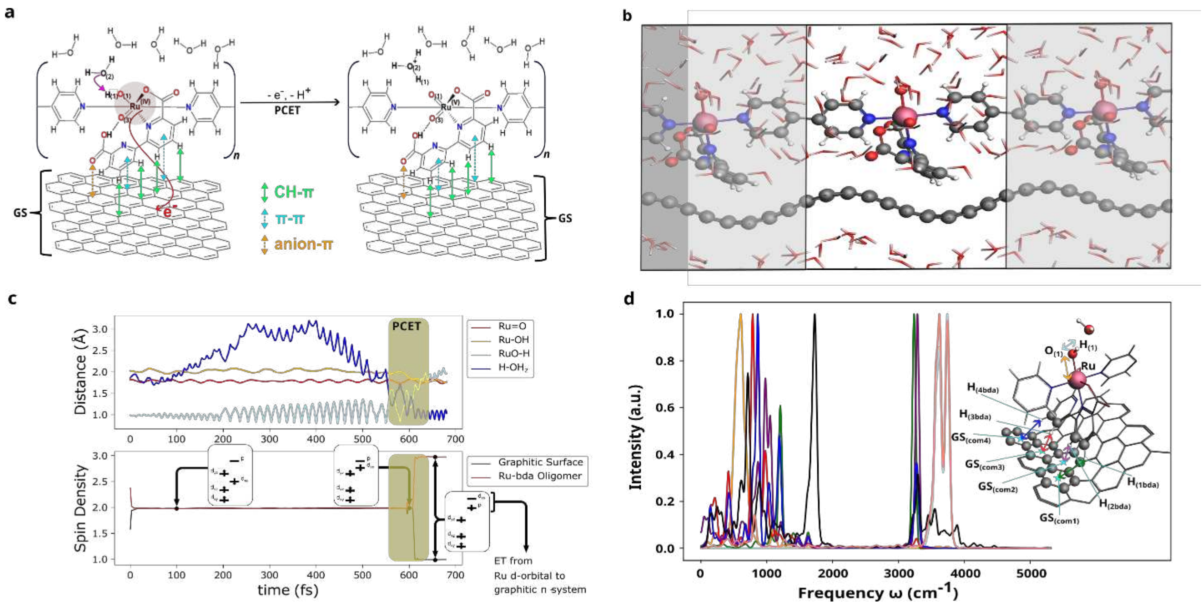
The oligomeric ruthenium-based water oxidation catalyst, Ru(bda), achieves experimental anchoring on graphitic surfaces via CH-π stacking interactions between its bda ([2,2'-bipyridine]-6,6'-dicarboxylate) ligand and the hexagonal rings of the graphitic surface (GS). [1,2] This anchoring mechanism regulates molecular coverage and promotes efficient catalysis of water oxidation to dioxygen. The oligomeric structure of the molecule provides multiple anchoring sites on the surface, significantly enhancing the stability of the hybrid catalyst-graphitic surface anode through dynamic bonding. [1,2] Nonetheless, the influence of this dynamic anchoring on the catalytic mechanism remains debated (Figure 1a). This study explores a key proton-coupled electron transfer (PCET) event in the catalytic cycle using DFT-based molecular dynamics (MD) simulations combined with metadynamics (Figure 1b,c). The CH-π stacking anchoring is crucial for stabilizing the hybrid system and facilitating the PCET, involving vibrational resonances between the anchoring bonds' movements and charge fluctuations at the catalyst–graphitic surface interface (Figure 1d). Additionally, the computational investigation reveals the presence of a quartet spin state intermediate that can transition to the experimentally observed, thermodynamically more stable doublet spin state. [3]



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Theoretical Investigations on Fe_2P-type Magnets: Effects of Si and Co Substitution on Physical and Magnetic Properties

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As a consequence of the resource criticality of rare-earth (RE) elements, a big focus is set on finding a rare-earth free magnet that fills in the gap between the commercially available ferrite and $Nd_2Fe_{14}B$ magnets. One potential candidate to fill in this gap are magnets based on the hexagonally ordered Fe_2P compound, which exhibits promising properties like a high magnetization and high uniaxial anisotropy. In this work, we performed density functional theory (DFT) calculations to investigate the influence of the substitution of P and Fe with Si and Co on the magnetic and physical properties of the Fe_2P compound. For a systematic understanding, physical properties like the formation energy at 0 K and the lattice constant, as well as intrinsic magnetic properties like the magnetization M_S and the Curie temperature T_C are screened starting from the binary structure of Fe_2P for each substitution. Furthermore, the combined effects of Si and Co substitution on the physical and magnetic properties are considered in quarternary $(Fe,Co)_2(P,Si)$ compounds with different Si contents. The resulting T_C trends for these quarternary compounds were further investigated by the calculation of J_{ij} energies, which revealed a positive influence of Si on the 3*f*-3*g* Fe interactions resulting in a significant increase of T_C. The substitution of Co on the other hand leads either in case of a low Si content to an overall increase or with a high Si content to a decrease of the 3*f*-3*f* and 3*g*-3*g* interactions and therefore to an increase or decrease of the T_C in dependence on the Si content, respectively.

Low-order scaling multicomponent methods for the description of nuclear quantum effects

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Nuclear quantum effects (NQEs) are relevant for a wide range of chemical phenomena, including photochemistry, proton coupled electron transfer reactions, and even in the description of common hydrogen bonds, just to name a few examples. The latter may require a quantum mechanical treatment of atomic nuclei, in particular the protons. Several schemes exist for this aim, many of them involving extensive PES calculations, which are then used for quantum or semiclassical dynamics, i.e. path integral molecular dynamics and instanton theory, among others.[1] All these methods have in common that the computational costs scale very unfavorably with the system size and the number of quantum nuclei.

Multicomponent methods offer an alternative. The latter uses wavefunction or density functional theory (DFT) to treat both (selected) nuclei and electrons at the quantum mechanical level and on equal footing. Among these, notable progress has been made within the nuclear-electronic orbital (NEO) formalism.[2] While the methods founded on the NEO framework seem promising for the systematic incorporation of NQEs, their practical application has been somewhat restricted due to the substantial computational cost associated with the existing algorithms. Recently, Hasecke and Mata reported and implemented in Molpro the use of local density fitting techniques in NEO Hartree-Fock calculations, achieving speed-ups by an order of magnitude and above with almost no penalty in accuracy.[3]

Here, we present the recent developments in the NEO framework within the group and currently available in Molpro.[4] In particular, the implementation of NEO-DFT with local density fitting, reparameterization of electron-proton correlation functionals within NEO-DFT, and the construction of nuclear basis sets together with their performance in simulating proton tunneling processes. Overall, the aim is to make multicomponent simulations efficient and accessible, extending the day-to-day quantum chemistry toolbox.

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Path Integral Monte Carlo Simulation on Molecular Systems with Multiple Electronic Degrees of Freedom

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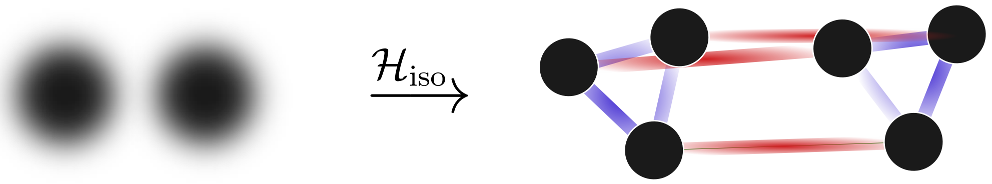
Statistical mechanics of many-body quantum systems is fundamental to our understanding of physical reality and of central importance for emerging quantum technologies. In this context, Path Integral Monte Carlo (PIMC) simulations allow for efficient sampling of static finite temperature properties in the canonical ensemble where classical simulations of quantum systems would otherwise require exponentially large resources.

The idea behind all these PI simulations is to map the original quantum system onto a purely classical one, described by a so-called classical isomorphic Hamiltonian, that on average exhibits identical statistical behavior. However, for molecular systems, electronic degrees of freedom are typically not included in this classical isomorphic Hamiltonian and thus it is assumed that the nuclei evolve on a single potential energy surface (PES), typically associated with the electronic ground state. This naturally results in the inability to properly describe molecules where multiple thermally accessible low-lying excited states are present.

Here we propose a generalized approach to Path Integral Simulations based on the previous work of Schmidt and Tully [1] that accurately considers multiple electronic states, including non-adiabatic effects in the diabatic picture. We will show how this, as usual, results in a classical system that is easily interpretable and computable.

Accordingly, we demonstrate an efficient Markov chain Monte Carlo scheme [2] and show that it can reproduce exact results for simple model problems and molecular systems like H_2 and C_2.



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Intramolecular Singlet Fission: Insights from Quantum Dynamical Simulations

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Singlet fission (SF) is a multiple exciton generation process where two triplet excitons are created out of a singlet exciton via a spin-allowed mechanism. [1] First invoked in the 1960s to rationalize the delayed fluorescence exhibited by some organic molecular crystals, [2] the interest in SF has gained momentum over the last decade in the context of energy conversion as it has the potential to overcome the Shockley-Queisser limit. [3] In this contribution, we analyze the mechanism of intramolecular SF (iSF) in a series of modified pentacene dimers covalently bonded to a phenylene spacer in ortho, meta, and para conformations using high-level ab initio multireference perturbation theory and quantum dynamical methods. [4-8] Our results allow us to determine the impact of the substitution pattern on the iSF mechanism, to characterize the relative contribution of the direct and mediated channels to the overall process and to reveal the instrumental role that vibronic coupling plays in the dynamics of iSF. [5,6] The impact that matter-light interaction in the weak coupling regime has on the iSF dynamics is also discussed. [7,8]

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Density-Functional Theory with σ-Functionals for Highly Accurate Energies and Molecular Properties

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σ-Functionals are a new type of functionals for the Kohn-Sham(KS) correlation energy based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem [1-3]. σ-Functionals are closely related to the well-known direct random phase approximation (dRPA). In the dRPA a coupling constant and a frequency integration of a function of the eigenvalues of the dynamic KS response function is carried out. In σ-functionals the dRPA expression in this integral is replaced by a function motivated by perturbation theory along the adiabatic connection [4]. This function is optimized with respect to reference sets of reaction and interaction energies in order to correct the errors resulting from neglecting the exchange-correlation kernel in dRPA.

σ-Functionals are applied in a post-self-consistent way using input orbitals and eigenvalues from a previous conventional DFT calculation, e.g. with the PBE functional [1] or with hybrid functionals (PBE0, B3LYP) [2,3]. σ-Functionals based on the latter yield mean absolute errors around or below 1 kcal/mol for reaction energies, barrier heights, and non-covalent interactions, thus reach chemical accuracy, and were shown to even slightly outperform the double hybrid functional DSD-BLYP-D3(BJ) for main group chemistry [5].

In Ref. [5] three setups of basis set combinations were proposed, which offer a good compromise between accuracy and numerical efficiency. The evaluation of the post-SCF total energy in a RPA or σ-functional method requires less computational time than a preceding hybrid DFT method, and thus can be carried out routinely for systems of practical relevance.

Besides calculating accurate energies, σ-functionals have been used to compute many chemical properties, such as geometries and vibrational frequencies (using analytic gradients of σ-functionals [6]) as well as NMR shieldings [7]. Also singlet-triplet gaps have been reported [8]. Although none of these quantities were involved in their optimization, σ-functionals do not only outperform conventional DFT methods and the dRPA, but can compete with high level methods such as double hybrid functionals and even coupled-cluster theory.

σ-Functionals have been implemented in several popular quantum chemistry codes (Molpro, Turbomole, ADF, PySCF, FermiONs++, VASP).

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Alternative Coupled Cluster Methods for Open-Shell Singlet States

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Non-standard coupled cluster methods to calculate open-shell singlet states of molecules are discussed. In particular, the fixed-reference [3] and two determinant coupled cluster [1] methods. Similarities of obtained numerical results of both methods and how they can be significantly improved by the distinguishable cluster approximation [2, 4] are highlighted. Numerous singlet and triplet excited states of closed-shell molecules will demonstrate the point. As potential interesting applications of the methods, calculations in diradical chemistry will be shown and perspectives to calculate magnetic exchange couplings and to study OLEDs will be opened.

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Dissociation Kinetics of Hydrated O_2^- Anions Through Master Equation Modeling

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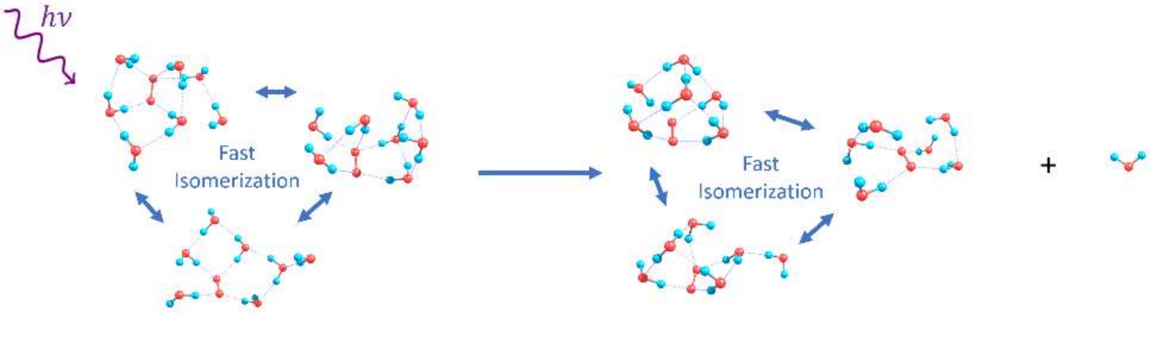
Aerosols are a crucial element towards a better understanding of atmospheric processes and climate change. However, the theoretical modeling of real-sized aerosols with proper quantum chemical methods is hardly feasible as the systems have sizes in the micrometer range. This leads not only to complicated electronic structure calculations, but also the exploration of the potential energy surface becomes increasingly challenging.

In this work, we take a step from small, well-defined systems towards slightly larger systems where the distribution of isomers at room temperature is already very complex. In $O_2^-(H_2O)_6$, we are already confronted with more than 1000 isomers which we obtain through a multi-step process using our genetic algorithm program,[1] different quantum chemical methods and a graph-based clustering algorithm.[2] We model the dissociation kinetics of $O_2^-(H_2O)_{1-7}$ using multiple-well master equation modelling, treating all isomers both for the reactant and the transition state on the same footing.[3] It has been shown previously that taking all accessible isomers into account significantly improves the description of the kinetics.[4]

We calculate the distribution of molecules over the different isomers and their energy. As expected, lower-lying isomers tend to be more populated than higher-lying ones. However, this correlation is far less strict than one might assume a priori. There are very low-lying isomers which are barely populated, and at the same time there are high-lying isomers which significantly contribute to the overall population. Based on this population analysis, we select the isomers which are relevant for the dissociation kinetics. With this sampling, the number of isomers can be reduced by 95 %, but at the same time the kinetics remain virtually unchanged.



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Benchmarking semiclassical methods for nonadiabatic dynamics using PySurf

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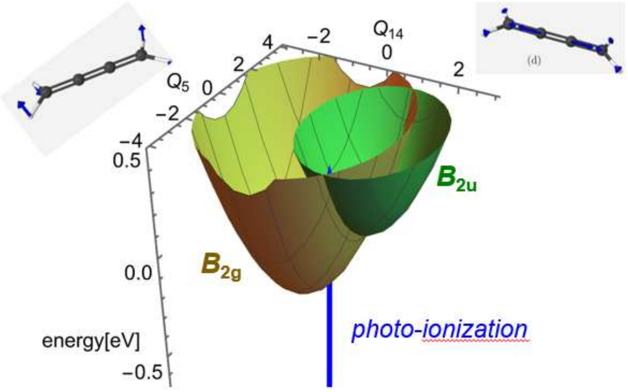
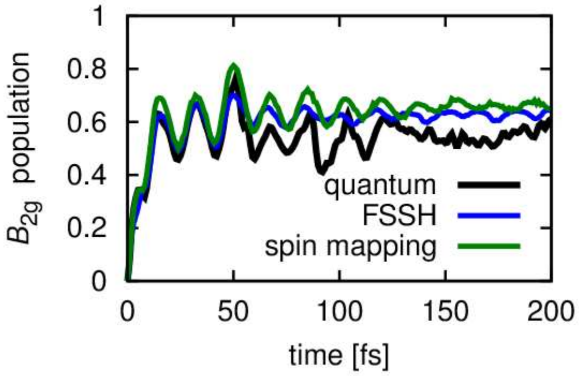
Photochemistry and photophysics involve molecular dynamics beyond the Born-Oppenheimer approximation, where the nuclear motion is coupled to radiationless electronic transitions. Quantum dynamical simulations, which allow a rigorous description of these phenomena, are computationally expensive for complex systems [1,2].
Therefore, mixed quantum-classical methods, where only the electronic states are quantized, are an area of intense development. Besides the widely used Tully's trajectory surface hopping method, new and more sophisticated approaches are constantly proposed, such as methods based on the Mayer-Miller mapping [3,4] or the mapping approach to surface hopping [5], to name a few.
This contribution presents PySurf [6] as a computational platform to implement and compare different types of quantum-classical approaches within a single package. The program implements both surface-hopping (Tully, Landau-Zener, MASH) and mapping approaches (Poisson-bracket mapping equation, spin-mapping, etc.), and is interfaced with different electronic structure codes.
Furthermore, the users have the possibility of providing model Hamiltonians in the same format as that used by the Heidelberg MCTDH code. This paves the way for systematic benchmarks of quantum-classical methods against exact quantum dynamics. The first benchmarks of different types of surface-hopping and mapping methods for pyrazine, butadiene and the PSB3 photoswitch will be illustrated.





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Refined Design Rules Based on Tuning the Excited State Energy Levels for Singlet Fission Chromophores

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Singlet fission (SF) in organic molecules has the potential to significantly enhance the efficiency of silicon-based photovoltaics by reducing thermalization losses. When one chromophore absorbs a photon and becomes excited to a singlet excited state, it may quickly relax to the lowest singlet excited state (S_1), share the excitation energy with another chromophore in the ground state (S_0), and generate a pair of lowest triplet excited states T_1 on the two chromophores, which exceed the Shockley-Queisser limit of ~35%. [1]

The development of design rules that enable the identification and synthesis of new singlet fission chromophores is arguably one of the most important challenges in functional organic materials research today. Tuning of excited state energy levels by substitution and benzannelation led to the rational and efficient development of compounds with optical SF activity. [2] However, strict energy conditions must also be satisfied. A positive energy driving force, S_1-$2T_1$, is preferred in practical applications to ensure that SF can occur. The energy level of T_2 should be twice as high as that of T_1, which then leads to a thermodynamically unfavorable triplet fusion. [3] In this work, novel SF-active chromophores are suggested to be tailored by changing the substituents to tune the $E(S_1)/E(T_1)$ energy ratio and meet stringent energy requirements.

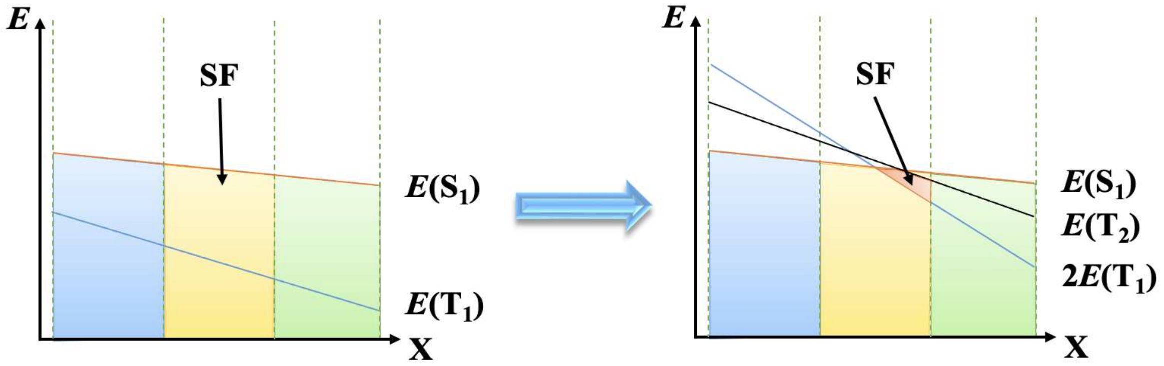

Figure 1: Schematic of curves of energy levels (*E*) vs. variable indexes (X).

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Hybrid vibronic coupling/molecular mechanics (VC/MM) and its application to surface hopping dynamics

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Photoinduced processes in molecules have a multitude of applications in, e.g., energy conversion, catalysis, or photobiology, and therefore are intensively studied. Unfortunately, their computational investigation is limited by the high cost of the required simulations, in particular when focusing on the effects of solvation, due to the large system sizes and long time scales involved.

Here, we present the hybrid vibronic coupling/molecular mechanics (VC/MM) approach [1] implemented in the Surface Hopping including Arbitrary Couplings (SHARC) software package [2]. VC models, e.g., linear VC or quadratic VC models, represent the excited-state potential energy surfaces of a molecule by coupled harmonic oscillators, thus providing a highly efficient description for rigid molecules in dynamics simulations [3]. We recently extended the VC approach by electrostatic embedding [1], enabling the inclusion of explicit solvent molecules analogous to QM/MM simulations. Due to the high efficiency of VC/MM, thousands of nonadiabatic trajectories can be simulated for many picoseconds for systems including thousands of solvent atoms. We show that in this way it is possible to reconstruct, for the first time, low-noise, three-dimensional, time-dependent, nonadiabatically-driven solvent distribution [4], allowing the observation of, e.g., the photo-induced breaking and forming of hydrogen bonds around different molecules.

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Quantum Dynamics of Electronic Coherences at Conical Intersections

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Conical intersections (CoIns) are currently regarded as a dominant mechanism underlying photochemical and photophysical transformations in molecular systems[1]. These are singular areas of the potential energy landscape where two (or more) electronic states intersect, resulting in strong (non-adiabatic) coupling between electronic and nuclear degrees of freedom. This causes the failure of the Born-Oppenheimer approximation, which in turn facilitates ultrafast internal conversion. The intricate interplay between electronic and nuclear degrees of freedom observed in the vicinity of these degeneracy regions exerts a profound influence on the system dynamics, making CoIns the pivotal event determining the outcome of molecular photoexcitation.

Due to their general importance, elucidating the intricate dynamics that occurs in the vicinity of CoIns is a grand challenge in theoretical chemistry[2-3]. In particular, the question of whether such degeneracy regions can give rise to vibronic coherences remains a matter of contention[4]. Symmetry considerations are typically invoked to predict the magnitude of such coherences. Specifically, when the electronic states that cross display different symmetries at the Franck-Condon (FC) point, the nuclear WP branched during the CoIn passage are orthogonal resulting in vanishingly small vibronic coherences. These symmetry considerations are applicable to minimal CoIn models but are unlikely to hold when realistic molecular systems are considered, given that the crossing seams are usually characterized by pronounced molecular distortions.

Here, we examine this aspect through a case study: the quantum dynamics of 2,5-dichlorofuran following optical excitation on the S_1 state. This system, analogous to its well-studied parent molecule furan[5], exhibits a competition between two mechanisms: namely ring opening (RO) and a ring puckering (RP). To perform wave packet propagation, an effective two-dimensional Hamiltonian comprising the RO/RP coordinates is constructed using high-level multireference electronic structure theory (via the XMS-CASPT2 approach). This approach allows for the accurate modeling of the electronic coherences that emerge at the two distinct conical intersections. It will be demonstrated that the activation of a chiral nuclear motion, such as the RP, induces intense electronic coherences even if the electronic states that cross show different symmetry at the FC point.

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A Thermodynamically Consistent Representation of Atomic Radii and Molecular Surfaces

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Molecular surfaces and atomic radii are fundamentally important quantities shaping multiple properties of atoms, molecules, and materials. Despite the fundamental importance and practical applications, precisely defining the surfaces of atoms and molecules as well as atomic radii has long been an open issue. In the present study, we bridge the gap between theory and experiment by combining the accuracy of advanced quantum chemical calculations with the empirical precision of experimental condensed-phase thermodynamics [1, 2]. By studying electron iso-density surfaces for different cut-off densities and across a spectrum of 104 molecules, ranging from simple hydrocarbons to more complex organic compounds, we find an excellent agreement between electron iso-density surfaces contoured at 0.0016 a.u. and high-precision experimental evaluations. Our findings not only validate Bader's elegant theory from a completely novel perspective, they also herald a new standard in defining atomic and molecular surfaces. We further extend the application domain to evaluate radii of atoms in molecules [3] as well as in their isolated states [4]. Finally, we discuss and demonstrate the importance and applications of atomic radii quantified via our developed methods.

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Machine learning potentials for molecular simulations of Pd(II) complexes in condensed phase

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Metal ions are central to many areas of chemistry, including (bio)catalysis, self-assembly, and charge transfer processes. However, computational modeling of their structural and dynamic properties in diverse chemical environments can be challenging for both force fields (due to accuracy) and ab initio methods (due to computational cost). To address this, we develop and apply machine learning potentials (MLPs) using Atomic Cluster Expansion (ACE) descriptors, employing a data-efficient active learning strategy based on accurate quantum chemical calculations. As a challenging model system, we investigate the structure and ligand exchange dynamics of Pd(II) complexes both in vacuum and in acetonitrile as explicit solvent. The trained MLP accurately reproduces equilibrium structures of the complexes, it captures structural changes between the metal ion and ligands in the first coordination shell, and it accurately describes the mechanism and free energy landscape of the ligand exchange reaction[1]. Taken together, the strategy presented here offers a computationally efficient approach to model metal ions in solution, opening the way for modelling larger and more diverse metal complexes relevant in biomolecules and supramolecular assemblies.

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A Multiscale Approach for Proton Conductivity Simulations in (Nanostructured) Fuel Cell Membrane Materials

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We present a multiscale simulation approach for the diffusion of small ions in disordered organic and inorganic materials. We combine ab initio molecular dynamics simulations and a Monte Carlo approach for an atom-level resolution of ion dynamics with quantum but with final length- and time-scales of micrometers and milliseconds.[1,2] While the ab initio part samples local ion transfer rates, the Monte Carlo part is responsible for actual long-range propagation of the ions.

In this talk, the multiscale approach is introduced and benchmarked for the solid acid compound class. [3] We provide atomistic explanations for the variations of the diffusion coefficients in the high-temperature phases of $CsHSO_4$ and CsH_2PO_4.[4] Our simulation method elucidates the relative importance of the two key components of the Grotthuss-type proton conduction mechanism, proton hopping and structural reorientation, as a function of the chemical/thermodynamic conditions.

As a proof-of-principle simulation, we have computed the proton conductivity of a nanostructured CsH_2PO_4 fuel cell membrane with respect to the porosity.[5] In the last part, we demonstrate how to extend our multiscale approach for more complex systems: a) simulation of proton conduction in $Cs_7(H_4PO_4)(H_2PO_4)_8$ which contains the exceptionally rare polycation tetrahydroxyphosphonium $H_4PO_4^+$ [6] and b) the description of hydroxide (OH^-) transport [7].

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Material property predictions by incorporating quantum chemical bonding information.

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Interactions between constituent atoms in crystalline materials have been shown to influence the properties of materials, such as elasticity, ionic and thermal conductivity, etc.[1–3] These interactions between constituent atoms, often quantified as bond strengths, can be extracted from crystalline materials using density-based[4], energy-based[5], and orbital-based methods. LOBSTER[6] is a software that relies on the orbital-based method to extract such bonding information by projecting the plane wave-based wave functions of modern density functional theory computations (DFT) onto a local atomic orbital basis. To garner a better understanding of how this bonding information relates to material properties on a larger scale, machine learning seems an obvious choice. However, for such data-driven studies, large quantities of data that are systematically generated, validated, and post-processed (feature engineering) in a form suitable for input in state-of-the-art ML models are often needed.[7] Here, we first present a workflow implemented in atomate2[8] that can generate such bonding-related data using the LOBSTER program with minimal user input and a post-processing tool, *LobsterPy*[9], which can summarize and engineer features that could be directly used as input for ML studies. Lastly, we demonstrate the utility of these newly generated features by building a simple machine-learned model to predict harmonic phonon properties using the bonding dataset[10] generated by us for 1500 materials. We find a clear correlation between the bonding information and the phonon property.

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How uncertain are predictions of condensed phase vibrational spectra from computational methods?

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Predicting condensed phase vibrational computationally requires an accurate theoretical modeling of the system of interest, including the explicit treatment of the chemical environment. Today, the two most common approaches to this are (i) molecular dynamics (MD) simulations and (ii) weighted ensembles of small clusters.

The latter approach can be realized in the low-cost yet robust quantum cluster equilibrium (QCE) framework, that we recently extended to model mixtures with an arbitrary number of compounds.[1] We demonstrate the accurate prediction of mole fraction-dependent infrared (IR) and vibrational circular dichroism (VCD) spectra[2], successfully reproducing experimentally measured IR spectra over the entire mixing range.[3] Additionally, we discuss the propagation of uncertainties from input to output within the QCE framework[4] in view of uncertainty quantification.[5]

Ab initio molecular dynamics (AIMD) simulations[6] provide access to vibrational spectra through a correlation function-based approach.[7] We demonstrate that this approach can elucidate complex chirality transfers in mixtures of molecular and ionic liquids,[8] validated by experimental measurements.

Lastly, considering the high computational costs of AIMD-based spectroscopy calculations, we elaborate on potential approaches for developing surrogate models. Therein, we focus on dipole moments and sampling the conformational space, two of the key factors governing bulk phase vibrational spectra.

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Lifelong Machine Learning Potentials

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Machine learning potentials (MLPs) can retain the high accuracy of underlying quantum chemical training data and enable simulations of extended systems with little computational cost. On the downside, the training needs to be performed for each individual system. However, extensions of MLP representations by learning additional data usually require demanding retraining on all training data to avoid forgetting of previous knowledge. Moreover, common MLP descriptors cannot represent efficiently many different chemical elements. As a consequence, a large number of MLPs has been trained from scratch in recent years.

We tackle these issues by the introduction of element-embracing atom-centered symmetry functions that are combined descriptors for structure and element information. In addition, we exploit uncertainty quantification to enable a continuously adapting lifelong machine learning potential (lMLP) [1] instead of a fixed, pre-trained MLP by ensuring a predefined accuracy level. To extend lMLP representations, we apply incremental learning strategies relying on data rehearsal, parameter regularization, and model architecture. Further, we propose the continual resilient (CoRe) optimizer [1, 2] for fast convergence and high accuracy in lifelong learning of deep neural networks on a continuous stream of new data. Moreover, we show that the CoRe optimizer outperforms many other state-of-the-art optimizers in diverse machine learning tasks.

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Inclusion of Nuclear Quantum Effects in Water from Room Temperature to Sub- and Supercritical conditions

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The study of high temperature water is important due to its usage as a green solvent, and as a coolant and modulator in nuclear reactors. Since hydrogen is essential in forming the hydrogen bonds that keep water together, and mediating Grotthuss chains necessary for many reactions, nuclear quantum effects (NQEs) remain essential in the study of water. NQEs in water are widely recognized as important for room temperature water, where differences are seen in both the structures[1] and the auto ionization constants[2] of isotopologues of water. While NQEs are found to persist at even suband supercritical conditions for light water (H2O)[3], NQEs are much less studied in this domain due to the difficulty of accurate modelling of water across large differences in pressure and temperature. All previously mentioned[1-3] were run using ab initio (AI) path integral molecular dynamics (PIMD), which, while computational expensive, is tractable with a GGA functional for a limited amount of pressure and temperature points in waters phase diagram. Investigating DFT functionals higher up the Jacob’s Ladder, which would be able to better describe van der Waals interactions important at high temperatures, are however intractable using AI-PIMD directly.
Recently machine learned potentials (MLPs) have been proposed as a method to obtain AI quality simulation results at a fraction of the computational cost. These do however require a robust training set from AI calculations of the system which needs to be studied. To allow for collection of this data set on the fly and to ensure that the ensemble distributions calculated remain those of the underlying AI model we introduce the self-learning path integral hybrid Monte Carlo with mixed ab initio and machine learned potentials (SL-PIHMC-MIX) method. This is based on previously proposed the self-learning hybrid Monte Carlo (SL-HMC) method [4]. SL-HMC is difficult to extend to larger systems and the PIMD domain, as the differences between energies calculated with the MLP and AI methods increase with system size. This problem is solved by the potential mixing in SL-PIHMC-MIX, though it requires re-weighting the obtained ensemble distributions. With this method implemented in the locally developed PIMD software, which has links to modern AI programs and MLPs, we are able to study water at a computational cost allowing us to examine NQEs for several temperatures and pressures in the sub- and supercritical domain.

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Ab initio Polaritonic Chemistry with Confined Infrared Light: Combined Insights from Perturbation and Wave Function Theory

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The emerging field of polaritonic chemistry employs optical Fabry-Pérot cavities as a light source in light-driven chemistry with the aim of going beyond traditional laser-based approaches.[1] Resonant vibrational strong coupling (VSC) between confined infrared (IR) cavity modes and molecular vibrations provides the conceptual cornerstone of vibro-polaritonic chemistry and is characterized by the formation of spectroscopically accessible light-matter hybrid states known as vibrational polaritons[2], which have been experimentally reported to intriguingly alter thermal ground state reactivity.[3]

In this contribution, I examine the role of nonresonant interactions between electrons and IR cavity modes in vibro-polaritonic chemistry based on the cavity Born-Oppenheimer (CBO) framework[4]. In the first part, I discuss how intra- and intermolecular electronic interactions in molecular ensembles can be altered under VSC[5] by combining CBO perturbation theory[6] with CBO Hartree-Fock and coupled cluster theories[7]. Intermolecular interactions are found to be augmented by non-trivial light-matter coupling components and interaction-specific cavity-induced long-range corrections, while intramolecular effects are observed to be small.[5]

In the second part, I discuss how nonresonant electron-cavity interaction effects provide access to an effective cavity mode response component in vibro-polaritonic IR spectra.[8] This response component connects to experimentally measured transmission spectra and allows for computationally extracting the characteristic IR spectroscopic double-peak signature of vibrational polaritons in complex multi-mode systems avoiding spurious molecular transitions.[8]

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Direct evidence for ligand-enhanced activity of Cu(I) sites

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Owing to the inefficiency of existing technological methods for the separation of hydrogen isotopologue, research has increasingly focused on adsorptive separation techniques. Hence, porous materials containing under-coordinated Cu(I) centres which exhibit a high affinity for dihydrogen adsorption, have emerged as promising candidates for efficient H_2/D_2 separation.[1,2,3] A benchmark material with such centres is the metal-organic framework (MOF) Cu(I)-MFU-4*l*, which achieved a selectivity of 11 at the relatively high temperature of 100 K. This high selectivity is attributed to a large difference in adsorption enthalpy of 2.5 kJ/mol between D_2 and H_2.[4] However, up to now, little is known about the substantial influence of the ligand environment and coordination geometry on the strength and isotopologue selectivity of hydrogen adsorption on the under-coordinated Cu(I) site. In this study, we explore this effect using gas-phase complexes $Cu^+(H_2O)(H_2)_n$ (with $n \leq 3$) as model systems. Through a combination of experimental and computational methods, we demonstrate a high isotopologue selectivity in dihydrogen binding to $Cu^+(H_2O)$, which results from a large difference in the adsorption zero-point energies (2.8 kJ/mol between D_2 and H_2 including an anharmonic contribution of 0.4 kJ/mol). We investigate its origins and the bond strengthening between Cu^+ and H_2 upon the addition of a single H_2O ligand. We discuss the role of the environment and the coordination geometry of the adsorption site in achieving a high selectivity and the ramifications for identifying and designing future materials for adsorptive dihydrogen isotopologue separation.

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q-vSZP: An Adaptive Minimal Basis Set Featuring a Novel Generally Applicable Charge Model for the Whole Periodic Table

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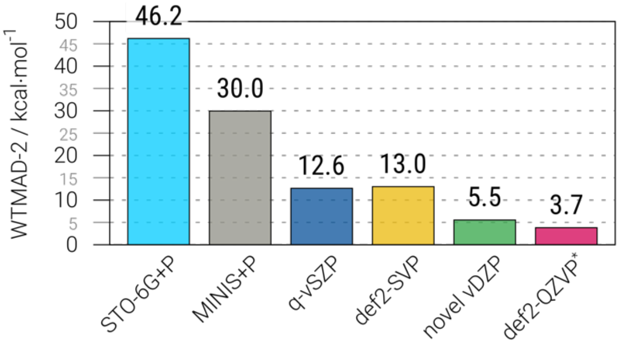
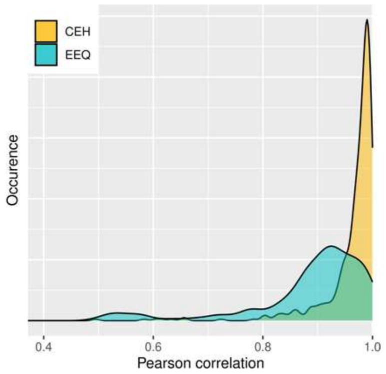
We introduce a novel atom-in-molecule adaptive minimal basis set called q-vSZP.[1] Unlike conventional basis sets that use identical Gaussian-type atomic orbitals (AOs) for atoms of the same type, q-vSZP assigns uniquely adapted AOs for each symmetry-unique atom. The effective AO is determined by the atom's geometrical environment (via coordination number) and its predetermined atomic partial charge, accounting for the essential "breathing" of AOs in molecules. The minimal q-vSZP basis provides significantly more accurate results than conventional minimal basis sets and rivals standard double-ζ basis sets like def2-SVP. This innovation paves the way for advanced semiempirical quantum chemical methods, overcoming the limitations of commonly used minimal basis sets.

A key component of this concept is the likewise new Charge Extended Hückel (CEH) model. It generates atomic charges (*q*) that are nearly as accurate as DFT partial charges, with mean absolute errors for *q* of approximately 0.02 electrons for organic molecules and up to 0.05 for electronically more complex systems. Consequently, the CEH model outperforms classical charge equilibration approaches such as EEQ (*right*) with only marginally higher computational effort, making it a valuable tool with relevance beyond its application in the q-vSZP basis set. Besides lanthanides, the model supports actinides by incorporating f-electrons within the valence space, thus encompassing the entire periodic table up to Z=103. The training dataset exhibits a diverse chemical composition, comprising "mindless" molecules and those with intricate electronic structures, including open-shell and highly charged species. This broad chemical diversity contributes to the CEH model's remarkable robustness and stability.





Left: WTMAD-2 values on the GMTKN55 data base for ωB97X-D4 combined with different basis sets (using adjusted D4 parameters). **Right**: Density plot of Pearson correlation coefficients per molecule between EEQ/CEH and Hirshfeld atomic charges obtained at the ωB97M-V/def2-TZVPPD level of theory for molecules in the MNSOL database.

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Multiscale Modelling of Photosynthetic Light-Harvesting in Photosystem I: The Impact of Natural and Artificial Environments

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Photosystem I (PS I) is one of the most efficient light-harvesting systems in nature. Its antenna complex of chlorophylls absorbs solar energy and transfers it to a reaction center, where the energy is used to drive one of the fundamental redox processes of photosynthesis. Understanding the high efficiency of this process requires an accurate evaluation of the chlorophyll absorption energies, affected by their natural environment (site energies), as well as the excitonic coupling between the pigments. Moreover, the molecular dynamics at physiological temperatures may be of relevance. However, this task poses a challenge to computational studies due to the large scale and complexity of the system.

We present a fully atomistic and dynamic computational model of cyanobacterial (*T. elongatus*) PS I [1]. In particular, we include the trimeric PS I complex in a solvated lipid membrane to describe the natural environment of the chlorophyll network as thoroughly as possible. With this extensive structural model, we sample geometries from classical trajectories and calculate site energies for each chlorophyll with the high-level DFT/MRCI method in a QM/MM framework. This approach allows to obtain accurate site energies and exciton couplings under explicit consideration of electrostatic interactions with the natural environment. Our results identify transient energy traps and barriers in the antenna complex and reveal a fundamental asymmetry in the reaction center.

Going beyond an understanding of the purely natural light-harvesting process to potential applications in artificial photosynthetic devices, PS I may be embedded in a metal organic framework (MOF) [2], capable of protecting the photosystem against harsher environmental conditions. In this context, we extend our model to include the MOF and perform molecular dynamics simulations for the bio-nanohybrid system. With the help of QM/MM calculations, we analyze the impact of the strongly interacting environment on the structure and function of PS I and discuss possible implications for future devices.

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Electric Dipole Polarizability Calculation for Periodic and Non-periodic Systems using Atomic-Orbitals-based Linear Response Theory

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The electric dipole polarizability is an important property to study the response of an atomic/molecular system in an external electric field. In this work, we present a comprehensive study of electric dipole polarizability calculations employing atomic-orbitals (AO) based linear response theory within the Kohn-Sham density functional theory (KS-DFT) framework considering both non-periodic and periodic boundary conditions. In that context, we adopt the optimization scheme introduced by Helgaker et al. [1] to obtain the single-electron AO-based density matrix. We then conducted a comparative analysis between the polarizability computed using the AO-based method and previously implemented molecular-orbital (MO)-based approaches in CP2K package. In the case of non-periodic boundary conditions, we implement the polarizability calculation using the length form of electric dipole operator in AO-based formalism. For the periodic case, we implement velocity representation of the electric dipole operator, and compare the results with those computed using the velocity form of electric dipole operator and Berry-phase formulation using MO-based response theory. We investigate a diverse set of systems, including 10 small and large molecules in the gas phase, liquid-phase systems with up to 256 water molecules, and the solid-state structures of anatase TiO_2 and bulk WO_3. All the polarizability results obtained from the AO-based solver exhibit good agreement with the MO-based results. Furthermore, the AO-based solver exhibits better computational scaling, making it suitable for the study of very large systems.

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Modelling Exciton Dynamics in Multiphotochromic Systems

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Molecular exciton dynamics underlie energy and charge transfer processes in organic multichromophoric systems. A particularly interesting class of the latter are multi*photochromic* systems composed of molecules capable of photochemical transformations. They feature both photophysical (*e.g.*, exciton localization, transfer, or trapping) and photochemical (*e.g.*, isomerization) processes. Understanding photoinduced dynamics of the multiphotochromic assemblies requires nonadiabatic treatment involving multiple exciton states and numerous nuclear degrees of freedom, thus posing a challenge for simulations.

In this contribution, we discuss exciton states and exciton dynamics in multiphotochromic architectures made of azobenzene — a prototypical molecular photoswitch. First, we address the effect of conformational disorder in the electronic ground state on the exciton localization of the ππ* and nπ* excitons. To do so, we perform Born–Oppenheimer adiabatic molecular dynamics simulations based on density functional theory (DFT), compute exciton states with time-dependent long-range corrected DFT, and characterize them with transition density matrix analysis. [1]

After that, we model photoinduced, nonadiabatic dynamics of azobenzene aggregates using an on-the-fly surface hopping (SH) approach combined with a supermolecular semiempirical configuration interaction singles (CIS) electronic structure method and equipped with the transition density matrix analysis to characterize exciton evolution. We quantify ultrafast exciton localization and transfer processes occurring during excited state dynamics upon ππ* and nπ* excitations as well as isomerization quantum yields in the aggregated state. [2,3]

Finally, we study how inclusion of double (D) excitations in addition to singles (S) into CI nonadiabatic dynamics simulations affect exciton dynamics of multiazobenzenes. In particular, we discuss exciton localization timescales, excited state lifetimes, and quantum yields obtained with CIS and CISD SH simulations. [4]

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Charge transport in organic semiconductors from a mapping approach to surface hopping

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Organic semiconductors have attracted considerable attention as an emerging class of materials for molecular electronics. Modern high-mobility materials are challenging to model since they defy both traditional delocalized band theory and localized polaron theory. Conventional methods to simulate the coupled charge-phonon system, such as Ehrenfest dynamics and fewest-switches surface hopping (FSSH) are also limited since they break the equilibrium of mixed quantum-classical systems.

In this contribution, I will present a simple way to overcome this problem. Based on a recently developed “mapping approach to surface hopping” [1,2], we propagate trajectories on the adiabatic state with the highest population. This approach is deterministic and free from overheating. Since it preserves the mixed quantum-classical equilibrium distribution, we can time-average to significantly reduce the number of trajectories needed for convergence. We apply this methodology to charge diffusion in crystalline rubrene [3] and find that it leads to a well-defined diffusion constant, without having to introduce the phenomenological relaxation time approximation (RTA). Our results give 30-60% higher charge mobilities than conventional RTA calculations and shed light on conflicting experimental measurements of the optical conductivity.

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Unraveling Multilevel Chirality with Vibrational Probes and Nuclear Velocity Perturbation Theory

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Chiroptical spectroscopy is an increasingly important and cost-effective method for the study of chiral compounds in the condensed phase. In recent years, vibrational circular dichroism (VCD) - the chiral form of IR absorption spectroscopy - has emerged as a highly sensitive probe of molecular conformation and environment. VCD exploits the chiral information hidden in the infrared (IR) fingerprints of the system, thus targeting the entire molecular scaffold with the wealth of absorption bands contributing to the spectrum. While this feature can be used to understand multilevel chirality in complex chemical systems, its potential can only be unlocked by realistic and efficient theoretical models.[1,2,3]

The interpretation of VCD spectra rests on two pillars: accurate ab initio calculations (at least at the DFT level) and accurate sampling of the conformational space of the molecular system. Therefore, ab initio molecular dynamics (AIMD), which provides both accuracy and sampling, is an attractive means of calculating VCD spectra. However, while the calculation of IR absorption requires only the electric dipolar response of the electrons to a vibrational transition, VCD relies additionally on the magnetic dipolar response.

Such calculations can be performed in the quantum perturbation framework, for which we use Nuclear Velocity Perturbation Theory (NVPT), which perturbatively reconnects the nuclear and electronic degrees of freedom.[4] In combination with AIMD simulations, this approach proves to be very powerful for predicting the chiroptical response based on time correlation functions. The interplay of the linear response of local Wannier orbitals, delocalized vibrational coupling, and periodic boundary conditions leads us to unravel the supramolecular chirality in the condensed phase.[5]

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Machine-Learning Force Field Simulations of Liquid Metal Catalyst Interfaces

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Heterogeneous catalysis still constitutes a vivid research area; a recently developed new concept are supported catalytically active metal solutions (SCALMS). In SCALMS, a metal with a low melting point like Ga or Sn acts as solvent, in which the catalytically active atoms like Pt or Ni are dissolved at low concentration [1,2]. When active atoms shortly arrive at the surface of the liquid, they act as isolated catalytic sites, since the gas phase reactants cannot enter the liquid metal. Within this concept, the advantage of heterogeneous catalysis - easy product separation - is combined with that of homogeneous catalysis - well defined properties of isolated reaction sites.

The simulation of SCALMS, however, is a challenging task, since the highly dynamical nature of the liquids render traditional force fields unsuitable and embedded atom potentials insufficient, since the reactions with gas phase species should be included as well to get the full picture. Direct DFT simulations, on the other hand, are also out of reach since the dynamical nature of the systems requires several nanoseconds of molecular dynamics for averaging. Further, processes like the formation of intermetallic compounds need simulation cells containing thousands of atoms. Machine-learning force fields (ML-FFs) are the method of choice to simulate SCALMS. Because ML-FFs do not rely on any preselected geometries or bonding situations, the description of the highly dynamical liquid and of the interactions with reactants is possible, their linear scaling further enables the simulation of large time and length scales [3].

This contribution presents a broad benchmark of different Gaussian process and neural network potentials [4] with respect to the description of liquid metal catalyst surfaces, including efficient learning strategies and performance studies on several physical observables. It further shows how ML-FF simulations can be used in combination with electronic structure calculations to explain trends in observed catalytic activities of different liquid metal catalysts [5]. Finally, it features the real-time observation of fascinating phenomena like intermetallic compound formation, being an important part of liquid metal catalysts. These compounds were formed during the simulations without being included into the training set, showing some extrapolation ability of ML-FFs.

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Quantum Information-Assisted Complete Active Space Optimization (QICAS)

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Automated active space selection is arguably one of the most challenging and essential aspects of multiconfigurational methods. If accomplished, it would elevate active space methods such as CASSCF to complete black-box machineries. As it turns out, this may be systematically achieved, by using precise quantum information tools for electronic structure analysis. In particular, based on a preceding low-cost calculation, suitable active orbitals can be selected in an *ab initio* manner based on their unique high entanglement profile.

In this work we take these promising ideas to the next level by proposing a quantum information-assisted complete active space optimization method (QICAS). Instead of just selecting active orbitals as the most entangled Hartree-Fock orbitals, we *transform* the active space by minimizing the entanglement of the complementary inactive orbitals, which results in remarkably accurate optimal active orbitals. For instance, for C_2, the energy of a post-QICAS CASCI calculation matches nearly exactly with the CASSCF one.

Accordingly, our study reveals and validates for the first time a profound empirical statement: the optimal inactive space contains the least entanglement. This in turns inspires an energy-free orbital optimization method which places most of the correlation within the optimal active space. For challenging systems, QICAS offers an ideal starting point, from which the number of expensive CASSCF iterations needed for chemical accuracy is greatly reduced.

Development of an RT-TDDFT program with k-point sampling in CP2K

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Progress in experimental techniques has been realizing control of excited-state properties and dynamics of molecules and solids [1,2]. *Ab initio* simulations are indispensable for the analysis of those phenomena to clarify the details of the underlying physics.

We report our development of a real-time time-dependent density functional theory (RT-TDDFT) program for periodic systems with **k**-point sampling in CP2K package [3]. The **k**-point sampling RT-TDDFT had been missing in CP2K though it is indispensable for efficient calculations of electronic band structures. RT-TDDFT has been established as a popular tool for excited-state simulations because of its efficiency in large-scale simulations, ability to reproduce real-time evolution of physical observables, and applicability to non-perturbative dynamics, though its adiabatic formulation has a certain limitation in accuracy. We exploit its strengths for the study of excited-state properties and dynamics of solids and surfaces. CP2K's efficiency in parallel computation, which is supported by a number of techniques including sparse matrix computation, is critically important for our purpose. We indeed observed higher efficiency compared to a Python-based RT-TDDFT program [4]. We report our benchmark calculations and some of our ongoing calculations.

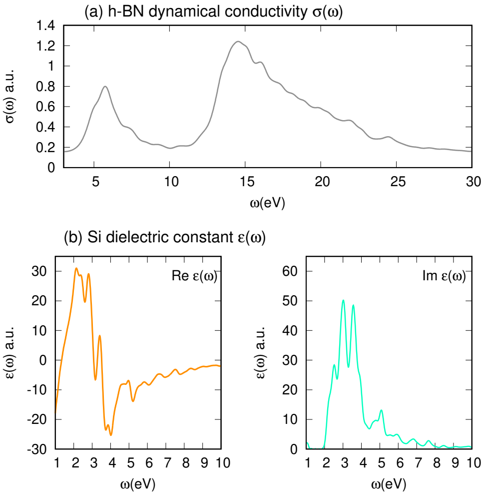

Figure 1: Optical absorption spectra as benchmark calculations. Panel (a) shows the dynamical conductivity of h-BN, calculated with LDA(VWN)/GTH-dzvp, **k**-point sampling $15 \times 15 \times 1$, and (b) dielectric constant of Si, calculated with LDA(PZ)/GTH-dzvp, **k**-point sampling $8 \times 8 \times 8$.

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Computational X-ray and Photoelectron Spectroscopy of Conical Intersections

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Conical intersections (CIs) determine the mechanisms and outcomes of many photochemical reactions. The direct spectroscopic detection of CIs is therefore one of the most ambitious – but also one of the most difficult – challenges in ultrafast molecular sciences. Theoretical insights into how the associated spectroscopic signatures might eventually be isolated are crucial on the way to this goal. [1]

We develop a computational protocol to design, predict and simulate direct signatures of CI passages during molecular photochemistry. We combine quantum molecular dynamics, computational spectroscopy, electronic structure theory and optimal control theory. First, we use highly accurate and efficient multi-configurational quantum chemistry at the CASPT2 level of theory to compute potential energy surfaces and molecular properties along the photochemical pathways. In the case of time-resolved X-ray spectroscopy that has recently been enabled by free-electron laser sources and provides novel windows into molecular dynamics, this includes core-hole states that participate in the probing process. We then propagate nuclear wavepackets according to the time-dependent Schrödinger equation including the passage through CIs. This gives access to the (multi-point) matter response functions used in the perturbative signal calculation, where *n* classical light fields induce an *n*th-order polarization in the matter. Finally, we use quantum optimal control simulations to shape the laser pulses involved in the spectroscopic pulse sequence. This allows to selectively enhance desired signals, which is especially critical for accessing the intrinsically weak vibronic coherences that form directly at CIs. [2,3]

We demonstrate our quantum-controlled spectroscopy approach on the photochemistry of 2,5-dichlorofuran. Like its parent molecule furan, 2,5-dichlorofuran exhibits two competing photochemical pathways upon optical excitation via ring opening and ring puckering. The validity of our molecular dynamics and spectroscopy simulations is verified by closely matching recent experimental observations. We show how direct signatures of the ring-opening and the ring-puckering CI, that have not been observed to date, can be separated in X-ray stimulated Raman and time- and angular-resolved photoelectron signals. Quantum-controlled X-ray and photoelectron spectroscopy allows not only to separate CI signatures from the usually dominating background of other, less interesting signatures, but even to distinguish two competing CIs from each other.

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Robust Design of Semi-Empirical Density Functional Approximations

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While density functional theory is the most widely used method to calculate molecular properties of medium and large sized molecules, vast majority of modern density functional approximations (DFAs) are unreliable for the calculation of vibrational properties. [1] This can lead to errors in frequencies, intensities and nuclear relaxation contributions to electric response properties of up to thousands of percent, especially in systems with low-frequency modes. We show that the fundamental origin of this problem lies in the unphysical oscillations of the real-space exchange-correlation energy density derivatives with respect to external perturbations. By directly connecting the magnitude of these oscillations to specific behaviors of the DFAs at different reduced density gradient values, we developed a strategy to design functionals that are robust for calculating molecular properties. Using this strategy, we designed DFAs which are loosely based on the mathematical structure of the ωB97 family of functionals, yet are robust for calculating molecular properties while achieving similar general accuracy as the base functionals. Finally, by adding purely density and density-gradient based range-separation of the correlation energy, we construct a DFA that is not only robust for the calculation of molecular properties, but also has a competitive edge in the general performance compared to state of the art density functional approximations.

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Graphene for environmental remediation: Interactions with nanoplastics in solution

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Nanoplastics (NPs), defined as plastic particles smaller than 1000 nm, have become a significant contaminant in aquatic environments. These particles originate from the degradation of larger plastic debris and polymer-based materials. Due to their small size and high surface area-to-volume ratio, NPs can adsorb a wide range of contaminants, including heavy metals and persistent organic pollutants, thereby acting as carriers of harmful substances throughout aquatic ecosystems. This property significantly amplifies their ecological impact, as these contaminants can bioaccumulate in the food web, adversely affecting aquatic organisms and potentially humans. The persistence of NPs in water bodies and their resistance to conventional water treatment processes underscores the urgency of developing effective removal strategies.

The current study addresses this critical issue by exploring the interactions between NPs and graphene, as a raw model for 2D materials-based membranes, utilizing atomistic molecular dynamics simulations. These simulations provide detailed insights into the dynamics of hydrophobic and hydrophilic polymers specifically polystyrene, polyethylene, and polyethylene oxide in various aqueous environments. The results reveal that graphene can effectively capture a range of polymers, highlighting its potential as a versatile material for NPs removal. The detailed analysis offers a comprehensive understanding of NPs behavior in different scenarios, demonstrating the superior performance of graphene in adsorbing NPs. Ultimately, the findings of this study represent a step forward in laying the groundwork for designing advanced materials and filtration systems capable of mitigating nanoplastic pollution in aquatic ecosystems.

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Modeling of Molecular Crystal Polymorphs: From Thermodynamics to Kinetics

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Understanding the thermodynamics and kinetics of molecular crystal polymorphs is critical for drug development, particularly in terms of molecular crystal structure predictions [1, 2]. Therein, highly accurate relative stabilities at a certain temperature are needed, since polymorphs often differ only by very few kJ/mol in their Gibbs free energies. However, high-level electronic structure calculations are often prohibitively expensive for relevant systems, especially when vibrational properties need to be accounted for as well. One way of circumventing expensive periodic calculations is the usage of a subtractive embedding scheme, where the periodic calculation is only performed using a lower-cost method and then monomer energies and multimer interaction energies are replaced by those of the high-level method. Beyond thermodynamics, understanding the kinetics of transitions between molecular crystal polymorphs is equally important, as many thermodynamically stable polymorphs are not observed experimentally due to kinetic inaccessibility. While force-field approaches [3] can provide approximate energy barriers for polymorph transitions, accurate transition barriers would require electronic structure methods.

Herein, we present a multimer embedding approach for energies, structures, and vibrational properties of molecular crystals incorporating up to trimer interactions [4]. We benchmark this approach for the X23 set of molecular crystals [5, 6] and approximate periodic PBE0+MBD calculations by embedding multimers into less expensive PBE+MBD calculations. By utilizing trimer interactions, we can describe lattice energies within 1 kJ/mol and cell volumes within 1 % of the canonical periodic PBE0+MBD result. Harmonic vibrational free energies can already be approximated within 1 kJ/mol at the monomer or dimer level. Hence, this approach will speed up or enable more accurate thermodynamic calculations of practically relevant molecular crystals. Furthermore, we investigate the kinetics of polymorph transitions by using a solid-state nudged elastic band (NEB) approach [7] in combination with a new interpolation method for generating appropriate initial structures along the transition path – enabling NEB calculations for crystals involving larger and quite flexible molecules.

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Tailoring UV-Vis Absorption via Aromaticity in (Sub)Porphyrins and (Sub)Phthalocyanines

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Understanding the structure-property relationship in (sub)porphyrin and (sub)phthalocyanine derivatives facilitates the design of new materials on demand. One of the main features of these systems are their optical properties, *i.e.* characteristic Soret and Q absorption bands, which depend on π-delocalization. A possible way to characterize differences in the π system is the theoretical description of the aromaticity, previously used to rationalize the non-optical properties of octaphyrins [1,2]. However, the high complexity given by the topological flexibility and the existence of multiple π-electron circuits makes it a challenging task [3]. In this work, we analyze the influence of structural differences on the aromatic character and the UV-Vis absorption spectra of eight (sub)porphyrinoids (Figure 1), including phthalocyanine and subpthalocyanine. We performed calculations at CAM-B3LYP/cc-pVTZ level of theory followed by global and local aromaticity descriptors, providing a qualitative relation between aromaticity and UV-Vis absorption spectra. Notably, we establish a direct correlation between the aromaticity of the external conjugated pathways and the Q bands. This insight is pivotal for pinpointing modifications in porphyrinoid structures that lead to marked shifts in UV-Vis bands. Our findings offer a strategic framework for designing novel phthalocyanine derivatives with custom-tailored properties.

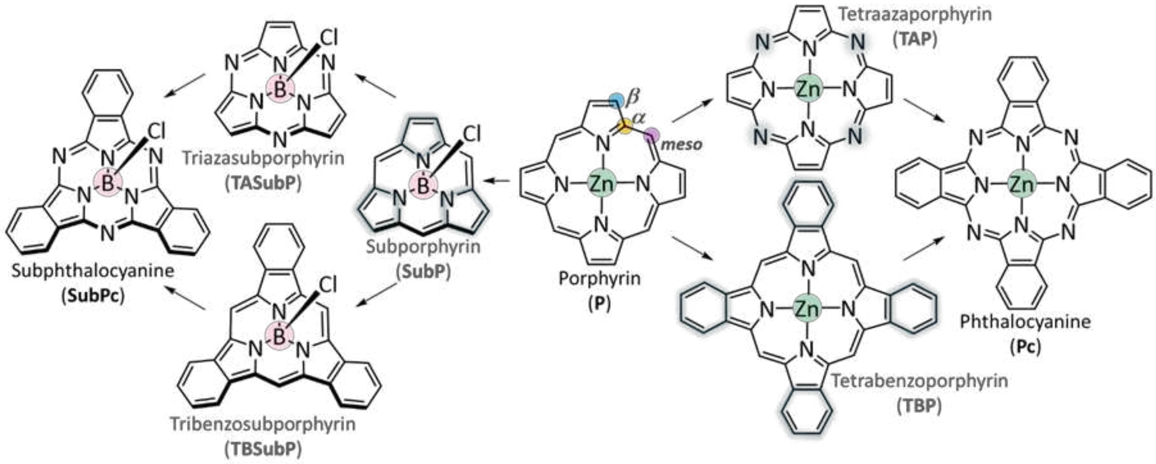

Figure 1. Metallo or B-X coordinated (Sub)porphyrins and (sub)phthalocyanines included in this study.

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Investigating electronic structure on the force-modified PES: Oxirane ring-opening reactions

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As materials are often subjected to external forces, controlling their force-response is highly relevant. In addition to increased resilience, more complex force-triggered behavior such as color change or chemical reactions are of interest. Particularly strained ring-systems such as oxirane can undergo mechanochemical ring-opening reactions. For a trans-substituted oxirane, the external force stimulus promotes the thermally allowed conrotatory reaction path, yielding an ylide structure as its product. For cis-oxirane, the thermal conrotatory pathway is inhibited by pulling force, and a sufficiently high force can fully suppress this reaction route. Instead, the mechanochemical reaction of cis-oxirane is disrotatory and thus symmetry-forbidden, suggesting a diradical transition state. We seek to provide insight into the electronic structure underlying these ring-opening reactions. For this, we compare the computationally very efficient broken-symmetry DFT method with different levels of multireference theory: CASPT2, MRCI-F12, and MRCC which we use to track the electronic character along the entire reaction path by analyzing active space orbitals and CI coefficients. This validates that the disrotatory ring-opening reaction proceeds through a diradical transition state and involves an orbital crossing. Along the reaction path, the frontier orbital energy gap decreases until it reaches a point where HOMO and LUMO are degenerate, equally occupied orbitals. The conrotatory reaction on the other hand shows no orbital crossing, and the transition state has only partial diradical character. Through constrained geometry optimizations using multiconfiguration methods we show the influence of external forces on the potential energy surface and the competing conrotatory and disrotatory reaction paths, while revealing zones of high diradical character along the symmetry-forbidden reaction coordinates. By performing these computations at different forces, we intend to show how transition states of force-suppressed reactions like the conrotatory ring-opening of cis-oxirane disappear from the potential energy surface in topological catastrophes.

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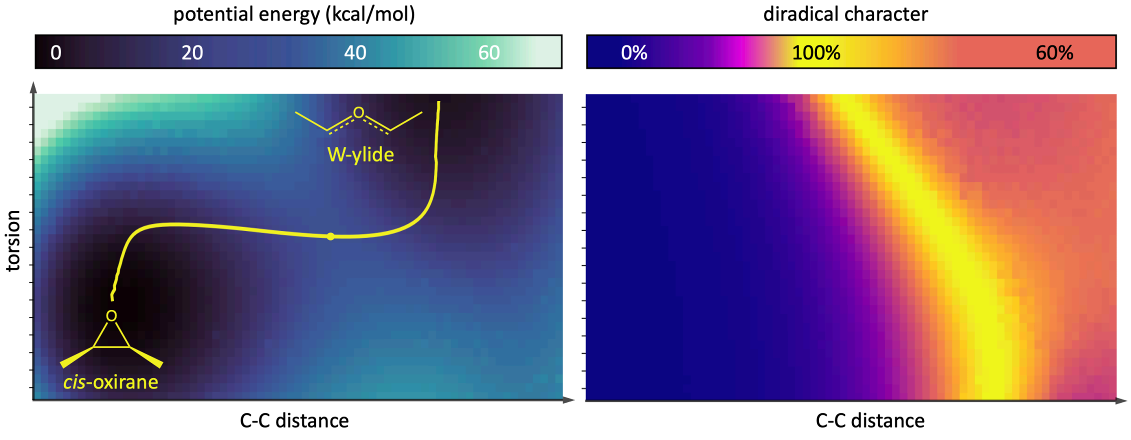

Influence of Ligands on the Stereoselectivity of a Cyclization Reaction

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The asymmetric 1,6-enyne-cycloisomerization reaction allows for the synthesis of biologically active cyclopropane compounds. [1] This reaction employs a rhodium-based catalyst with an N-heterocyclic carbene (NHC) ligand with varying side chains. Density Functional Theory (DFT) was utilized to assess the impact of these side chains on the reaction.

The investigated reaction mechanism follows the three-step mechanism described by T. Nishimura, wherein annulation occurs at the second step.[1] The metal center acts as an electrophile here and activates the triple bond of the reactant. The reaction barriers increase in height for larger side chains at the NHC ligand as steric hindrances increase and stabilizing interactions decrease. The energy difference between these barriers also increases with ligand size, resulting in an increase in enantioselectivity. In contrast, no such correlation could be found with the electronic influence of the NHC ligand.

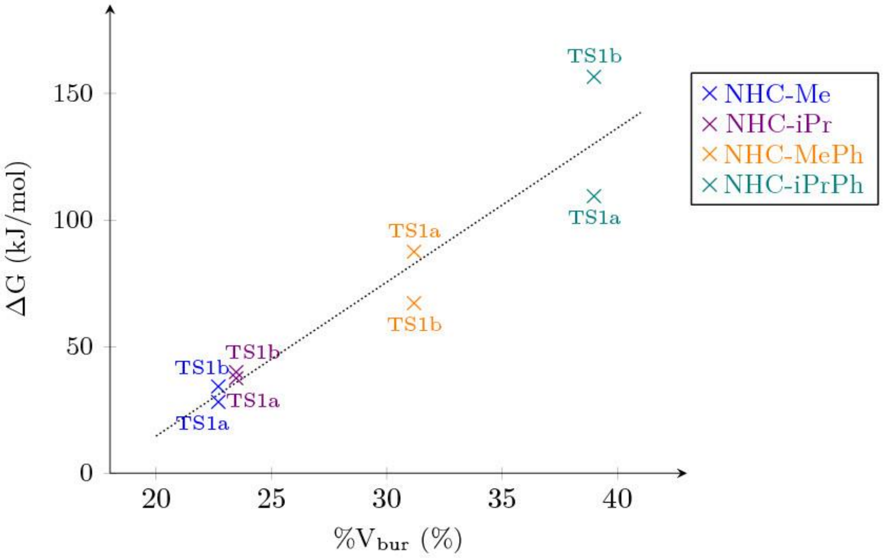

Figure 1: Graph of the energy of the first transition states for all NHC ligands plotted against their 'buried volume'. A linear fit function is employed to better visualize the occuring trend and plotted as the black line. The values for the 'buried Volume' are taken from H. Clavier *et al.*[2]

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Simulating Surface Reactivity with a Cluster-Based Embedding Approach

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Copper surfaces show great potential as catalysts for the conversion of carbon dioxide into valuable products. Although there is tremendous interest in such systems, designing efficient catalysts remains challenging due to an insufficient understanding of the underlying reaction mechanisms. In this regard, quantum chemical calculations offer insights into the complex electronic structure, but they are limited by either high numerical costs or reduced accuracy inherent in many efficient electronic structure methods.

To address this, we propose to use cluster models in combination with the projection-based embedding theory, which has the potential to provide a balanced compromise between accuracy and efficiency. In projection-based embedding theory, the system is partitioned into an active subsystem, where the numerical efforts are focused, and an environmental subsystem, treated at a lower level of theory. The system partitioning is based on our recently developed ACE-of-SPADE algorithm (1). This algorithm has been proven to enable consistent active orbital selection even for such challenging systems as transition metal clusters with many delocalized and (near-) degenerate orbitals by tracking the molecular orbitals' evolution along a reaction pathway.

In this work, we present a benchmark study validating the accuracy of the embedded cluster approach for calculating the binding energy of different CO_2 reduction products on Cu(111)-clusters. First, we validate the accuracy and reliability of cluster models for calculating the binding energies of small molecules on copper surfaces, considering different cluster geometries, sizes, and electrostatic environments. Then, we demonstrate that the proposed QM/QM embedding strategy allows us to considerably improve the accuracy of the binding energies compared to periodic plane-wave calculations, conducted at the lower level of theory. To further increase numerical efficiency, we adapt the ACE-of-SPADE algorithm to consider only the initial and final state of a reaction, effectively reducing the analysis to discrete endpoints rather than evaluating the entire trajectory. This algorithm proves to be particularly robust for small active cluster sizes.

The projection-based embedding theory, together with our ACE-of-SPADE algorithm, shows high potential for studying chemical reactions on metal surfaces due to its ability to balance accuracy and numerical demands efficiently.

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Rovibrational configuration interaction for astronomically relevant molecules

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Rovibrational spectroscopy plays an important role in the fields of atmospheric sciences, astrophysics and astrochemistry. The sulphur counterparts of oxygen-containing molecules, such as thioformyl cyanide and thiopropynal, which have been recently identified in the interstellar medium, are an emerging topic of significant interest. We performed rovibrational configuration interaction calculations (RVCI) to produce high-resolution infrared spectra of the fundamental bands, overtones, hot bands and combination bands of these compounds [1,2]. The effect of temperature on the hot bands has been studied in detail. Furthermore, the computational benefits in terms of memory requirements and CPU time due to the block diagonality of the rovibrational matrix arising from the symmetry of the rovibrational wavefunction were investigated. It was found that a substantial number of the coefficients of the rovibrational eigenfunctions are negligible and can be discarded in subsequent parts of the RVCI calculations. The compressed sparse column (CSC) method was utilized to store the sparse eigenfunctions, which enhanced the efficiency of the program with regard to CPU time. The combined implementation of symmetry and sparsity reduced the CPU time by almost one order of magnitude.

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Enhancing Doxorubicin permeability and Reducing Toxicity Using Deep Eutectic Solvents: Insights from Molecular Dynamics Simulations

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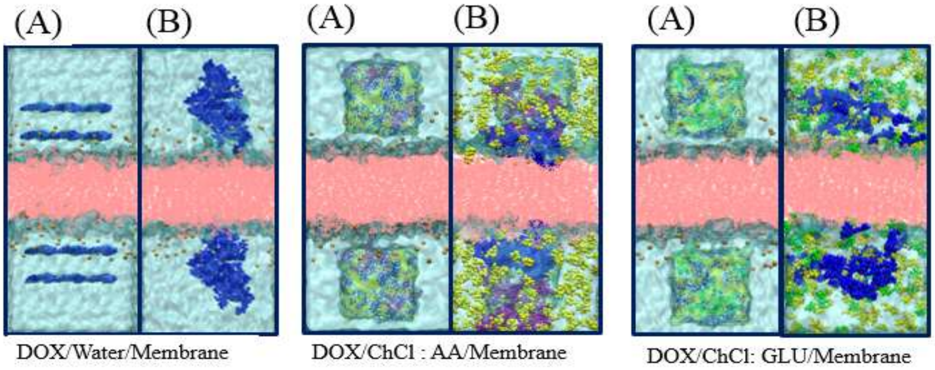
Abstract: The efficacy of doxorubicin (DOX), a cornerstone chemotherapy agent, is often compromised by its limited blood circulation time, poor permeability, and off-target toxicity, including cardiomyopathy. [1] This study explores the utilization of choline chloride (ChCl)-based deep eutectic solvents (DES) to enhance DOX delivery and reduce its systemic toxicity.

Using advanced molecular dynamics simulations, the interactions between DOX and a model cancer cell membrane was analyzed in three distinct solvent environments: water, ChCl:Ascorbic acid (AA), and ChCl:Glucose (GLU). Our simulations employed the GROMACS software and Amber 99SB force field [2] to provide a comprehensive understanding of the solvent effects. Radial distribution function (RDF) and mean square displacement (MSD) analyses were conducted to evaluate DOX aggregation and membrane penetration, respectively.

The results indicated that DES significantly mitigate DOX aggregation compared to water. Specifically, ChCl:GLU demonstrated the lowest degree of DOX aggregation, followed by ChCl:AA, whereas water showed the highest aggregation. This reduced aggregation in DES correlates with enhanced membrane permeability of DOX, as evidenced by the MSD analysis, which revealed a superior penetration profile in ChCl:AA, followed by ChCl:GLU and water. After 300 ns of simulation, DOX molecules exhibited substantial membrane penetration in DES environments, implying enhanced drug bioavailability and reduced cytotoxicity. Our findings underscore the potential of ChCl-based DES to revolutionize chemotherapy by improving drug solubility and permeability while minimizing adverse effects. This novel approach could pave the way for more effective and safer cancer treatments.



DOX/Water/Membrane

DOX/ChCl : AA/Membrane

DOX/ChCl: GLU/Membrane

Figure 1: Snapshots of the three systems at 0 ns and 700 ns. **Color code:** blue: DOX, Cyan: Water, Pink: cancerous membrane, Yellow: ChCl, Purple: AA, and Green: GLU.

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The influence of temperature on the structure of aqueous solutions of natural dyes

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Modern experimental and theoretical-computational studies of the possibilities of extracting natural and artificial dyes from aqueous media are closely related to the study of the features of their interaction with water, the features of changes in these interactions under the influence of external conditions (radiation of various natures, changes in temperature, pressure, etc.). The process of dissolving a dye in an aqueous environment is closely related to the restructuring of the hydrogen bonds of the water itself, the formation of free space around the dissolved molecule, and the formation of hydrogen bonds between the dissolved substance and water. One of the oldest and most common dyes used in the textile industry is indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$). The presented work is devoted to studying the characteristics of interaction with water using the molecular dynamics method. All simulations were executed using an packages DL_POLY_4.06 and DLPOLY_FIELD. The potential parameters for describing the interaction between the atoms of the indigo carmine with the atoms of the water molecules are calculated using the Lorentz–Berthelot combination rule.

As a result of the analysis of the obtained trajectories, radial distribution functions and the Wenta-Abraham parameter were calculated for various interatomic interactions between the atoms of water molecules and indigo carmine. Analysis of the calculated radial distribution functions and the Wenta-Abraham parameter shows that the dissolution of indigo carmine in water leads to the formation of free space around the dissolved molecule and a change in the local density of the water structure in the vicinity of the dissolved substance. At the same time, the value of the first hydration sphere around the indigo carmine molecule is about ~2.7 Å. The second hydration sphere around the indigo carmine molecule is poorly defined can be described as the space between ~2.7 Å and ~5.0 Å. Temperature changes have practically no effect on the size of the first and the second hydration spheres around the IC molecule. All of calculation show that the coulomb interaction between indigo carmine and water atoms may lead to the formation of HB-bonds with lengths from ~1.9 Å to ~2.1 Å. In this case, part of the water molecules, due to the strong Coulomb interaction, can be quite close to the dissolved dye without the formation of hydrogen bonds. It has also been established that the observed structural changes can be attributed to the change in the shape of water clusters. The dissolution of indigo carmine leads to a further decrease in the local ordering of the liquid system with increasing temperature.

IHD302: Assessing Quantum Chemistry Methods for Inorganic Heterocycle Dimerizations

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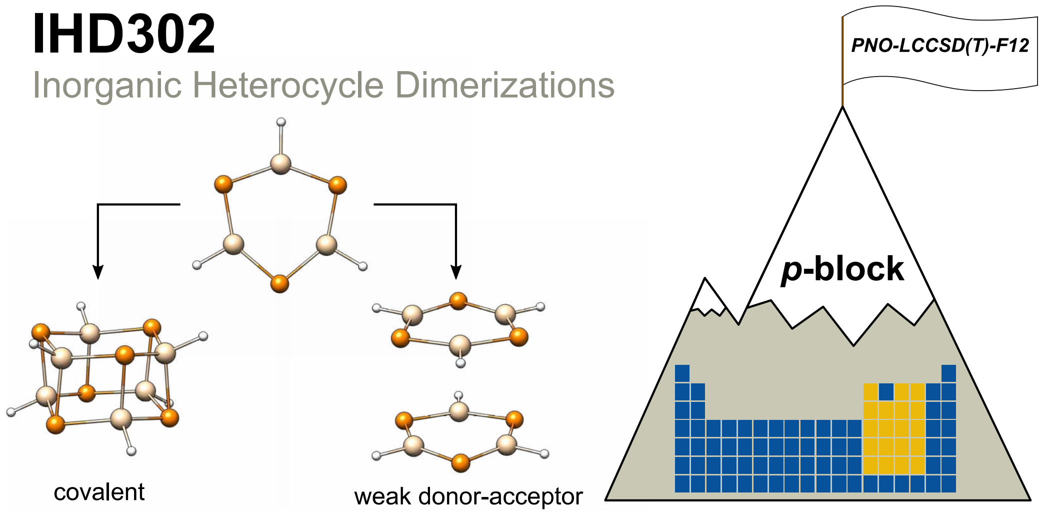
Compounds containing inorganic p-block elements are commonly used in various chemical fields, such as frustrated Lewis-pairs (FLP) and optoelectronics. To accurately describe these systems, theoretical methods like density functional theory (DFT) must be thoroughly assessed beforehand, but high-quality reference data is scarce. In this work, we present the IHD302 benchmark set, which contains 604 dimerization energies for 302 "inorganic benzenes" composed of non-carbon p-block elements from main groups III to VI, up to polonium.[1] This set can be divided into two subsets: structures bound by covalent bonding and those bound by weaker donor-acceptor interactions (cf. Figure). Reference reaction energies were computed using state-of-the-art explicitly correlated local coupled cluster theory, termed PNO-LCCSD(T)-F12/cc-VTZ-PP-F12(corr.), with a basis set correction at the PNO-LMP2-F12/aug-cc-pwCVTZ level.[2] We evaluated 26 DFT methods with three different dispersion corrections and the def2-QZVPP basis set, five composite DFT approaches, and five semi-empirical quantum mechanical methods on the IHD302 benchmark set.



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Improving Quantum Chemical Solvation Models by Dynamic Radii Adjustment for Continuum Solvation (DRACO)

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Computational modeling of processes in solution requires additional models to account for solvent effects. Widely used examples are the implicit solvent models CPCM, COSMO, SMD, and COSMO-RS, which model the electrostatic interactions of solvation via surface charges on a three-dimensional solute cavity. The cavity is constructed by overlapping atom spheres based on fixed atomic radii assigned per element. This can limit the models' ability to adapt to the electronic structure of the solute, potentially reducing the maximum achievable accuracy.

With the Dynamic Radii Adjustment for COntinuum solvation (DRACO) approach,[1] we aim to address this limitation by using precomputed atomic partial charges and coordination numbers of the solute atoms to adapt the solute cavity. DRACO is compatible with major solvation models, significantly and robustly improving their performance at virtually no extra computational cost, especially for charged solutes.

Combined with the purely electrostatic CPCM and COSMO models, DRACO reduces the mean absolute deviation (MAD) of the solvation free energy by up to 4.5 kcal mol^{-1} (67%) for a large data set of polar and ionic solutes. Even in combination with the highly empirical SMD model, it improves the MAD for charged solutes by up to 1.5 kcal mol^{-1} (39%), while neutral solutes are slightly improved (0.2 kcal mol^{-1} or 16%). The DRACO interface is available with two computationally efficient atomic charge models, enabling fully automated, out-of-the-box calculations with widely used software packages like *ORCA* and *TURBOMOLE*.

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Surface Hopping Molecular Dynamics Simulations for Reaction of Pyrene and CH_3Cl

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Graphene and aromatic hydrocarbons, such as pyrene, are of significant interest not only for their fundamental electronic properties as prototypical two-dimensional materials but also for their applications in nanoelectronics and sensing. Pyrene, known for its exceptional opto-electronic properties, is pivotal in various photo-responsive materials. Their planar structure and strong π-π stacking interactions often render graphene, pyrene and pyrene-containing molecules insoluble in water and organic solvents, presenting opportunities for heterogeneous catalysis.[1,2] Also, there is significant interest in tuning the (opto-)electronic and other properties of these materials, with functionalization being a promising approach to achieve this.[3]
In this work, we perform nonadiabatic (Surface Hopping (SH)) molecular dynamics (MD) simulations for pyrene-CH_3Cl and investigate the fragmentation and formation processes. Specifically, we: (i) model the electronic structure of the pyrene-CH_3Cl system using configuration interaction singles (CIS) based on molecular orbitals (MO) obtained from a self-consistent field calculation with floating occupation (FO) numbers[4] using the Austin model 1 (AM1)[5], (ii) incorporate the Lennard-Jones (LJ) potential to account for intermolecular interactions, (iii) reveal the nature of the excited states, (iv) calculate the electronic spectra for selected MD snapshots, and (v) model nonadiabatic dynamics using SH, considering both excitation of non-covalent pyrene-CH_3Cl complex and excitation of pyrene covalently modified with CH_3 and Cl. The following questions are addressed: 1. What are the observed changes in the population of excited states as a function of time? 2. How does the bond length of C—Cl in CH_3Cl and the bond length of C—Cl between CH_3Cl and pyrene, and the C—C bond length between CH_3Cl and pyrene change during dynamics? 3. What is the computational absorption spectrum of free pyrene, and how does it change after the approach of CH_3Cl to pyrene? 4. What is the role of LJ potential applied to all considered potential energy surfaces throughout the SH calculations? 5. How might our findings guide the controlled modification of pyrene-CH_3Cl structures for specific applications? 6. What is the stability and quantum yield of products for the titled reaction?

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Revisiting the Kanamori-Goodenough-Anderson rules for magnetic property prediction

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Recently, machine learning of magnetic properties of transition-metal compounds has attracted large interest due to environmental and availability issues of rare-earth-based functional magnetic materials. Surprisingly, bond-angle-derived features were not found to be relevant for magnetic structure prediction in previous studies using DFT-computed labels.[1, 2] This contrasts with a well-known magnetism heuristic, the Kanamori-Goodenough-Anderson (KGA) rules of superexchange. These semiempirical rules predict the sign of the nearest-neighbor magnetic interaction in insulators based on the bond angle, orbital symmetry and orbital occupancy.[3, 4] They can be simplified further to only take into account the bond angle of neighboring magnetic sites (KGA rules of thumb).[5] We review magnetic interaction trends within the *MAGNDATA* database,[6, 7] the largest collection of experimentally determined magnetic structures. Observed trends can be rationalized in the light of the KGA rules of thumb and their follow-up studies. We find similar trends for other systems than oxygen-connected, octahedral transition metal sites. Building on our analysis, we engineer bond-angle-derived features for machine learning of magnetic structures. We introduce a new, informative label for predicting magnetic structures that can be extended to magnetic sites and structures of arbitrary complexity: the parallelity score *p*. For a single magnetic site, it is defined as the fraction of neighboring magnetic moments aligned parallel to it. Averaging the *p* scores of all sites in the magnetic unit cell gives the structurewise *p* score. An antiparallelity score *ap* can be defined accordingly. Bond-angle-derived features are found to be highly relevant for the prediction of *p* and *ap* scores. We demonstrate the predictive power of an *ap* and *p* score model in combination with a magnetic propagation vector model as a step towards full magnetic structure prediction.

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Investigation of mechanochemical transformations under the impact of uniaxial pressure

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Mechanochemical reactions are chemical processes that occur under the influence of external forces. While there are established theoretical models to describe mechanochemical transformations under the influence of a pulling force, there is currently no established method for the *ab initio* simulation of the impact of uniaxial pressure onto molecular systems.

Here, we want to introduce a new approach to allow the simulation of uniaxial pressure on molecular systems. A force acting on each atom individually is applied to push the molecule along the z-axis into the plane created by the *x*- and the *y*-axis, see Figure **1b**. The strength of the force acting on each of the atoms depends on the distance of the atom to the *xy*-plane. With this approach, the mechanism of the so-called *Flex Activation* is investigated. *Flex Activation* allows the release of small molecules from a polymer without destruction of the polymer backbone. Methods to simulate a pulling force on a molecular system were not able to explain the occurrence of *Flex Activation*.[1-2] Simulating the external force as a uniaxially acting force, however, reduces the activation energy and can therefore explain the *Flex Activation* mechanism.

In addition to the scission of covalent bonds, the formation of such bonds under the influence of uniaxial pressure is investigated. It is expected that for these processes the activation energy of the chemical reaction does decrease in dependence on the increasing uniaxial force.

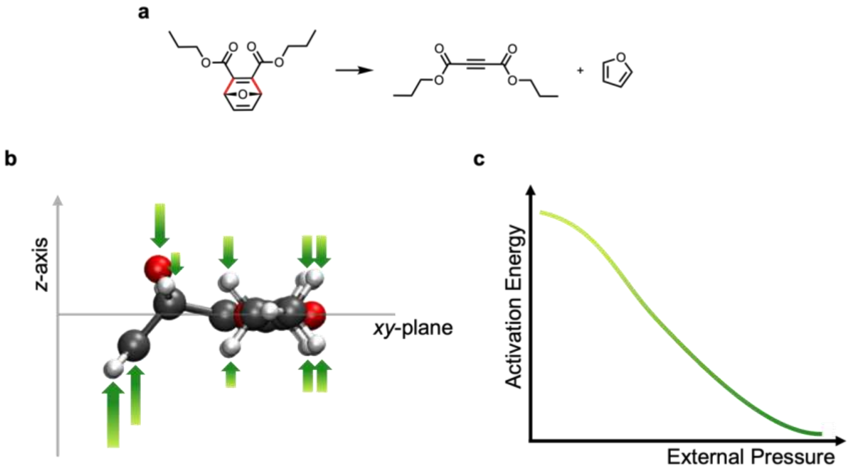

Figure 1: **a**: Examined reaction of an oxanorbornadiene-based mechanophore.[3] **b**: Schematic representation of the application of the model for simulating uniaxial pressure. The force is applied to each atom separately. The green arrows indicate the strength of the force acting on an atom. **c**: Effect of uniaxial pressure on the activation energy. With increasing force, the activation energy decreases.

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Current Approaches for Electrolyte Modeling at the Electrode-Electrolyte Interface

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Electrocatalysis plays a central role in advancing sustainable energy technologies and addressing environmental challenges. Fuel cells, water electrolysis and industrial electrosynthesis are some examples that are gaining growing interest in clean energy conversion and storage. Computational methods provide precious insights that are often challenging to obtain through experimental means alone and hence aid catalyst design strategies. The accurate modeling of the electrode-electrolyte interface is crucial for describing electrochemical systems [1] and represents one of the main challenges of computational electrocatalysis.

In principle, ab initio molecular dynamics (AIMD) is the most accurate method, but its high computational cost is often prohibitive, making this approach unfeasible for general applications. One way to reduce the computational cost is to treat the electrolyte region classically while maintaining a quantum description for the electrode and the reactive site. However, for this mixed quantum mechanics-molecular mechanics (QM/MM) approach, an accurate force field and a reliable approximation of the quantum/classical boundary are required.[2] Additionally, MD simulations require a representative sampling of the configurational space to be reliable, which is very challenging to achieve due to the multicomponent nature of the system and the strong ion concentration gradients at the interface. Implicit solvation models are computationally cheaper and have the advantage of already accounting for ensemble averages. Poisson–Boltzmann (and its variants) is the most widespread model, and it has been implemented in various electronic-structure software. [3] The reference interaction site model (RISM) and classical density functional theory (cDFT) are two less common but promising alternatives that model solvation by incorporating information from the radial distributions of the solvent and the electrolyte at the interface. [2,3]

In this contribution we present a comparison of the different state-of-the-art approaches to modeling the electrode-electrolyte interface, highlighting each model’s main advantages and disadvantages.

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Benchmarking DFT-based excited-state methods for intermolecular charge-transfer excitations

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Intermolecular charge-transfer plays a crucial role in biological processes and energy conversion applications, where the energy excess acquired by means of light absorption is moved across molecular units. However, understanding the mechanism behind these photoinduced processes is a complex task due to the high precision required, especially when dealing with large molecular systems.

In this benchmark study[1], we test computational methods that are scalable for this purpose and assess their accuracy. Our reference results are derived from highly precise calculations obtained with wavefunction theory which limits the size of the benchmark systems. On the other hand, the methods we have identified are based on density-functional theory (DFT) and can here be applied to much larger systems. Investigated excited state DFT methods are both time-dependent DFT[2] (TD-DFT) and orbital-optimized DFT[3] methods (OO-DFT, also known as ΔSCF).

In general, the best results are achieved with orbital-optimized methods, even though convergence issues negatively affect their performance[4]. Among these, the maximum overlap method[5], when used with the initial MOs as reference orbitals[6], proves to be the most numerically stable variant. Additionally, a combination of optimally-tuned range-separated hybrid functionals and relatively small basis sets can provide a reasonable wavefunction economically when using time-dependent density functional theory. This wavefunction can then be recalculated with orbital-optimized methods to refine the ICT energy estimation.

Since these rapid calculations are particularly appealing for high-throughput screening applications, our follow-up studies focus on improving the numerical stability of the SCF algorithms used for OO-DFT, either by starting the iterative procedure with a better guess MO set or by making the SCF algorithm more robust to the variational collapse of the electronic wavefunction onto undesired excitations.

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Computational Insights into Ion Solvation in Battery Electrolytes using DFT and Semi-Empirical Methods

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The performance of lithium-ion and sodium-ion batteries is critically influenced by the solvation-shell structure of the solvated ions in electrolyte solution. In this work, we conduct a detailed computational investigation of ion solvation using Density Functional Theory (DFT) and semi-empirical methods to perform a sensitivity analysis of the employed methods with respect to different computational parameters, such as choice of a solvation model, density functional or conformational analysis approach.

For lithium-ion batteries, the cluster-continuum model is employed, where the explicit solvation shell of the lithium ion is immersed in an implicit pure ethylene carbonate (EC) solvent. We perform DFT calculations with B3LYP/6-31G(d,p), consistent with the methodology detailed in Ref. [1]. The implicit solvation is included by conductor-like polarizable continuum (C-PCM) and Poisson-Boltzmann solvation models within the Q-Chem electronic structure package [2]. By applying a series of refined corrections to the gas and solution phase binding free energies, we aim to replicate and extend the findings of Ref. [1]. Our further analysis focuses on the sensitivity of binding energetics to the choice of DFT functionals and parameters of the implicit solvation models, providing insights into the accuracy and reliability of these computational methods.

We extend our analysis to sodium-ion batteries and examine the conformational energies of explicitly solvated sodium ions in N-methylformamide (NMF) electrolyte. Previous studies indicate a systematic overestimation of conformational energies with the GFN2-xTB method for clusters $Na^+(NMF)_n$ with n = 5-8 [3]. To address these discrepancies, we refine the procedure of the conformational analysis by re-optimizing the geometries of these clusters using DFT at the wB97X-V/def2-TZVP level. Additionally, we employ a permutation-aided Kabsch algorithm [4] to eliminate generated duplicative structures. This approach aims to produce more accurate low-energy conformers for the sodium solvation clusters, enhancing the reliability of the GFN2-xTB method for conformational analysis.

By applying these refined techniques to various ions and electrolyte mixtures, we aim to achieve more accurate simulations, contributing to the understanding of ion solvation in battery electrolytes with first-principles simulations.

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Implementation of Density Matrix Purification Methods with GPU-Offload Tailored to Consumer-Grade Hardware

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For semi empirical electronic structure methods, solving the Roothaan-Hall equations by means of diagonalization of the Fock matrix is generally the computational bottleneck.[1] Alternatively, a density matrix **P** can be constructed directly without solving for the orbitals. Density matrix purification (DMP) schemes start from a guess density matrix **P** that fulfills the anticommutation with the Fock matrix. **P** is then purified iteratively until idempotency is achieved, preserving the symmetry of **P** and a trace equal to the number of electrons.

We present a C++ library implementing 2nd order trace-correcting (TC2) [2] DMP among others. The computational bottleneck for DMP methods is the matrix-matrix multiplications needed to construct the purification polynomials. The highly parallel architecture of graphics processing units (GPUs) can be exploited to noticeably speed up this operation. In this context, a C++ linear algebra library with GPU-offload capability was written and is published separately to allow code reusability.

The potential of consumer-grade GPUs can be leveraged by maximizing the amount of single precision (FP32) operations. Therefore, a tailored mixed numerical precision (MP) scheme is proposed composed of two main approximations. **P** is split up in a diagonal and off-diagonal tensor, where the off-diagonal matrix is stored in FP32. Additionally, an incremental scheme is used for matrix transformations between orthogonal and non-orthogonal basis. The transformation of the increment is performed in FP32.

Our DMP library is interfaced to the *tblite* codebase. We demonstrate that this MP TC2 DMP implementation is faster than LAPACK (intel oneMKL) and cuSOLVER diagonalization for molecules with more than 2000 basis functions using the GFN2-xTB[3] Hamiltonian. The numerical precision of the energies and gradients is not impacted by the MP scheme compared to full double precision computations.

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Fast and generalizable generation of transition state guess structures via system-specific force fields.

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Calculating transition states (TS) and rate constants is essential for studying chemical reactions and their kinetics. Kinetic models based on complex reaction networks require the near-automatic determination of rate constants from a large number of underlying transition states.

We present a TS search method that efficiently generates an initial TS guess for further saddle-point optimization, for example with density functional theory (DFT) methods. This approach employs system-specific force fields (FFs) of the reactant and product structures, created by fitting the FF Hessian to a quantum mechanically derived Hessian. These FFs are then used to construct a TS FF, which is employed for the calculation of the initial TS guess. Subsequent saddle-point optimization of this guess geometry by DFT leads to obtaining the correct transition state in 80% of the cases of a well-established benchmark set [1]. The presented approach may be a very efficient alternative to more elaborate path optimization techniques as the growing string [2] or the nudged elastic band [3] method.

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Challenges in Molecular Simulations of Stratum Corneum Permeation

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Human skin is a complex, multilayered organ of millimeter thickness. Its barrier function resides almost completely in the topmost layer, the stratum corneum (SC).[1] This barrier against the permeation of chemicals in SC lipid matrix is investigated by employing atomistic, force-field-based molecular dynamics (MD) simulations.
We carried out our study on the short periodicity phase (SPP)[2] of the SC lipid bilayer and also compared our results with “simple” 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) membrane. As conventional MD simulations cannot sample permeation through lipid bilayers due to high free energy barriers, we employ a range of enhanced sampling techniques, including umbrella sampling, metadynamics and adaptive biasing force calculations. Nevertheless, extensive sampling on microsecond timescales is necessary to converge potentials of mean force in all of these techniques. We present various structural and dynamical metrics which show that SC membranes are much more solid-like than the commonly studied, fluid-like POPC membranes, necessitating long time scale sampling. Extensive sampling also reveals slow dynamical changes in the membrane structure due to flipping of lipids which leads to long-living asymmetries. All these challenges make simulating SC membranes much harder than common fluid-like systems. We demonstrate how these methodological differences impact permeabilities.

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Hybrid Fermion-to-Qubit Encodings

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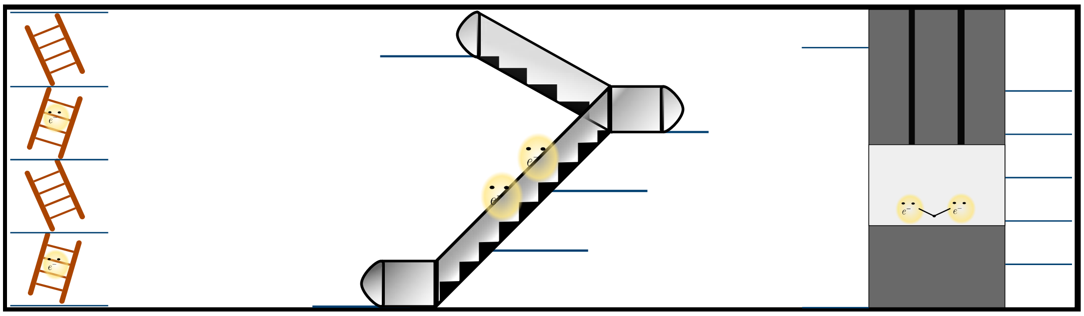

One of the most popular algorithms for nowadays Quantum Computers is the Variational Quantum Eigensolver (VQE), which aims to approximate a Hamiltonian's ground state. In this algorithm, an initial guess is built whose expectation value is measured. Then, the guess is optimized through a classical computer until convergence. Constructing efficient quantum circuits that accurately represent the target state is crucial for a good result and in order to minimize the VQE iterations. Different homomorphisms exist to encode the molecular electronic information into the qubits. Most of them relate each electron with one qubit and deal with the anti-symmetry in the operations. However, other methods exist which approximate the system pairing all the electrons in bosonic quasi-particles. In practice, it consists of encoding electron pairs into qubits and allowing only those operations that respect this all-paired orbital occupancy.

In this work, a hybrid encoding has been developed which allows splitting the Fock space into two subspaces, one fully Fermionic and one Quasi-Bosonic. For this purpose, the Molecular Hamiltonian is split into three parts; a fully fermionic, a fully Bosonic, and an interaction Hamiltonian between both subspaces. An immediate consequence is Hamiltonian simplification since part of the operators are reduced, driving to fewer operator strings. On the other hand, some improvement take place when compiling the circuits. Other improvements rely on the qubit reduction due to the Bosonic subspace, and a decrease in the amount of orbitals subject to the anti-symmetry, reducing the computational cost of the remaining Fermionic operations. Moreover, the main advantage relies on the electron excitations between the two subspaces. Not all of them will be allowed, but for those that they are, they will be compiled into significantly shorter circuits. For example, a semi-paired excitation (two electrons paired excited to different orbitals) will be compiled into a circuit half as deep.

This will open the door to a new type of chemically designed ansatzes for nowadays Quantum Computers with a better balance between molecular description and computational resources. Where each subspace could be adapted to the problem of study based on chemical intuition or estimated through algorithms.

Integrating Hückel and PPP-Model Hamiltonians with pCCD Approaches in PyBEST

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In quantum chemistry, theoretical models are crucial for understanding electronic structures and molecular behaviour. 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, utilising 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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Electronic structure and optical properties of substituted adamantanes

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The development of new, efficient, and sustainable light sources for a variety of applications is an ongoing process, in which the light emitting or light converting materials range from classic inorganic phosphors and semiconductors for LED applications and their organic equivalents to a plethora of different molecular phosphors.

Organic chemical compounds consisting of substituted adamantanes (AdR_4) were shown to exhibit a nonlinear optical response, which depends on the degree of ordering of the solid compound. [1,2] In particular, $AdPh_4$ exhibits white-light generation in the amorphous state and second-harmonic generation in the crystalline one. Furthermore, the nonlinear optical properties of adamantane-based materials strongly depend on the organic groups R bonded to the cluster core. [2] Despite the rich experimental findings on the structural and optical properties of these compounds, the mechanism of the nonlinear response is not fully understood.

In the present contribution, the electronic structure features of a series of isolated molecules consisting of an adamantane core and common organic substituents are systematically studied with the use of various DFT and *ab initio* methods. The calculated descriptors (ionization potential, electron affinity, fundamental and optical gaps, *etc.*) are analyzed in order to find a correlation with nonlinear optical properties of corresponding chemical systems available from experiment. The design of novel adamantane-based materials exhibiting nonlinear optical response is discussed from the perspective of performed electronic structure calculations. [3]

The work was supported by DFG within the framework of FOR2824.

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Excited State Dipole Moments from ΔSCF: A Benchmark

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Oriented external electric fields can be used to modify the relative energies of excited states and their properties[1], which can be exploited to tune the photophysics/photochemistry of molecules[2]. Information about the charge distribution in a given excited state is important for this, and one way of expressing the charge distribution in an approximate and concise manner is the excited state dipole moment μ_{Exc}. While the ground-state dipole moment μ_{GS} can be calculated quite accurately with hybrid DFT (5-10% MAE, PBE0)[3], time-dependent density functional theory (TDDFT) has been found to only be captured with sizeable errors (60%)[4] in terms of μ_{Exc}. Recently, ΔSCF methods have gained renewed attention as a way to access excited states as an alternative to TDDFT, as they offer access to the electronic structure in a more straightforward way,[5,6] as ground-state methods for calculating molecular properties are available.

Here, we investigate excited-state dipole moments of small to medium-sized molecules using ΔSCF methods and compare them to reference data from the literature as well as TDDFT and wave-function-based calculations.[4,7,8] We focus on HOMO-LUMO excitations which can be converged comparatively easily with ΔSCF as well as double excitations. The latter are available from ΔSCF calculations, in contrast to TDDFT calculations.

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Predictive Modelling of Transition Metal Catalyzed Cross-Coupling Reactions Using Machine Learning Techniques

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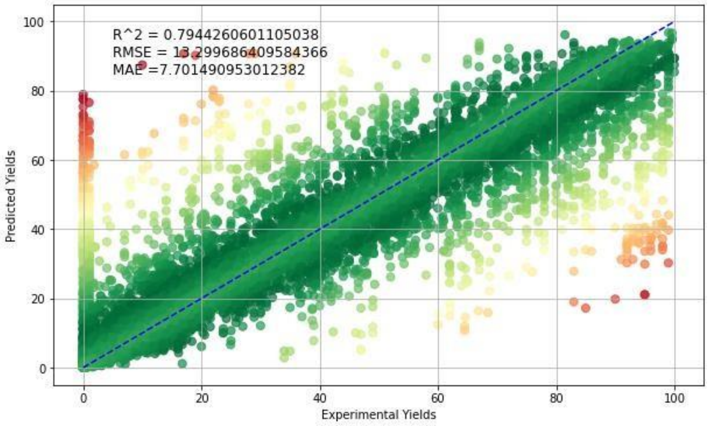
The development of transition metal-catalyzed cross-coupling reactions has been a significant advancement in organic chemistry, primarily due to their crucial role in facilitating the construction of carbon-carbon and carbon-heteroatom bonds. The determination of reaction yields, a crucial aspect of chemical research, has historically relied on experimental procedures. However, the integration of advanced machine learning techniques has revolutionized this field, streamlining and enhancing the processof evaluating reaction outcomes.

Constructing an accurate predictive model for reaction yields that can be applied across diverse categories of cross-coupling reactions remains a formidable challenge. However, this study has meticulously curated an extensive dataset encompassing a wide range of yields of cross-coupling reactions catalyzed by transition metals, achieved through rigorous literature mining efforts. This research employed regression analysis, utilizing various feature engineering techniques. Among them, the DRFP featurized Random Forest model with hyper parameter tuning achieved an R-squared value of 0.79. By releasing an open-access dataset comprising cross-coupling reactions catalyzed by transition metals, this study is expected to make a significant contribution to the advancement of predictive modelling for sustainable transition metal catalysis, thereby shaping the future direction of synthetic chemistry.



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Electroweak perturbations of rotational constants in chiral Bismuth-containing molecules

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In conventional quantum chemistry, the equilibrium structure of a molecule is found by minimising the total energy of the system with respect to the positions of the atoms. This energy is derived from an electronic Hamiltonian containing only electromagnetic interactions and the kinetic energies of the electrons. If one moves to a relativistic description and takes into account the electroweak interactions between electrons and nuclei, in the case of chiral molecules, the equilibrium structure found using the previous method is no longer correct. However, as the effects are small, the electroweak interactions only slightly distort the molecule and the structural change can be predicted using the gradient of the parity-violating potential. The beauty of this geometrical perturbation lies in the fact that changing the atomic positions leads to a change in the moment of inertia tensor, and therefore in the rotational constants of chiral molecules. The effects are opposite in the left- and the right-handed molecule [1] and the differences can, at least in principle, be measured by means of rotational spectroscopy. We aim at the detection of such shifts in molecules containing heavy atoms, like Bismuth, in which the perturbation is promisingly large. Shifts of rotational constants induced by the weak interaction energy (also called parity-violating potential) were already obtained for other molecules in earlier works [2,3]. In this study, we attempt the prediction of changes in the rotational constants of a selection of chiral molecules containing Bismuth, taking into account also the vibrationally averaged equilibrium structure. A prerequisite for such calculations is the knowledge of the gradient of the parity-violating potential, which is analytically available [3] and already implemented in our research group.

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Polymer degradation with molecular reaction discovery

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Automated reaction discovery is an upcoming field in computational and theoretical chemistry, which can e.g. use ab initio molecular dynamics (AIMD). It allows the determination of different reaction pathways starting from a defined molecular system to build a reaction network. However, MD by its nature is a short-time method, so reaction-enhancing techniques need to be used to facilitate rare events and speeding up reaction discovery. Various approaches have already been developed to accelerate MD, such as nanoreactor molecular dynamics, which uses external forces in order to enhance chemical reactivity.[1] In this work, we use this method to investigate the degradation of polyethylene, polypropylene, and mainly polystyrene. These synthetic polyolefinic plastics constitute a substantial portion of the global plastic waste, necessitating the development of effective recycling process, such as depolymerization into monomers and small molecules. Experimentally, this process can be achieved using a ball-millreactor.[2] To ease and enhance experimental investigations, a combination of AIMD simulations and kinetic modeling is employed to elucidate the degradation process. AIMD simulations contribute to the discovery of novel reactions, while kinetic modeling is instrumental in identifying the most efficient degradation pathways. During the simulations for polystyrene, numerous molecules and reactions were identified, corroborated by existing literature.[3] The primary reaction of significance involves the depolymerization of the polymer chain into styrene monomers. Additionally, the presence of oxygen molecules led to an experimentally observed oxygen attack on the polymer chain. Further depolymerization led to the formation of molecules observed in the simulation, including styrene, benzaldehyde, acetophenone, ethylbenzene, and cumene. These molecules can subsequently undergo repolymerization to form new plastics or other materials such as fuels, styrene monomers, or pharmaceuticals.

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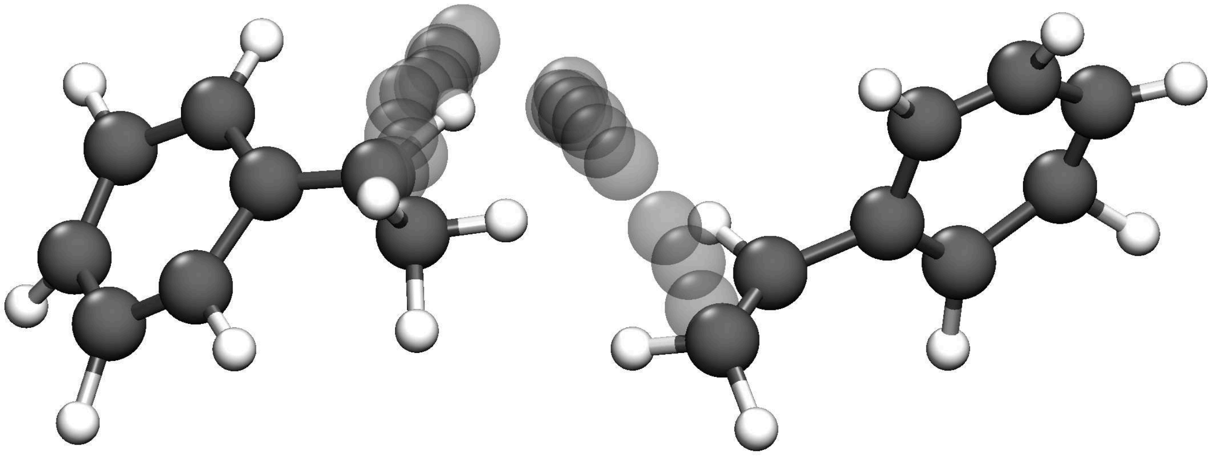

Energy decomposition analysis for excited states

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Chemical bonds are one of the most important heuristic concepts in chemistry and are often used for explaining reactivity. For this purpose, the bonds are mostly given a character like ionic, covalent, metallic, etc. Most chemical bonds have a mixed character, whereby this is not observable. Because of that model methods like Energy Decomposition Analysis (EDA) are needed for the analysis of bonds. EDA methods split up the bonding energy into different parts, which corresponds to chemical concepts like electrostatic, Pauli repulsion, and orbital interaction. By comparing the sizes of this different parts, the bonding character can be determined. But most EDA schemes are only for the ground state. Excited states are also interesting because photochemistry is a large research field. Thereby light is used as a reagent. In the excited states, the molecules change properties like structures, higher energy, and occupation of antibonding orbitals. Because of that reactions are possible, which does not work in the ground state. For a better understanding of such reactions, EDA for the excited state would be useful. Up to now only the Absolute Localized MO(ALMO)-EDA[1] and General Kohn Sham (GKS) EDA[2] scheme can be used for excited states.

Our Idea is now to combine the Morokuma-Ziegler-EDA scheme[3,4,5] with linear response TDDFT. The advantage of Morokuma-Ziegler EDA over both is that other aspects are analyzed due to the different decomposition of bonding energy. The basic idea of this new method is to calculate the excitation energy for the different intermediate states. For this purpose, their excitation matrix is determined. The method uses two variants for the calculation of excitation. First, the eigenvalue problem of the excitation matrix is solved by Davidson approach. The other variant determines the matrix-vector product of this matrix and the excitation vector of fragments.

This method is implemented in ADF. As testing system exciplexes are used, since in these only a fragment is excited. The excitation of one fragment leads to a bond with the other fragment. So there is no question of splitting the excitation. After testing the new method was applied to oligomers of pentacene due to their Singlet fission properties. In singlet fission, a monomer goes into an excited singlet state. This interacts with others, resulting in two triplets coupled with one another to form a singlet. These can then decouple. The advantage of this excitation is that it is spin allow but de-excitation spin forbitten. This means that such a system could be used for more effective charge separation in solar cells. We aimed to use the new method to understand the interaction of the excited momomer with the others and to gain an insight into the mechanism.

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How (Not) to Cage an Electron within a Molecular System

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The notion of a (molecular) electron cage was coined for the unique hosting capacity of perfluorocubane[1], suggesting the encapsulation of an electron within the highly symmetric molecular framework. Extensions to this occurrence of the perfluoro cage effect (PCE)[2] have been found in a variety of different cage structures, showing a remarkable transferability within the chemical subspace of prismanes and fullerens. Our investigation of the electronic structure within the molecular cage of perfluorocubane does not support the hypothesis of an caged electron as the common cause of the unique electron affinity characteristic for the PCE. Instead, we observed a central confining nodal surface within the spin density for perfluorocubane as well as any other radical anions of the aforementioned chemical subspace. The association of the spin density to the singly occupied molecular orbital (SOMO) of a corresponding Kohn-Sham reference system, by potential reconstruction, enables us to construct a quantitative single-particle model that captures analytically the main tendencies of the symmetry and size dependence on the electron affinity. The derivation is solely based on the nodal variational principle[3] and thereby explains the effectiveness of a confined particle model for the PCE without any reference to an caged electron. The demonstration of the complementarity between the hosting mechanisms in PCE systems and color centers of alkali halid clusters as well as silsesquioxane radical anions, provides further evidence for the uniqueness of the PCE systems.

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Revealing the Molecular Origin of Anisotropy around Chloride Ions in Bulk Water

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A clear picture of the local solvation structure around halide anions in liquid water remains elusive. This discussion has been stimulated by pioneering simulation results that proposed a “hydrophobic cavity” around anions in the bulk, which is analogous to air at the air-water interface. However, there is also sound experimental and theoretical evidence that halide ions are rather symmetrically solvated in the bulk, leading to a different viewpoint. Using extensive ab initio molecular dynamics simulations of an aqueous Cl^- solution, we indeed find an anisotropic arrangement of H-bonded versus interstitial water molecules. The latter are not H-bonded to the anions and thus do not couple much electronically to Cl^-. The resulting purely electronic anisotropy of the local solvation environment correlates with that structural anisotropy, which however should not be understood as an empty cavity–as it would be at the air-water interface–but rather contains interstitial water molecules.[1]

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Topological Frustration Triggers Ultrafast Dynamics of Monolayer Water Confined in Graphene Slit Pores

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The ultrafast dynamics found within water monolayers confined in narrow slit pores has broad implications from physics to biology to technology. Here, the molecular mechanism underlying ultrafast diffusion in monolayer water is found to be strikingly different from that of both, bulk and interfacial water. The significant population of dangling (or free) O-H bonds pointing toward the two walls, caused by the geometric restriction due to such extreme confinement, leads to topopogical frustration within the residual H-bond network of the monolayer. This provides a novel, ultrafast channel for diffusion of water molecules based on instantaneous kicks due to dangling bonds dynamics, while residing in a stable H-bonded solvation shell, thus without exchanging any such H-bonded partners by large angular jumps as required in bulk or interfacial water.

Modeling Sulfur Based Polymer Cathodes for Li-S Batteries: Structural Analysis and Raman Characterization

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The optimization of lithium-sulfur batteries highly depends on the exploration of novel cathode materials. Here we focuse on the development of sulfur/carbon co-polymers as a promising class of cathodes to replace crystalline sulfur. These co-polymers offer a flexible atomic structure and a potential for high reversible capacity. In particular, we dive into the investigation of poly(sulfur-n-1,3-diisopropenylbenzene), (S/DIB). Our exploration begins with a comprehensive analysis of the atomic structure of sulfur-n-1,3-diisopropenylbenzene co-polymers, using density-functional theory calculations. The primary goal was understanding the local structural properties, with a focus on identifying the optimal sulfur chain length ($\mathrm{S}n$ with $n = 1 \cdots 8$) bridging two DIB units. Our findings reveal a preference for shorter sulfur chains $n \sim 4$ in DIB-$\mathrm{S}n$ -DIB co-polymers. Subsequently, we complement our findings with ab initio Raman spectroscopy simulations and experimental Raman measurements. This combined approach facilitates the identification and characterization of various sulfur/carbon co-polymers with distinct sulfur contents. We demonstrate that S/DIB co-polymers featuring short and long sulfur chains exhibit distinguishable Raman activity in the 400-500 cm^{-1} range, providing crucial insights into their structural composition. Significantly, the results presented herein apply to the fully charged state of the cathode. Furthermore, we extend our investigation to explain the discharge state of the battery, focusing on the transformation of sulfur co-polymer cathode materials upon lithiation.
Specifically, we explore how sulfur chains evolve during lithiation and perform the same ab initio Raman spectroscopy methodology for their characterization.

Extensions of auxiliary function ansatz for quantum-inspired simulation of non-Condon effects

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Vibronic transition profiles of molecules with high-symmetry often cannot be fully assigned within the first-order Herzberg-Teller approximation, thus necessitating the inclusion of second order terms. A recently derived scheme employing auxiliary functions approximates the non-unitary transition dipole moment operator as a linear combination of Gaussian operators [Jnane. et al. ACS Photonics 8, 2007 (2021)]. However, an extension to simulate finite-temperature effects is missing. Herein, we provide this extension, and also modify the scheme such that not only transition probabilities but also amplitudes can be extracted. We apply our developments to the simulation of selected molecular systems.

ωB97M-3c: A small basis composite DFT method for the computation of large systems

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We introduce a new “-3c” composite density functional (DFT) method called ωB97M-3c. Almost 10 years after the release of the first 3c method (HF-3c [1]), we are circling back to the application of a small basis set for a substantial speed-up in computation time. The method is based on the popular ωB97M-V range-separated hybrid density functional [2] together with a fitted D4 dispersion correction [3] and an adaptive polarized minimal basis set, which has been specially optimized in molecular DFT calculations [4]. The savings in expensive polarisation functions must be compensated for the appropriate description of the anisotropic electron density distribution, which is why we employ the idea of atomic correction potentials (ACP) as proposed by DiLabio [5]. These one-electron potentials are very cheap to compute and can be readily used like regular effective core potentials (ECP). With this new method, we make the computation of supramolecular complexes and proteins up to 2000 atoms routinely possible at the range-separted hybrid DFT level.

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Chirality Signatures in Linear Combinations of Hydrogenic Wave Functions

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Chirality in chemistry is often intuitively connected to the three-dimensional spatial distribution of nuclei in molecules, seen in a molecule-fixed coordinate system.

We investigate the signatures of chirality in a strongly reduced representation of a chiral system, specifically in linear combinations of hydrogenic functions [1,2], since such single-center expansions are able to represent also chiral distributions of, e.g., electrons, depending on the choice of quantum numbers and coefficients in the expansion.

We show which minimal linear combinations are chiral—and for which aspect of the system, i.e. wave function, probability density or probability current density—and explain simple rules for the identification and construction of such chiral systems.

It then becomes evident that the molecule-fixed perspective, while intuitive, does not always present the most sensible approach to chirality, especially when the system is rotationally averaged in the laboratory-centered perspective.

We discuss parity-odd, time-even properties of this model system [3] and their dependence on the selection of quantum numbers, including spin. This fundamental approach to chirality of linear combinations of hydrogenic wave functions not only furthers the understanding of chirality in molecules, but is also a natural model for Rydberg states, especially in atoms.

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Quantum chemical calculation of mass spectra via automated transition state search

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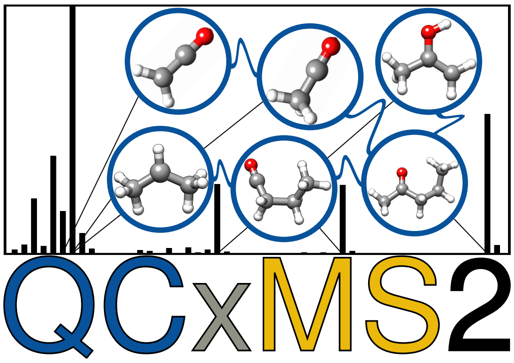
Mass spectrometry is a powerful analytical tool used in many areas of chemistry such as metabolomics, drug discovery, and environmental sciences. Due to the enormous complexity of the many possible fragmentation pathways, the annotation of spectral peaks, even for small molecules, is very complex and in many cases unsuccessful. In this context, mass spectra predicted by quantum chemistry can help to elucidate unusual or unknown fragmentation pathways. To this end, a new method called "QCxMS2" for the routine calculation of EI mass spectra is presented as a successor to the established QCxMS program. [1], [2] The QCxMS2 workflow is based on the automatic generation of possible fragmentation pathways and the calculation of the corresponding reaction barriers using efficient quantum mechanical methods. According to transition state theory, the mass spectrum is calculated from the relative rates of the fragmentation reactions. Subsequent fragmentations via cascade reactions and ion tracking according to the ionization potential obtained from ΔSCF calculations were adopted from the QCxMS method. Compared to the old approach, based on extensive sampling via molecular dynamics simulations, for which only approximate semiempirical quantum mechanical methods are feasible, in QCxMS2, the reaction barriers can be systematically improved at the density functional theory level. This enables the calculation of mass spectra with unprecedented accuracy at reasonable computational costs. For a test set of 14 small to medium-sized organic and inorganic main group molecules (10 to 24 atoms), the computed spectra using ωB97X-3c barriers on GFN2-xTB geometries yield a good average entropy similarity score of 0.71 compared to experimental spectra.



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Achieving Pressure Consistency in Mechanochemical Simulations of Chemical Reactions Under Pressure

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The development of computational methods capable of simulating molecules under pressure is a very important yet challenging task, as pressure plays a significant role in today's chemistry. The extended hydrostatic compression force field (X-HCFF) as well as the extreme pressure polarization continuum model (XP-PCM), the gaussians on surface tesserae simulate hydrostatic pressure (GOSTSHYP), the hydrostatic compression force field (HCFF), and the generalized force-modified potential energy surface (G-FMPES) can be summarized as a group of electronic structure methods capable of simulating the effects of pressure on a target system. These methods allow the investigation of changes in chemical bonds, vibrational frequencies and absorption properties as well as the investigation of chemical reactions and spin crossover processes induced by pressure.[1]
Within this group of methods X-HCFF is a mechanochemical approach, in which a cavity is used to exert pressure on a target system.[2] This cavity is set up to represent the Van-der-Waals (VDW) surface of the system by joining spheres sized according to the respective atomic VDW radii. The pressure is applied in the form of forces acting perpendicular to this cavity, ensuring a hydrostatic exertion of pressure. Optionally, the size of the cavity can be scaled using a scaling factor. This is important as the surrounding medium inducing the pressure generally is at a distance greater than the VDW radii of the system's atoms.[3] We have observed that the scaling factor can influence the results of calculations in X-HCFF, e.g. the critical pressure required to make a chemical reaction barrier-free and this dependency is undesirable for the method. To counteract this effect, we have developed a rescaling formalism for the forces applied, allowing us to greatly decrease the scaling factor dependency of the pressure. This formalism reduces the empiricism of the X-HCFF approach and boosts its predictive power.

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Automatized Eigensolver for General One-body Potentials

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With quantum dots being a popular research topic following the 2023 Nobel Prize in Chemistry, the need to solve the Schrödinger equation for quantum dots has become increasingly important. Due to the variety of shapes and sizes of quantum dots, the potential is often complex and highly dependent on their properties. With this variety, it is difficult to find a sparse set of basis functions that can efficiently represent all quantum dots. For this reason, an adaptive real-space approach based on multiwavelets is used. This allows the dynamic generation of basis functions based on the given potential of the quantum dot. A method for the automatic generation of system-adapted initial guesses is developed and integrated into the automatized eigensolver for general one-body potentials. This automatized eigensolver is written using MADNESS, which ensures a high level of performance and accuracy.

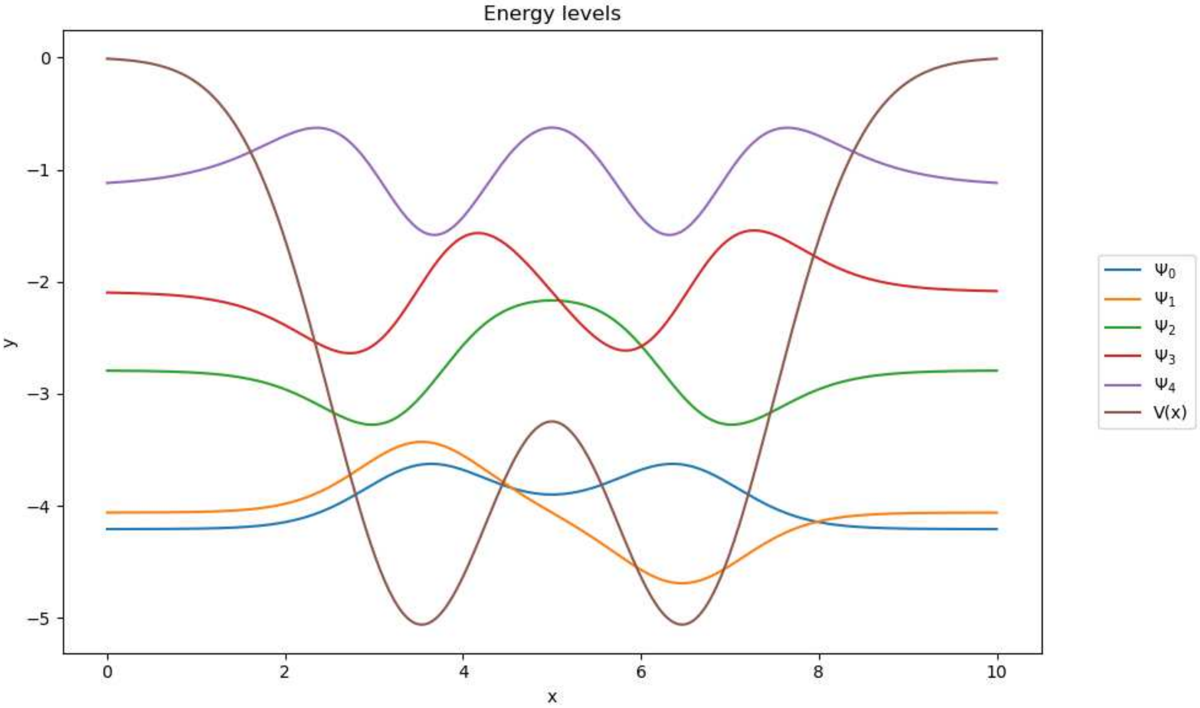

Figure 1 Visualization of a double-well potential and its eigenfunctions at different energy levels

Non-adiabatic Molecular Dynamics Simulation of Charge Transfer in Organic Semiconductors Using Trajectory Surface Hopping Approach

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In recent years, trajectory surface hopping methods have become increasingly popular for studying charge and exciton transport in organic semiconductors (OSCs). Our study focuses on investigation of the charge transport in different class of OSCs using non-adiabatic molecular dynamics simulation methods, particularly on the performance of the Fewest Switches Surface Hopping (FSSH) framework. Additionally, we utilize a fragment orbital approach to model the charge transfer Hamiltonian where, Density Functional Tight Binding (DFTB) method used to estimate the Hamiltonian elements. It has been shown that, DFTB is 2-3 orders of magnitude faster than Density functional Theory (DFT) method[1]. We have computed the charge mobilities of different OSCs with a specific focus on halogenated tetraazaperopyrenes (TAPPs). In TAPPs we examined the effect of halogen groups on the charge transport properties. Furthermore, we are modeling OSCs as thin films in polycrystalline phases to analyze the influence of grain boundaries on mobility compared to intrinsic values. Through our comprehensive analysis, we contribute to the identification of efficient methods for calculating charge transport mobilities in OSCs, providing valuable insights for advancing the field of organic semiconductor research.

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COOX: A Constraint-Based Orbital-Optimized Excited State Method for Valence and Core Excitations

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The quantum-chemical description of electronically excited states is an indispensable tool in the natural sciences. Predictions of vertical excitation energies, excited-state properties, and potential energy surfaces – often by means of linear-response time-dependent density functional theory (LR-TDDFT) – are routinely used to aid the interpretation of experimental spectra and to further the understanding of photo-induced reaction mechanisms. The need to overcome some of the central limitations of LR-TDDFT has sparked a resurgence of orbital-optimized excited-state methods, including constrained DFT (cDFT) approaches [1]. Recent advancements in the form of "excited cDFT" (x-cDFT) [2] and "transition-based cDFT" (t-cDFT) [3] have been used to extend the scope of cDFT, but are subject to some limitations of their own regarding the types of attainable states and physical correctness of excited-state properties.

We herein present COOX [4], a new constraint-based orbital-optimized excited-state method which aims to facilitate the accurate description of arbitrary excited states with physically sound excited-state properties within the framework of cDFT. Our COOX method uses a single constraint in the form of a projector onto the static part of the LR-TDDFT difference density and is shown to provide properties such as difference densities and excited-state forces that are in good agreement with higher-level methods, particularly including states with significant double-excitation character, while retaining similar levels of accuracy as existing orbital-optimized methods for vertical excitation energies. The adherence to an Aufbau principle further allows for the straightforward inclusion of post-SCF correlation methods such as the direct random phase approximation or the derived σ-functionals [5], which we illustrate through an application to the *cis*/*trans*-isomerization of azobenzene. A simple modification of the COOX constraint also enables the variational computation of core-excited states with substantially improved algorithmic robustness compared to the popular ΔSCF method and mean errors well below 1 eV, thereby facilitating the simulation of near-edge X-ray absorption spectra without the need for manual alignment to experimental data [6].

We therefore expect COOX to be widely applicable for the targeted variational computation of arbitrary excited states as well as for non-adiabatic molecular dynamics.

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An Automated Reaction Discovery Approach via New Atomic Frontier Orbital Features

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Exploring a complete reaction network based on known chemical mechanisms or experimental results requires enormous manual work. Various algorithms have been developed to facilitate the effort and predict reaction paths. [1,2] The Key step of automated reaction discovery lies in identifying many potentially important elementary reactions without human interference. Considering the localized nature of chemical reactions, we have developed atomistic reactive descriptions from semiempirical electronic structure theory. In addition, a complete reaction simulation algorithm is proposed: For each predicted elementary step, the reaction coordinate is constructed incorporating steric hindrance and buried volume. Subsequently, newly generated structures are screened to identify those that are thermodynamically accessible and then enable undergo a new elementary reaction search. To maintain low computational costs, both reaction site prediction and reaction simulations are conducted at the semiempirical tight-binding level [3], with structural and energetic corrections applied using low-cost density functional theory (DFT) methods [4]. The performance of this algorithm is demonstrated for different known reactions, some of which are difficult to describe using, e.g., well-established Fukui functions.

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Ab-Initio Simulation of Photoreactions

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The study of chemical systems and their reactions through molecular dynamics simulations is gaining growing interest. Ab-initio molecular dynamics (AIMD) involves describing the motion of the nuclei using classical Newtonian mechanics while treating the electron cloud quantum mechanically via density functional theory. This approach was pioneered by Roberto Car and Michele Parrinello with the development of the Car-Parrinello Molecular Dynamics (CPMD) program. Simulating photoreactions, which involve excited states, presents a significant challenge compared to ground-state simulations. Here, we combine restricted open-shell Kohn-Sham theory with AIMD to simulate photochemical reactions. Our method successfully confirms a textbook principle for photochemically induced halide substitution of aromatic compounds: For the example of chlorine and toluene, we observe homolytic bond scission and show that the reaction takes place on the side chain of the aromatic system. Photochemical reactions are also used in the synthesis of silver nanoparticles. One method is the photochemical reduction of trisilver citrate. Our simulations of the photochemical reduction of silver citrate help us to expand our understanding of nanoparticle formation at the atomic scale.

Quantum chemical calculations on $Pt_nH_{2n}^-$ clusters

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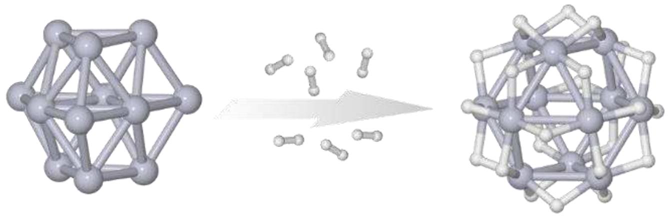

Heterogeneous catalysts consisting of Pt-nanoclusters supported on metal oxide surface exhibit quite versatile catalytic properties and are widely applied in automotive catalytic converters, in catalytic oxidation and reduction reactions, and for emission control [1]. Such nanoclusters have high catalytic activity and show diversity in a small energy range. A thorough study of the gas-phase cluster structure is needed to understand the underlying mechanisms of the surface reactions. In the current study, we combined trapped ion diffraction spectroscopy with density functional theory to analyze the effect of hydrogen on Pt_n^- structures in the gas phase. Clusters ranging from $Pt_6H_{12}^-$ to $Pt_{13}H_{26}^-$ were studied. The results showed that spin-orbit coupling influences the structures and the energetic ordering of the isomers. Among all the clusters, $Pt_{12}H_{24}^-$ exhibits unique properties [2]. One of its isomers possesses a cuboctahedral cage structure which is stable irrespective of the low coordination number of the Pt atoms. The structural analysis of such a structure revealed that bridge-bound hydrogen atoms stabilize the structure through strong interactions with the neighbouring Pt atoms by multi-center bonds resulting in higher charge transfer and thus high binding energy. The electronic effects show the presence of all-metal aromaticity.

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Compound Screening of Hetero-atom Bridged NBDs

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Tuning the properties of desired molecular solar thermals (MOST) is the central challenge of the development of efficient MOST applications. Facing the vast compound space spanned by possible substituents on the central ring of a norbornadiene (NBD) compound is not only synthetically impossible but also very expensive for high-level theoretical screening procedures. Here we employ a computational screening protocol based on semi-empirical (GFN2-xTB & sTDA-xTB) methods for the investigation of a large space of substituted hetero-atom bridged NBD compounds. We employ the previously introduced solar conversion efficiency as scoring function for these compounds.[1,2] The most promising candidates are eventually re-evaluated at higher level of theory ((TD)DFT/M06-2X/def2-SVPD). These results obtained using the fast screening procedure agree qualitatively with the ones obtained with the more time consuming higher-level computations.

Based on these findings, we suggest new compounds for synthesis within the data set for future real-life comparison. We also demonstrate that the substitution is more decisive for the NBD's properties than the choice of the bridge atom.

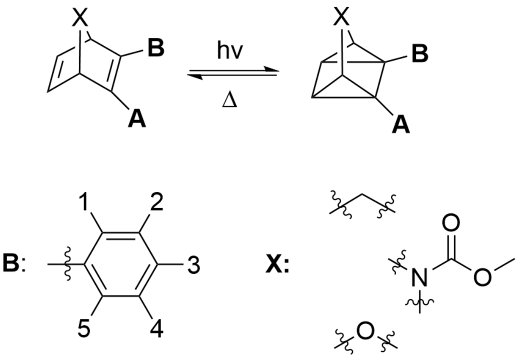

Figure 1. Hetero-atom bridged NBDs with substitution pattern.

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The Effect of Bias and Electrode Temperature on Magnetoresistance in a Chiral Molecular Junction: A First-Principles Study

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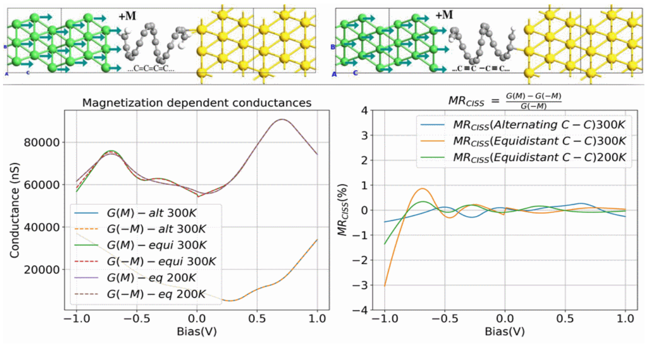
Electrons travelling through chiral structures are selected according to the helicity of the chiral structure and the electron's spin orientation. The effect is best known as chiral-induced spin selectivity (CISS) [1-2]. The underlying physical mechanism is still under debate. To help elucidate this mechanism, a non-equilibrium Green's function method, combined with a Landauer approach and density functional theory, is applied to carbon helices contacted by nickel and gold electrodes to mimic the experimental setup. This results in magnetoresistance (MR) [3] with different electrode electronic temperatures, which is important in the context of understanding recent experiments taking consideration of temperature effects [4-5]. While the MR is usually calculated in experiments by taking the difference of currents with opposite magnetization directions, report suggests that [6] to facilitate Julliere's model [7], the CISS MR should be calculated by taking the difference of magnetization-resolved differential conductances. Our results [3] suggest that indeed temperature plays a cruical role as the CISS MR increases with temperature similar as in experiments [4-5]. Thus, understanding CISS MR in a model helix junction could be a key component in understanding the CISS measurements.



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Electrochemical oxidation of UV filters: A first-principles molecular dynamics study

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A theoretical model is proposed to study the oxidation mechanisms of the organic UV filters benzophenone-3, **BP3,** and benzophenone-4, **BP4**, during electrochemical water treatment utilizing Car-Parrinello Molecular Dynamics. Factors such as the amount of solvent to be included and how to design the system with the least possible intervention are discussed. The stages of the proposed model consist of the optimization of the geometries by density functional theory methods, the equilibration of the structure immersed in a water box, the inclusion of the reactive species, and the analysis of the reaction energies of each reaction pathway. The ab-initio molecular dynamics simulations lead to several products, and some trends can be identified, in accordance with the well-known reactivity rules of organic chemistry. We conclude that the model is valid for predicting potential oxidation products of these organic UV filters and hope to extrapolate the model to other compounds. We also believe that the products proposed in this work are intermediates in longer oxidative pathways. [1, 2]

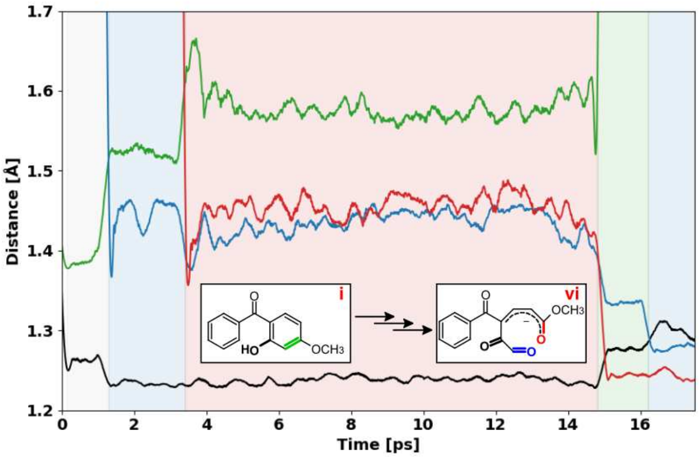

Figure 1: Evolution of interatomic distances between reactive species of a BP3 (i) simulation. The color of each line corresponds to the bonds highlighted in the structures. The bond formation, bond cleavage, and changes in bond order during the reaction can be followed throughout till the formation of structure vi.

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Assessing the dynamics of hemithioindigo-based photoswitches using multi-state molecular mechanics

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In the realm of nanotechnology and molecular engineering, photoswitches play a key role as structural elements converting light into mechanical work. In particular, switchable chromophores embedded in complex molecular environments – such as molecular machines and self-assembled monolayers on surfaces – offer unique opportunities for the precise control of material properties and molecular motion. [1] A relatively new but emerging class of photoswitches is based on hemithioindigo (HTI) chromophores, which feature high thermal bistability, bright absorption bands in the visible region of the electromagnetic spectrum, and chemical durability. Upon photon absorption, HTIs readily undergo double bond isomerization, resulting in the formation of either *cis*- or *trans*-isomers. By using HTI photoswitches as core structures, future photoresponsive (nano-)devices are accessible via HTI functionalization to tailor the light-induced motion, aggregation, and self-assembly on substrate surfaces. [2]

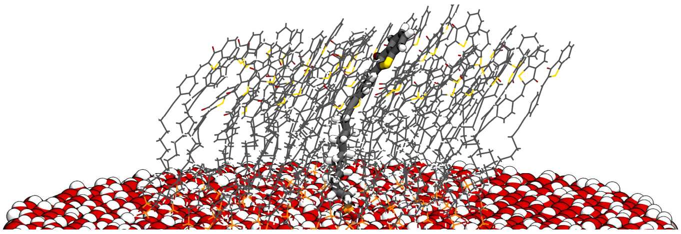

Fig. 1: Ensemble of HTI-based photoswitches on aluminum-oxide surface.

In principle, excited state dynamics simulations can be an appealing tool for investigating devices and structural elements featuring photoswitchable molecular motifs. However, in most light-responsive devices, the motion of the photoswitch is strongly coupled to a complex environment – e.g. explicit solvent shells or ensembles of photoswitches – requiring an atomistic treatment of 1000s of molecules paired with ns-scale dynamics. While this presents a significant challenge for a fully *ab initio* treatment, an approximate approach, as suggested by Duchstein et al. for azobenzene chromophores, involves multiple molecular mechanics models, each describing a separate electronic state under consideration. [3] Here, we present an adaption of this methodology to the widely employed hemithioindigo chromophors. This is demonstrated for cyclic photoswitching dynamics in different explicit solvation environments, gaining atomic-scale insight into energetic and kinetic effects. In-depth mechanistic understanding is achieved through committor analyses in combination with predictive modeling of the relaxation to either the S_0-*cis* or S_0-*trans* state, respectively.

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Impact of torsion angles on the photophysical properties of TADF emitters with donor-acceptor-systems

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Thermally activated delayed fluorescence (TADF) emitters are crucial for organic light-emitting diodes (OLEDs) because they enable high efficiency by facilitating the conversion of triplet excitons into fluorescent singlet excitons, significantly enhancing the light emission without requiring heavy metal atoms. Accurate calculation and prediction of the electronic and photophysical behavior of TADF emitters are essential for optimizing these properties and ensuring the development of more efficient OLEDs.[1]
The torsion angle between the donor (D) and acceptor (A) segments plays a substantial role in influencing these key properties, including the energy gap between singlet and triplet states, oscillator strength, and spin-orbit coupling. These properties include the energy gap between singlet and triplet states, oscillator strength, and spin-orbit coupling.[2] In response to these insights, our study focused on calculating rotational energy profiles to examine how these angles influence conformer-rotamer ensembles.[3] Additionally, we investigated the efficient conversion of triplet excitons into fluorescent singlet excitations in TADF emitters. Employing density functional theory combined with multireference configuration interaction (DFT/MRCI)[4], we characterized the excited states of DA-TADF emitters, such as phenothazines or triarylamines with a dicyanobenzene moiety. These emitters display charge-transfer states and a remarkably small adiabatic $T_1 - S_1$ energy gap, crucial for efficient TADF functionality.[1,3]

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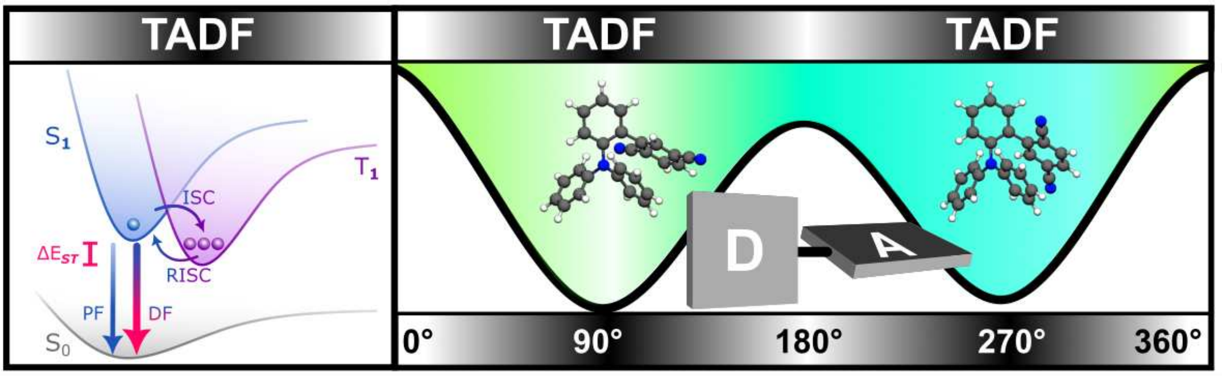

Spectroscopy and Nonadiabatic Dynamics of the Cations of Adamantane, Amantadine and 1-Cyanoadamantane: Violation of the Energy Gap Law?

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Diamondoids are the carbon cage molecules which have gained prominence in interstellar chemistry [1] as well as in medicinal chemistry and industrial applications[2]. The fundamental unit of these diamondoids is adamantane (Ada). The cations of diamondoids have also become a subject of interest due to their potential role in interstellar chemistry [3,4]. Studying their electronic spectra and photo-induced dynamics can provide insights into the chemical behavior of the molecules under the influence of light. In our research, we explore the electronic spectra and nonadiabatic dynamics of adamantane derivatives containing two different nitrogen groups, (one electron donating group (NH_2) and one electron withdrawing group (CN)) on the adamantane cage, namely, amantadine (Ama) and 1-cyanoadamantane (Ada-CN). Using Tully's Surface Hopping approach [5], combined with Thiel's semiempirical configuration interaction method (OM3/CISD) [6], we investigate the nonadiabatic molecular dynamics and determine the lifetimes of the excited states of the cations. We also looked into the possible ultrafast fragmentation and rearrangement channels of these molecules and tried to understand the behaviour under various excitation energies. We compared the relaxation rates and fragmentation outcomes [7] with our previous results for Ada^+[8]. For both Ada^+ and Ama^+, our simulations demonstrate that upon excitation with near-infrared to ultraviolet photons, the cations rapidly undergo internal conversion to the ground (doublet) state (on a time scale of 10-100 fs depending on initial excitation energy), while it takes longer time (~ 120-300 fs) in case of $Ada\text{-}CN^+$ to populate the ground state. Despite of having lower excitation energy, $Ada\text{-}CN^+$ takes more time to relax to the ground state. Therefore, determination of the rate of internal conversion may not be straightforward at first glance, as the well-known energy gap law may not be directly applicable in studying the internal conversion rate of these systems. A careful examination of the participating states and nonadiabatic couplings may be necessary to elucidate the nature of the relaxation processes.

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Influence of the Quality of the Hessian Matrix on the JEDI Strain Analysis

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The JEDI (Judgement of Energy Distribution) strain analysis allows for the quantification of mechanical stress distribution across the relevant degrees of freedom in a molecule [1, 2]. This requires *i.a.* the Hessian matrix of the molecule's relaxed state in internal redundant coordinates. With the calculation of the Hessian being the rate determining step, we investigated the influence on the quality of the JEDI strain analysis when reducing the Hessian to a certain set of elements as well as using a frozen density matrix approximation when calculating second derivatives. Calculations were performed for a set of five molecules using several semi-empirical methods as implemented in SCINE sparrow [3, 4] and compared to calculations done with the quantum chemistry program Gaussian 16 [5]. The associated Python module facilitating the use of the JEDI strain analysis with SCINE sparrow calculations will be available soon.

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Basis pruning concepts within rovibrational configuration interaction (RVCI) calculations

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The *ab initio* calculation of rotational and rovibrational spectra with rovibrational configuration interaction (RVCI) theory is highly sensitive to various parameters, including the quality of the multidimensional potential energy surface, the expansion of the *μ*-tensor within the Watson Hamiltonian and the chosen set of vibrational state wavefunctions. Consequently, these quantities need careful monitoring and optimization in the usual workflow to yield reliable results, necessitating both expensive test calculations and high user control. Within configuration interaction approaches, the number and proper selection of the used basis functions are crucial. In the here employed RVCI theory, a direct product of rotational and vibrational basis functions is used, with the latter corresponding to state functions from preceding vibrational configuration interaction (VCI) calculations. While the rotational basis has an upper limit of meaningful functions, the vibrational basis is, in principle, unlimited. The choice of vibrational basis size significantly impacts rovibrational state energies and computation time, requiring a balance between completeness and computational efficiency [1].

Here, we present a screening technique that limits the vibrational basis functions to only those with a significant impact on the final RVCI state energies in specific spectral regions. This approach mirrors configuration selection in VCI theory, where a large initial configuration space is screened to identify meaningful configurations for the VCI matrix setup [2]. Similarly, we screen a large space of vibrational wavefunctions based on their impact on rovibrational state energies. To identify important basis functions quickly and effectively *prior* to the VCI calculation, we use approximate VMP2 wavefunctions. Consequently, a VMP2 test wavefunction is added to the selected set when it changes the monitored RVCI eigenvalues above a threshold, repeating this process until convergence is reached. We assess the performance and user-friendliness of this scheme by comparing the automatically generated vibrational basis set with computationally demanding benchmark calculations of the rovibrational spectra of thioketene (H_2CCS) and cyclopropenone (C_3H_2O).

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Using High Pressure Conformational Sampling Within the CREST Program to Model Piezochromic Molecules

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We present a new standalone library, to calculate the PV term for molecules, where the volume V is calculated as the volume of overlapping van der Waals spheres centered at each atom. We linked our library with the Conformer-Rotamer Ensemble Sampling Tool (CREST), which is a powerful software mainly focused on computing ensembles of molecular systems using Grimme's GFN*n*-xTB methods, (*1*, *2*) to calculate the molecular enthalpy

$$H = E_{\text{GFNn−xTB}} + PV. \tag{1}$$

This procedure allows conformational sampling for molecular systems at elevated pressures.

We investigate the pressure-induced isomerism of the propeller-shaped molecule Tetra(4-methoxyphenyl)- ethylene (TMOE). Previous experimental studies reported that TMOE exhibits piezochromism, i.e. molecules changing color upon exposure to high pressures, and observed a significant darkening in its fluorescence and Raman spectra above 1 GPa. (*3*) Ab initio DFT calculations from this studies, suggested that the darkening is caused by a change in the dihedral angle between the phenyl units and the central ethylene. Our findings indicate, that TMOE isomerizes from a propeller to a sandwich shape at pressures above 3 GPa. The isomerization is accompanied by a significant reduction in intensity for both Raman active vibrations as well as electronic excitations and affects the molecular ensemble at pressures above 2 GPa. While the model overestimates the necessary pressure to initiate the isomerization, we find that it explains the spectroscopic changes well.

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Development of a low-scaling density fitted NEO-DFT implementation

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In recent decades, quantum chemistry calculations have become indispensable for understanding chemical systems, aiding spectroscopy and uncovering the mechanisms of organic reactions. However, classical methods treating nuclei as point charges encounter limitations, especially when treating light atoms, due to the influence of nuclear quantum effects (NQEs). These include various phenomena such as kinetic isotope effects or anharmonicity in vibrational motion and play a vital role in proton-coupled electron transfers (PCETs).[1–3]

We focus on the utilization of the nuclear electronic orbital (NEO) method,[4] aiming at the quantum mechanical treatment of protons. As has been shown in previous works of our group, the application of density fitting (DF) to NEO wavefunction methods such as NEO Hartree-Fock (NEO-HF) yields significant improvements in the computational performance.[5] In this contribution we present our own development of a density-fitted NEO-DFT implementation.

Comparison of standard implementations to our approach shows significant speedups. Furthermore, calculated gas-phase proton affinities exhibit lower root mean square deviations from experimental results. This observation is confirmed by comparison with DF-NEO-DFT calculations by Rodriguez et. al.[6] For future works, we aim at not only including local DF methods as done for NEO-HF, but also implementing multistate NEO-DFT (NEO-MSDFT).[7]

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Solvent Effects in Electron Transfer Reactions: Dynamics of Nascent Aqueous Halides and Dielectric Properties of Nano Confined Water

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Photoinduced electron transfer (ET) plays an important role in many fields, including catalysis and biology, and nonequilibrium solvent dynamics may play an important role in such processes. As a simple model system, we simulate the non-equilibrium solvent dynamics following photoionization of solvated halides in water. This is achieved with adaptive buffered hybrid quantum mechanics / molecular mechanics (QM/MM) molecular dynamics simulations [1]. Our simulation results are compared to data obtained from experimental [2] extended X-ray absorption fine structure (EXAFS) analysis [3]. Another interesting aspect of water in the context of solvent-controlled ET is its dielectric properties. The dielectric constant of water in nanoconfinement is greatly reduced as water volume decreases. Theoretical simulations [4] so far show reduction of the dielectric constant with decreasing volume but do not accurately reproduce absolute values shown in experiments [5]. Our goal is to study spherical nanoconfined water and find a suitable simulation setup to reproduce experimental values.

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Constructing a H_2S Oxidation Reaction Network via Active Learning and Accelerated Molecular Dynamics

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Atmospheric chemistry, characterized by a multitude of radical reactions, results in the formation of intricate reaction networks. Constructing these networks poses significant challenges due to their inherent complexity. Our approach extends the established Nanoreactor method (NMD)[1], by incorporating the Diffusion Accelerated NMD (DA-NMD) method for improved sampling of reaction spaces. The method operates in two distinct phases: a contraction phase, during which an external force pushes the molecules to the center, and an expansion phase, where an external force is used to accelerate molecular diffusion. To further improve the development of reaction networks, we integrate a machine learning-based active learning scheme inspired by the work of Zhang et al. [2]. This scheme features two main components that are built with the SpookyNet architecture[3]: the 'Exploratory Sampler' and the 'Committee.' The Exploratory Sampler continually generates new molecular configurations using the DA-NMD. These new configurations are then evaluated by the Committee, which assesses their deviation from expected predictions. Structures that exhibit significant deviations are flagged for single point calculations using density functional theory. This allows an iterative refinement and enrichment of the training dataset. The continuous feedback loop ensures that our model adaptively improves, focusing computational resources on the most informative and chemically diverse structures, thereby accelerating the construction of accurate and comprehensive reaction networks.

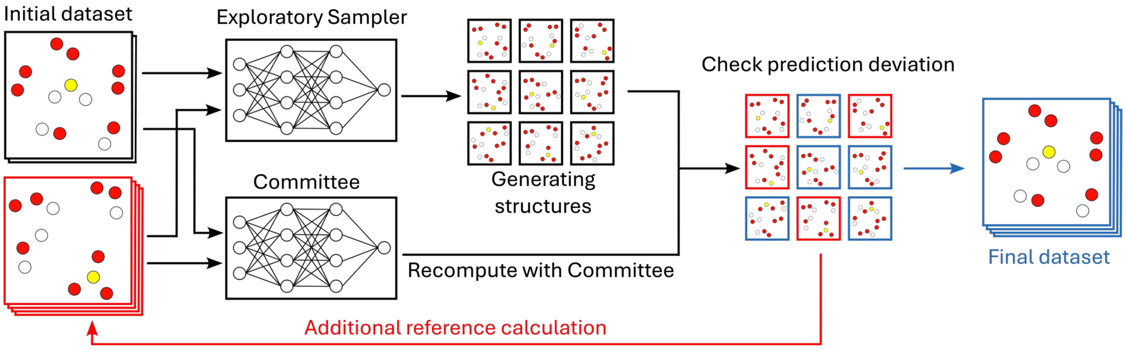

Fig 1: Active learning scheme with the 'Exploratory Sampler' and 'Committee.' The Exploratory Sampler continuously generates new structures for evaluation, while the Committee refines the model through iterative feedback, leading to an optimized final dataset.

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Reference States in Nuclear Ensembles: Dealing with the Reordering and Mixing of Electronic States

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A common approach towards predicting electronic properties such as absorption spectra of a molecule is to solve the electronic structure for a single geometry. In past years, theoretical studies on the influence of molecular vibrations on the electronic properties have become more feasible even for a large molecular systems. A popular way to account for vibrational effects on the electronic properties is the nuclear ensemble method, where a thermally populated ensemble of distorted geometries is generated and a large number of single point calculations is carried out on each of those to obtain the spectrum of the ensemble.
An inevitable effect in such ensembles is that the electronic states of the individual members will change their energetic ordering or the character of their wavefunction (a so-called mixing of states). Consequently, insights into how much certain states contribute to the absorption spectra will be hampered, although such information may be crucial to estimate the photophysical properties of certain systems.
To address this issue, we herein introduce a set of reference states, which are simply the electronic states at the optimized geometry, and use these states to analyze the ensemble. For each geometry in the ensemble we define the transformation to the set of reference states through wavefunction overlaps.
This methodology is applied to the $\mathrm{Chl_{D1}Pheo_{D1}}$ and $\mathrm{P_{D1}P_{D2}}$ pigment pairs in Photosystem II. The ensemble method provides the necessary insight into the distribution of charge transfer character along the energy axis. The reference states we introduce help to uncover the individual state contributions. We find that the $\mathrm{Chl_{D1}Pheo_{D1}}$ pair exhibits an almost uniform distribution of charge transfer density over the energy range of the visible spectrum. We identify this pair to be a much more prominent candidate for the initial charge separation than the usually discussed central $\mathrm{P_{D1}P_{D2}}$ pair.

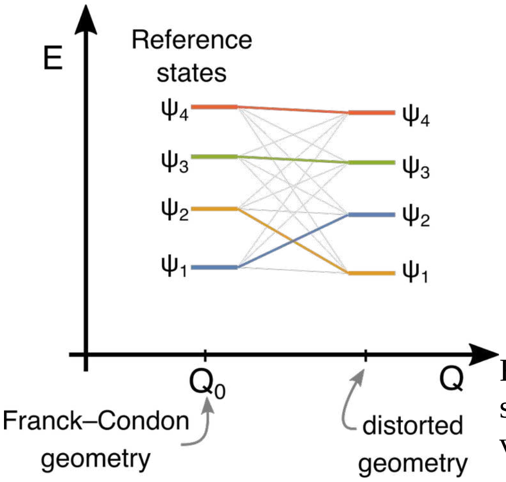

Figure 1: Schematic illustration of maping the reference states onto the electronic states of the distorted geometry via wavefunction overlaps.

Strong Anisotropic Electronic Coupling between Gold Surfaces and Interfacial Water

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Understanding the intrinsic properties of solid/electrolyte interfaces is crucial for comprehending the behavior of catalysts, capacitance, reactivity, and the anomalous behavior of confined water. However, probing electrochemical interfaces buried between electrodes and electrolytes is notoriously challenging. In particular, the intrinsic properties at metal/water interfaces remain unclear. Using ab initio molecular dynamics (AIMD) simulations with a large supercell we find that strong electronic interactions between water molecules and gold metal surfaces govern the structure of water molecules and charge transfer. Specifically, dangling OH groups adjacent to the gold surface exhibit orientation-dependent electronic polarization and charge transfer. These findings hold significant importance for tailoring the electrochemical properties of metal-aqueous interfaces, with broad implications ranging from sensing to electrochemistry.

Automating the implementation of internally-contracted multireference coupled-cluster methods using an Open Source stack

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Coupled-cluster theory is a very common choice for the computation of highly accurate results. Yet, there exists a range of interesting molecular systems (e.g. open-shell systems) for which the standard coupled-cluster methods break down: those with multireference character. In such cases, approximating the wavefunction with a single configuration (as done in Hartree-Fock theory) is no longer viable – not even for qualitative investigations. Instead, a multiconfigurational ansatz has to be used, which is incompatible with standard coupled-cluster theory. Therefore, a generalization to the multireference case is needed.

While there exist different formulations of multireference coupled-cluster (MRCC), only internally-contracted MRCC[1] (icMRCC) shows all characteristics desirable in applications to real-world problems. Although very pleasing from an application's point of view, icMRCC comes with a significant challenge for developers: the resulting equations are orders of magnitudes more complex than the ones encountered in conventional coupled-cluster theories. This makes any attempt at manual implementation futile. Instead, the derivation of working equations and the implementation thereof has to be automated.

We present such an automation framework, realized within the SeQuant[2] ecosystem, which is available as Free and Open Source Software (FOSS). We illustrate important concepts required for the automation, e.g. a tensor network canonicalization algorithm. Finally, we give a perspective on how we think our new framework can improve our existing icMRCC implementations[3] and also how we could provide FOSS variants with minimal maintenance overhead.

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Exploring Photodynamics in Complex Environments through Semi-Empirical Methods

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An interface between SHARC (Surface Hopping including ARbitrary Couplings) [1, 2] and MNDO (Modified Neglect of Diatomic Overlaps) [3, 4] has been implemented with the aim of simulating the photoisomerization of photoswitchable molecules in complex environments. Conventional single-reference methodologies are unsuitable for describing the cis-trans isomerization phenomenon, thereby necessitating the utilization of a multi-reference approach. Multi-reference semi-empirical quantum chemistry methods represent a suitable approach for simulating the photoisomerization of large molecules due to their computational efficiency and scalability. The OM2 (orthogonalized method 2) method, which employs the MRCI (multi-reference configuration interaction) approach, was selected for this purpose. However, even the fastest semi-empirical methods are not capable of treating systems of arbitrary size. For example, it is not feasible to simulate the target molecule solvated in water in a reasonable amount of time. To mitigate this, a hybrid QM/MM (quantum mechanics/ molecular mechanics) approach becomes invaluable [5, 6].

Azo-escitalopram was first synthesized by Cheng et al. and has shown promising results as a photo-switchable SSRI (selective serotonin reuptake inhibitor), a class of drugs used to treat depression and other neuropsychiatric disorders [7]. In order to gain deeper insight into the switching mechanism of azo-escitalopram and how it is influenced by the environment, simulations of this molecule in gas-phase and water have been made. We also plan to investigate the switching behavior of azo-escitalopram in the binding pocket of the serotonin transporter. Photoswitchable compounds represent a promising class of drugs that could allow for spatiotemporal control of drug activity, thus potentially resolving the most pressing issues in pharmacology such as poor drug selectivity, including side effects, emergence of resistance and environmental toxicity. The development of photoswitchable SSRIs could provide a valuable tool for studying the spatial and temporal effects of these drugs in the brain, thereby enhancing our understanding of their mechanism of action and potential therapeutic applications [7].

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Quantum Monte Carlo Algebraic Diagrammatic Construction with Dense-Sparse Partitioning and Importance Ranking

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Quantum Monte Carlo Algebraic Diagrammatic Construction (QMCADC), recently developed as a stochastic extension of second-order ADC schemes for the polarization propagator, has been reformulated to combine deterministic and stochastic processes, dividing the configuration space into dense and sparse subsets. In this approach, dense configurations, including contributions from the sparse set, are propagated deterministically, while projections onto the sparse set are calculated stochastically. Additionally, stochastic projections are screened using importance ranking criteria, reducing the effective variational space to include only significant configurations and thus accelerating convergence. This work demonstrates the efficiency of the proposed method by targeting the excitation energies of the first electronic excited states of some exemplary molecular systems with singlet and triplet spin symmetries. Furthermore, the bias resulting from importance ranking screening and the distinct roles of the parameters introduced in the method are discussed. Our calculations show that integrating deterministic propagation with stochastic projections within the dense-sparse partitioning, enhanced by importance ranking, provides an efficient and versatile framework for solving the ADC Hermitian eigenvalue problem with a significantly reduced memory footprint[1,2,3].

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Real space path integral framework for the spin-phonon problems and the spin-Peierls phase transition

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Heisenberg model is a common approach for treating the interaction of spins on a lattice, typically investigated either using Exact Diagonalisation (ED) or some of the numerous approaches based on the Quantum Monte Carlo (QMC), like the Stochastic Series Expansion (SSE). In the simplest of views, the Heisenberg model assumes that the lattice is stationary and the couplings between the spins constant, which should otherwise depend on the positions of the coupled spins. Problems which go beyond this assumption are referred to as the spin-phonon problems. Models used to tackle these kinds of problems are often simplified, unrealistic and may contain various approximations and numerical issues. Here, a new general framework without sign problem in the real space has been developed, which can be used to formulate methods specific to the problem of interest. The real space part of the framework is based on path integrals in the first quantisation, which can also take Ab Initio potentials. The electronic part can be handled in different ways, depending on the problem, e.g. one can use ED to define a method based on Molecular Dynamics to analyse the motion, or may use SSE to get an efficient QMC sampling of the electronic properties. With path integrals, one can analyse both classical and quantum cases at finite temperatures. One class of spin-phonon problems is the spin-Peierls dimerisation, where the system spontaneously dimerises because the lowering in the electronic energy overcomes the increase in the potential energy. Here, the framework is applied to the dimerisation problem to illustrate the various angles that the rich behaviour of these systems can be observed and analysed from, qualitatively and quantitatively.

Magnetic Fields in Turbomole: One-Component Implementation, Functionalities, and Performance

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Our everyday experiences revolve around weak magnetic fields within the region of microtesla up to decatesla. However, field strengths of up to 100 kilotesla are observed within the vicinity of magnetic white dwarfs – the regime where magnetic and electronic forces are of equal order of magnitude. Therefore, the level of theory requires a general approach beyond perturbative treatment to enable the computation of molecules and their properties from weak magnetic fields to such extreme conditions.

Turbomole's program package already provides a two-component (2c) framework for calculations within magnetic fields. However, a one-component (1c) approach is sufficient in many cases and less expensive. Therefore, the 1c framework has been made available within the dscf module of Turbomole by expanding the existing algorithm to handle complex algebra for Hartree-Fock and DFT calculations. Different functionalities, to allow an interplay between the 1c and 2c methods, have been implemented as well as algorithms to reduce computational costs. The perfomance of the 1c approach has been shown to be faster than the 2c approach. Future work is aimed to provide RECPs in the 1c framework, hence enabling calculations with heavy atoms in magnetic fields.

Towards Accurate Modeling of Thermally Activated Delayed Fluorescence Emitters: Computational Investigations of Cyanoarenes

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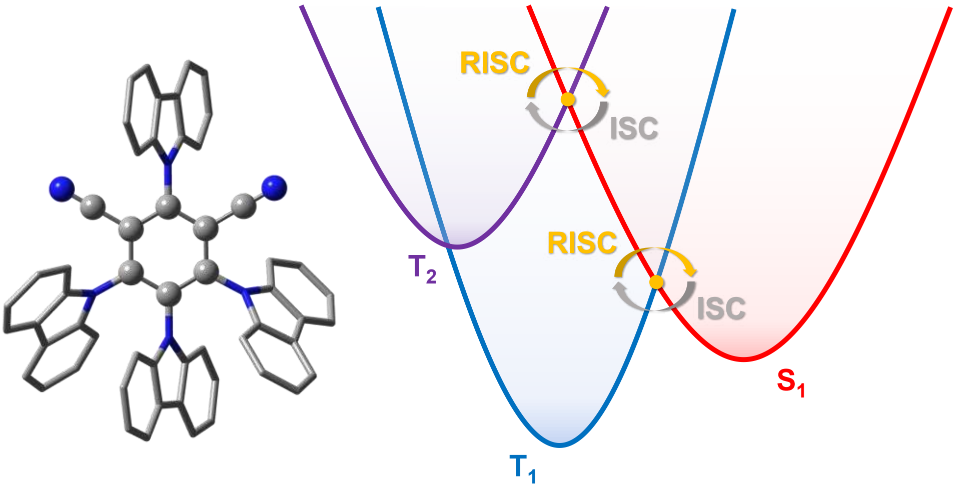
Due to the low efficiency and high cost of many conventional fluorescent and phosphorescent materials, there is increasing interest in emitters based on thermally activated delayed fluorescence (TADF) in the field of organic light-emitting diodes. The underlying mechanism involves a thermally activated reverse intersystem crossing (RISC) process from triplet to singlet states, enabling delayed fluorescence with high quantum yields.[1]



In preliminary work on this topic, we could already show good agreement of computed singlet-triplet gaps with experimental results in a simple TD-DFT framework for 4CzIPN and a halogenated derivative.[2] More recently, however, the role of additional, higher triplet states in this interconversion has become an active topic of discussion, complicating the established approach.[3]

As an initial step to accurately model these processes in donor-acceptor cyanoarenes, e.g. 4CzIPN, we are working on a comprehensive benchmark. Additionally, this work follows up on the new understanding of TADF by using a recently proposed TD-DFT-based methodology to assess RISC rates,[4] for which the minimum energy crossing points between S_1 and the relevant triplet state have to be optimized.[5]

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Aperiodic defects in periodic solids

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Standard computational approaches to modelling of defects in solids rely on periodic supercells. In real solids, however, the distance between defects can be much bigger than is affordable computationally within the supercell model. At the same time, the unphysical mutual proximity and periodic repetition of the defect's images lead to spurious artefacts, especially if the defect is polarized, charged or/and open-shell. To circumvent the problems of the periodic defect model altogether we introduce a "defectless" embedding [1], where a fragment with the defect is embedded in the periodic mean field of the pristine lattice. We demonstrate that this approach is much more physically reliable than the standard periodically repeated defect model and allows for a very fast convergence to the thermodynamic limit.

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On the Performance of DFT/MRCI to describe Excited States of Thermally Activated Delayed Fluorescence Emitters

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We assess the performance of density functional theory (DFT) in conjunction with multireference configuration interaction – DFT/MRCI[1] – to describe the lowest excited states of thermally activated delayed fluorescence (TADF) emitters. We demonstrate that the energy gap ΔE_{ST} between the S_1 and T_1 excited states can be predicted with mean absolute deviations of 0.06 eV in the vertical approximation for emitters of the recently proposed STGABS27 benchmark set.[2]

Vertical emission energies can be computed with average deviations of 0.20 eV, which falls within the experimental uncertainties. Here, solvation effects based on a state-specific polarization field[3] and a perturbative non-equilibrium correction term[4] from an external calculation are required to achieve this accuracy. While this strategy improves emission energies, state-specific equilibrium solvation, and adiabatic conditions at the excited state geometries worsen the agreement for the experimental energy gaps. This is mainly attributed to an imbalanced description of the external solvation treatment with DFT/MRCI. For a broader overview, we compare our results to those obtained with ΔSCF approaches. Here, it is found that the explicit orbital relaxation, available with ΔSCF schemes helps to improve the accuracy even more, compared to relaxation effects included in the CI-type procedure. While we do not obtain the accuracy of ΔSCF approaches for adiabatic gaps, DFT/MRCI can be used in a black-box fashion and serves as an excellent method to estimate the energy gaps from a vertical calculation.

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Investigating protein dynamics of chaperone Hsc70 and Huntington-Disease related $\mathrm{Htt}_{\mathrm{Exon}}1\mathrm{Q}_{\geq 36}$-fibrils

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Even though a lot of progress in understanding and treatment has been made over the past century, neurodegenerative diseases like Alzheimer or Huntington Disease remain a scourge to mankind. We here present a workflow for the investigation of a trimeric protein complex consisting of co-chaperone DNA-JB1, chaperone Hsc70 and the HttExon1[Q>36] which is responsible for the outbreak of the Huntington's disease. [1] The workflow consists of a combination of multiple advanced molecular dynamics sampling methods in order to accurately represent the dynamics of the ATP catalyzed defribrilisation process.

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Efficient Exploitation of Numerical Quadrature in Explicitly Correlated F12 Theory

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Explicitly correlated methods are powerful tools for overcoming the basis set incompleteness error by directly incorporating the electronic cusp behavior into the underlying wavefunction description.[1-4] However, due to the sheer number of terms arising in explicitly correlated theories that cover multiple orbital spaces, the cost of the correction can easily exceed the computational effort of the corresponding correlation method. This is especially true for second-order Møller–Plesset perturbation theory (MP2), where an additional F12 correction is typically several times more expensive. The primary computational bottleneck in this context arises from exchange-type intermediates, despite CABS-RI and density fitting techniques being commonly used to reduce computational costs.

To address this issue, we recently published an alternative method for computing the exchange-type F12 contribution, showcased for the example of the most expensive exchange term in RI-MP2-F12 theory.[5] We introduced a linear scaling atomic orbital-based algorithm that combines numerical quadrature (NQ) with CABS-RI. Additionally, we implemented a robust distance-dependent integral screening scheme based on integral partition bounds, which drastically reduces the number of required three-center-one-electron integrals.[6]

With errors below 1 μE_h and evaluations that are two orders of magnitude faster for chemically relevant systems, our new approach surpasses the standard density fitting/CABS-RI approach in terms of accuracy and efficiency. Furthermore, our NQ/CABS-RI ansatz requires significantly less computation time than the corresponding RI-MP2 calculation. We also demonstrate near-linear scaling through calculations on linear alkanes, achieving an 817-fold acceleration for $C_{80}H_{162}$ and an extrapolated 28,765-fold acceleration for $C_{200}H_{402}$, reducing computational time for the latter from 229 days to just 11.5 minutes. Our approach can also be adapted to the remaining MP2-F12 terms, which will be the focus of future work.

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Combining Molecular Dynamics and Computational Spectroscopy for Systems in Soft Condensed Phases

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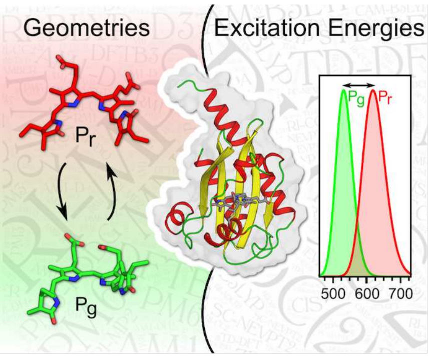
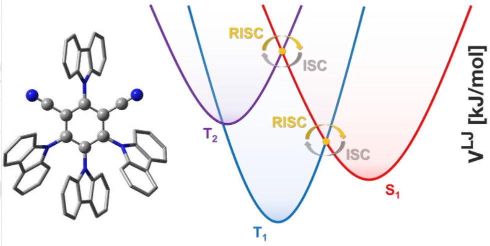
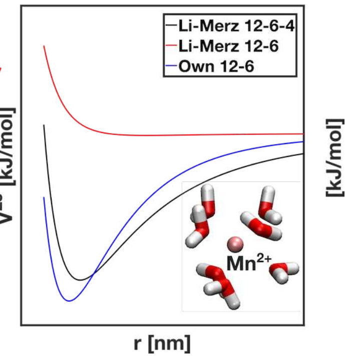
Molecular dynamics is a wide-spread simulation technique, which (i) we have employed to elucidate photochemical and -physical processes based on potentials from electronic structure calculations[1,2] and (ii) can be used to obtain structural insights into biological macromolecules like proteins and DNA using classical force fields. Complementary to this, computational molecular spectroscopy allows to establish structure-property relationships. For example, our calculations aided in assigning chemical shifts and hyperfine couplings to atoms of chromophores inside proteins.[3,4] In our research, we have also combined both in the framework of quantum mechanics/molecular mechanics (QM/MM) simulations to understand the molecular origin of the difference in optical absorption between the photoproduct (Pg) and dark state (Pr) of the photoreceptor protein Slr1393.[5]







In Augsburg, we are, on the one hand, working on unravelling the mechanisms leading to thermally activated delayed fluorescence in donor-acceptor cyanoarenes[6] by employing QM and QM/MM to describe the properties of these molecules in molecular aggregates. On the other hand, we perform simulations of biological macromolecules in solution. For this, we are working on the parameterization of metal ions, e.g. Mn^{2+}, which is a prerequisite for classical MD. This will pave the way towards assessing the influence of salt concentration on the structure of biological macromolecules.

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`ElemCo.jl`: A Julia package for the electronic structure of molecules and solids

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A new Julia package `ElemCo.jl` for the electronic structure of molecular systems is presented. The main focus of the package is on electron-correlation methods, which are essential for the accurate description of the electronic structure. The package is designed to be easy to use and to provide a high level of abstraction to the user. Inputs are Julia script files, which can also be used to define custom methods or access the package's internal functions.

The package provides a wide range of methods, including the closed-shell and open-shell coupled-cluster methods CCSD, CCSD(T), CCSDT, distinguishable-cluster approaches, DCSD and DC-CCSDT,[1, 2] the density matrix renormalization group (DMRG) method, etc. Furthermore, the package includes, e.g., the two-determinant coupled-cluster and frozen-reference coupled-cluster methods,[3, 4] which can be used to calculate excited states, and tensor-decomposed distinguishable-cluster methods,[5] which can be used to calculate ground-state energies of large systems.

The one- and two-electron integrals can either be computed (using the LibCInt library[6]) or read from a file in the FCIDUMP format, including the possibility to read similarity-transformed (transcorrelated)[7] or embedded Hamiltonians.

```
using ElemCo
geometry="N1 0.0 0.0 0.0
          N2 0.0 0.0 2.1"
basis="vdz"
@dfhf
@cc dcsd
```

```
using ElemCo
fcidump="N2.FCIDUMP"
@cc dcsd
```

Figure 1: Example scripts for the calculation of the N_2 molecule using the DCSD method.

The package is open-source and available via the Julia package manager or on GitHub at `github.com/fkfest/ElemCo.jl`. Documentation can be found at `elem.co.il`.

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Tailoring quantum chemistry for vibrational spectroscopy: Vibrational embedding theory

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Vibrational spectroscopies have become crucial for understanding structures and processes in life sciences. Computing vibrational properties accurately, including anharmonicity and nuclear quantum effects, is computationally intensive, even for medium-sized molecules. Fortunately, interpretation of experimental results often requires only a limited part of the spectrum, making multilevel approaches highly desirable. Still, such approaches are rather sparse in the field of vibrational structure theory.[1]

With vibrational embedding theory[2], which we present, a multilevel approach is addressed where a reduced number of vibrational degrees of freedom are embedded in the potential of the remaining environmental modes. This concept can be applied to correlated as well as response subset treatments. The environmental description may be obtained from either a mean-field (VCCinVSCF) or correlated (VCCinVCC) treatment of the environmental degrees of freedom. The latter includes correlation within all subsets but describes their interaction in a mean-field manner.

We apply these multilevel approaches to water wires in bacteriorhodopsin, exploring different partitioning schemes for the embedding approach: In the local partitioning of the vibrations, the modes dominated by motions in the same spatial region are correlated, whereas, in the energy-based partitioning, modes of similar fundamental frequencies are correlated. We compare with full reference calculations, where we obtain better agreement for the local partitioning than for energy-based partitioning.

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A nearly complete treatment of the effect of non-adiabaticity on rovibrational energies of H_3^+

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In this report significant contributions of non-adiabaticity for the rovibrational bound states up to 25000 cm^{-1} and total angular momentum J=0 - 20 of H_3^+ are investigated. A coupled-perturbed full configuration interaction (CP-FCI) treatment is applied to calculate all couplings between electronic states caused by the nuclear motion. These derivative couplings were evaluated up to the second order by means of a perturbation treatment, and include all nuclear Cartesian first and second derivatives of the electronic wavefunctions. In particular, the coupling of special derivatives with respect to r and R in the Jacobi coordinate representation are more significant than thought. The perturbation approach is especially optimal for the treatment of weak non-adiabaticity in case of rovibrational energies in H_3^+, and had not been available before for H_3^+ or other triatomics. Using exclusively Gaussian basis functions for CP-FCI appears to be sufficient, because explicit correlated wavefunctions are already used for all other potential energy contributions.

Our work is an extension of earlier non-adiabatic investigations based on first derivative couplings of electronic states that led to the concept of geometry-dependent effective nuclear masses and which needs only a single potential energy surface for the dynamics. The implementation allows to include all non-adiabatic effects up to the order of $1/\mu^{-2}$, μ being the reduced nuclear mass. Our treatment works for any isotopologue and for the whole PES. By this treatment a further reduction of deviations to experimental data for most rovibrational levels to less than 0.1 cm^{-1} is possible. For the related transition frequencies, 1366 of 1720 known rovibrational transitions in H_3^+ have deviations less than 0.1 cm^{-1} without using any empirically adjustable parameters or optimizing the nuclear mass for a specific transition. For many questionable assignments (deviations > 0.3 cm^{-1}) of observed transitions in H_3^+ a new labeling is proposed [1].

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Structure motifs in interpretable quantum algorithm design

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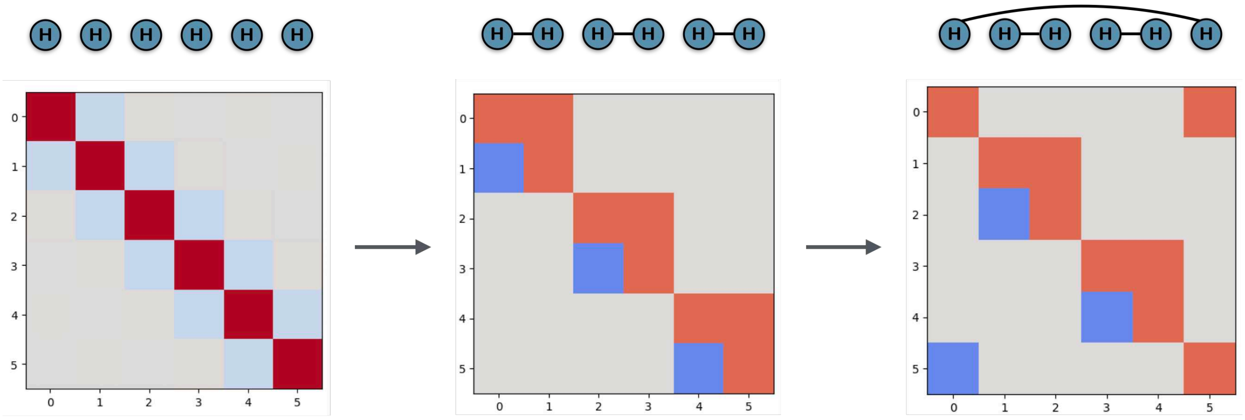

One of the most studied algorithms for modern quantum computers in chemistry applications is the Variational Quantum Eigensolver (VQE). This hybrid quantum-classical algorithm combines state preparation on a quantum computer with optimization on a classical computer to efficiently approximate the ground state energy of a quantum system.

State preparation involves constructing an ansatz, a series of parameterized quantum gates, to represent the system's wave function. A crucial aspect is designing ansätze that are accurate, resource-efficient, and interpretable.

In this context, an important heuristic is the Graph-Based Circuit Design. It encodes the system chemical information in a series of graph structures, where vertices represent atoms and edges represent interactions between them. These structures are inspired by Valence Bond Theory, i.e. each vertex has one edge in order to produce only paired interactions between atoms. Each of these graphs is then translated into parametrized quantum gates of topology: basis change - double excitation - backward basis change.

This heuristic satisfies the three requirements stated before, especially due to local connectivity.

This work introduces a method to analyze the orbital space transformation induced by the basis change process, aiding in the ansatz interpretability. This is given by leveraging the matrix representation of a subspace rotation operator, also called Givens rotation.

In addition, some possible extensions of this ansatz are presented in order to show its flexibility and accuracy. These are obtained using quantum gates which produce more general basis change and electrons double excitations compared to the graph structures.

Introducing Hyperreactor Dynamics for Efficient Reaction Space Exploration

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In recent years, first-principles exploration of chemical reaction space has provided valuable insights into intricate reaction networks. Here, we introduce *ab initio* hyperreactor dynamics, which enables rapid screening of the accessible chemical space from a given set of initial molecules, predicting new synthetic routes that can potentially guide subsequent experimental studies. Inspired by the computational nanoreactor introduced by Martínez and coworkers [1], *ab initio* molecular dynamics simulations of a periodically contracting spherically-confined molecular system are enhanced by different hyperdynamics bias potentials to increase reactivity [2]. Hereby, mild conditions are employed to circumvent the problem of thermal decomposition of products as observed before [3].

The advantages and flexibility of the hyperreactor approach are first showcased on an HCN toy model, where the interplay between the two biasing strategies is investigated and excellent temperature control is achieved. Furthermore, we apply this method to prebiotic systems on the formation of glycinal and acetamide in interstellar ices [4], as well as on an aqueous non-enzymatic DNA nucleoside synthesis [5], and retrieve results in line with recent experimental findings.

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Introducing Regioisomeric Engineering for Multi-Charge and Spin Stabilization in Two-Electron Organic Catholytes - A Combined Theoretical and Experimental Study

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Developing multi-charge and spin stabilization strategies is fundamental to enhancing the lifetime of functional organic materials, particularly for long-term energy storage in multi-redox organic redox flow batteries. Current approaches are limited to incorporating electronic substituents to increase or decrease the overall electron density or bulky substituents to shield reactive sites sterically. [1, 2] To further expand the general molecular toolbox, we introduce regioisomeric engineering as a novel charge and spin stabilization strategy that considers the electronic and steric contributions from all substituents based on their relative placements within a conjugated system.

Density functional theory (DFT) calculations reveal that the strategy operates by redistributing the charge and spin density while also highlighting the critical role of aromaticity in charge stabilization. Moreover, we propose Gimarc's rule of topological charge stabilization (TCS) [3] to be a computationally simple yet insightful tool for qualitatively assessing the relative stabilities of positional regioisomers in near-planar π-systems for future studies targeting optimal battery design. Finally, our computational analysis of potential decomposition pathways challenges current state-of-the-art conformational workflows, indicating issues related to the conformational sampling of large, bulky systems.

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Transcorrelated Embedding for Molecular and Periodic Systems

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We present a transcorrelated embedded fragment model to treat local defects inside molecular and periodic systems. The fragment itself is defined as a set of localized occupied and virtual orbitals corresponding to a Hatree-Fock solution. These orbitals serve as the basis for the in-fragment post-HF treatment. The Jastrow factor for the transcorrelated method is optimized for the full system, which means that some part of the electronic correlation is already incorporated into the effective embedding field of the fragment, which makes our approach a high-level embedding method.

As an application of the embedded fragment approach, we investigate the dissociation of a fluorine atom within fluorinated cyclohexane and within a fluorinated graphane sheet. We use the Distinguishable Coupled Cluster method with doubles and triples as post-HF method. Both systems have substantial amount of dynamic and static correlation, which is typical for real defects. In particular, we investigate and compare the behavior of the dissociation curves in dependency on the fragment sizes between low-level Hatree-Fock embedding and our high-level transcorrelated embedding.

Size Consistency and Transcorrelation

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The transcorrelated method (TC) is applied in the context of strongly multi-reference regimes, in particular for the description of bond breaking in N2. We find modifications to the approach are needed for the stretched geometries, both to the choice of the form of the Jastrow factor J and to the Slater expansion |D0⟩. By using the wave function calculated from a (size-consistent) ab initio post-Hartree-Fock method such as full configuration interaction quantum Monte Carlo (FCIQMC) as |D0⟩ then using the same method on the TC Hamiltonian, we find our calculations to be highly accurate.

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Problem-Specific Semi-Empirical Methods: Evaluating Optimization Algorithms

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Semi-empirical methods like Parameterization Method 6 (PM6) are valued for their efficiency in computational speed compared to ab initio methods such as Density Functional Theory (DFT). Using empirical data from diverse molecules, these methods offer broad applicability but may lack accuracy for particular chemical structure classes and properties. We aim to enhance the accuracy of semi-empirical methods by optimizing their parameters to more closely align with specific molecular properties, with a particular focus on a dataset consisting of dicopper complexes. [1,2]

By using DFT calculations as a reference, we explore different local and global optimization algorithms like the Nelder-Mead method or the Basin Hopping algorithm, which are tested for their efficiency and performance in fine-tuning the semi-empirical parameters.

We also consider that this tailored approach, while significantly improving PM6's performance on targeted properties, may alter its accuracy on other attributes not considered in the parameter adjustment. [3]

This investigation not only advances the understanding of parameter optimization in semi-empirical methods but also contributes to the broader effort of creating training sets for machine learning approaches with optimized semi-empirical parameters.

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Theoretical Investigation of Grignard Addition to Ketones with X-ray Spectroscopy

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The addition of Grignard reagents to ketones is a well-established organic reaction, that is used to create to C-C bond. Nevertheless, a comprehensive understanding of its mechanism and its details is only beginning to emerge. X-ray spectroscopy is a special tool for distinguishing between competing pathways, due to its high selectivity and sensitivity.

We studied the concerted mechanism of the addition of methylmagnesium chloride (CH_3MgCl) to acetone in tetrahydrofuran with X-ray spectroscopy. We have simulated the spectra of different molecules in solution. We employed electronic structure methods to calculate the X-ray absorption spectra at the Mg K- and L_1-edges, and the X-ray photoelectron spectra at the Mg K-edge, for a range of organomagnesium species. These species coexist in solution as a result of the Schlenk equilibrium.

The simulated spectra reveal that individual species can be distinguished throughout the different stages of the reaction. Each species exhibited a distinctive spectral feature that can be used as a characteristic marker in solution. Furthermore, the absorption and photoelectron spectra consistently demonstrated a blue shift as the reaction progressed from reagents to products.

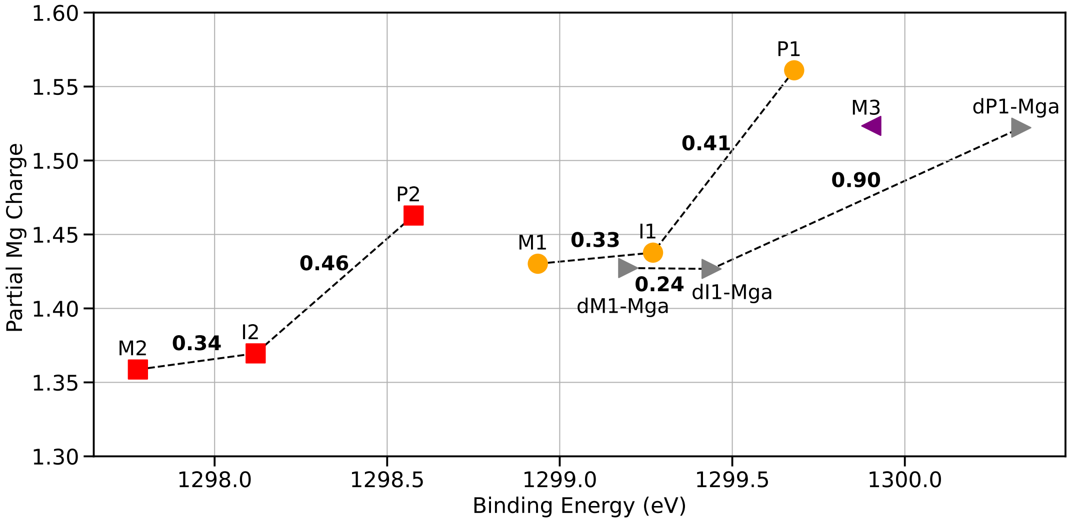

Figure 1. Correlation between the ΔKohn-Sham/B3LYP binding energies (eV) of Mg 1s electron and the local partial charge on magnesium for different species in solution. Dashed lines indicate Δ binding energies reported in bold. M indicates starting structures. I intermediates of reaction, P products, and d indicate dimers.

Investigating the impact of proton irradiation on organic semiconductor PTCDA

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Proton irradiation can damage materials in several ways. High-velocity protons eject atoms from crystals, creating defect sites, breaking chemical bonds, forming blisters, and causing amorphization and embrittlement of the material. [1–3] This study investigates the effects of proton irradiation on the organic semiconductor PTCDA, aiming to understand the underlying mechanisms of damage and degradation. Key questions addressed include: (i) How can different simulation approaches be combined to develop a comprehensive physical model of proton interaction with materials? (ii) What are the key degradation mechanisms of materials exposed to proton radiation? (iii) How can proton mobility in materials be evaluated using simulation tools, and how does it contribute to strain in materials? To answer these questions, we utilized several simulation methods, including molecular dynamics (MD) and ab initio molecular dynamics (AIMD) for analyzing dynamic behavior, density functional theory (DFT) for modeling structure and spectroscopic properties, Stopping and Range of Ions in Matter (SRIM) [4] for examining ion interactions and damage to materials, and the Judgement of Energy DIstribution (JEDI) [5, 6] anaylsis for assessing strain energy induced by impacting protons.

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A New Approach to Study the Bonds in [1.1.1]Propellane with Probability Density Analysis

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The singlet state of [1.1.1]propellane is energetically favored over its triplet state. Various explanations for this phenomenon have emerged over the years. Some argue, based on valence bond theory, that the stabilization originates from a central bond between the bridgehead carbon atoms.[1] Others, using molecular orbital approaches, attribute this effect to π-bonds along the wing bonds rather than a σ-bond.[2]

Using probability density analysis, the electron positions that locally maximize the many-electron probability density $|\Psi|^2$, as well as the exchange paths connecting these maxima, are investigated. Recently, two-center two-electron bonds have been studied and explained by the exchange of two opposite spin electrons.[3] Analyzing the local maxima and exchange paths in singlet and triplet [1.1.1]propellane revealed multiple differences between the two systems. Different electron arrangements that locally maximize $|\Psi|^2$ and different spin correlations for these arrangements are observed in the singlet case compared to the triplet case. Additionally, the exchange paths connecting these maxima differ. In singlet [1.1.1]propellane, highly unusual concerted pairwise electron exchanges involving up to six electrons can be observed, which is not the case for the triplet wave function. Understanding these differences helps explain the origin of the stabilization of the singlet state over the triplet state.

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High-Density Self-Assembly of N-Heterocyclic Carbenes on Au (111)

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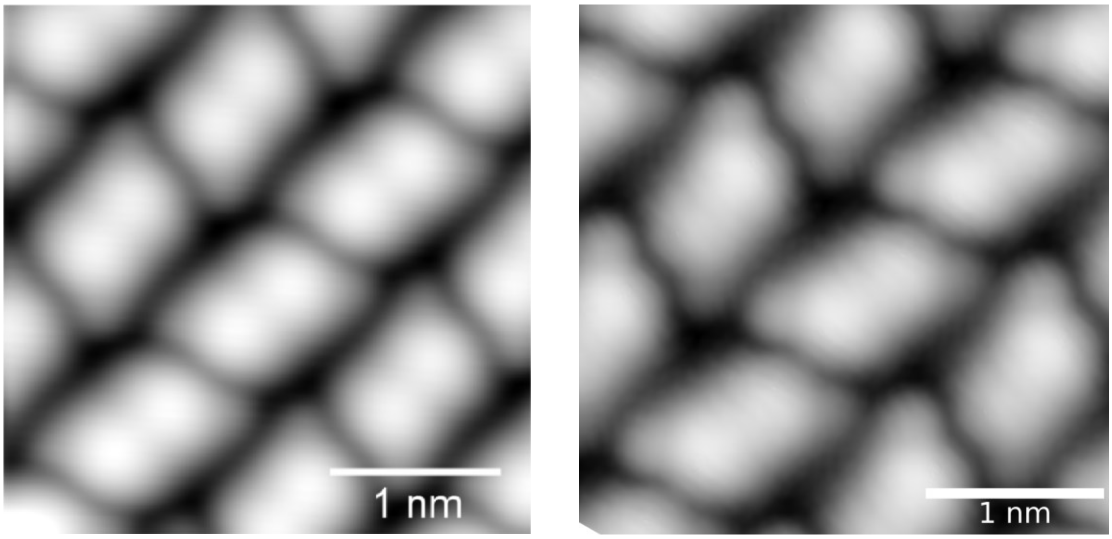
We investigate the structure of self-assembled monolayers (SAMs) of functionalized N-Heterocyclic carbenes (NHCs) on the Au (111) surface by means of density functional theory (DFT) calculations employing periodic boundary conditions. NHC SAMs are promising candidates for the selective functionalization of metal surfaces in applications such as semiconductor manufacturing via area selective atomic layer deposition.
We investigate the monomer adsorption motif of an NHC using PBE+D4 in a slab approach and find good agreement with the known experimental and theoretical observations of adatom bound NHCs on Au (111). [1,2] Systematic screening of possible dimer positions reveals the interplay of attractive dispersive (NHC-NHC) and electronic (adatom-adatom) interactions, contrary to chemical intuition, focusing on steric repulsion. Challenged by experimental observations, we use the obtained dimer configurations in a range of experimentally derived surface cells to understand the long-range order of the SAM. A dimer-stacking motif, represented by a tetramer unit cell packing exhibits a distinctive pattern, reproducing experimental STM results.



Left: Experimental STM picture of NHC on Au(111). Right: Simulated STM picture of dimer stacking using a tetramer unit cell.

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Challenges in the Calculation of the Dielectric Constant of Water in 2D Nanoconfinement using Molecular Dynamics Simulations

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The static dielectric constant is reduced in nanoconfined systems. This phenomenon is observed in various different systems, among the most investigated ones being nanoconfined water: While bulk water has a high dielectric constant (around 80 at ambient conditions), its value decreases to 2 in channels with a height of 1 nm. [1] Experimental measurements of dielectric constants of nanoconfined systems are known to be challenging. Therefore, Molecular Dynamics (MD) simulations are a valuable tool for interpreting experimental results. In order to calculate the dielectric constant, it is required to obtain either the polarization or the total dipole moment of the water molecules for each simulation step. The simulations can either be performed at zero electric field or at zero electric displacement, or at finite values of the electric field/displacement; fluctuations of the polarization are used in the former and the variation of polarization in the latter cases for the computation of the permittivity. [2] Depending on these electrostatic boundary conditions, simulation times between hundreds of picoseconds or even microseconds are cited in the literature in order for the static dielectric properties to converge. [3,4] Hence, careful evaluation of simulation parameters like simulation time, choice of thermostat, water concentration, or the simulation box size is needed. Apart from the required large configuration samplings which especially impose a challenge for quantum mechanical based MD simulations, further problems arise due to various existing definitions of the confined water volume which has a huge influence on the calculated permittivity. [5] The aim of this work is to evaluate the impact of the different parameters on such computations, and to propose an outlook on possible solutions for the stated challenges.

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Hydrogen isotope effects on chemical bonding in Boron cluster complexes

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The concept of chemical bonding stands is central for the discussion of properties and reactivity in chemistry. As chemical bonding is an inherently quantum mechanical effect, analyses naturally focus on the electronic structure of molecules and materials. However, for light nuclei, the quantum nature of the positively charged nucleus can play a significant role. The quantum nature of nuclei influences the chemical bonding properties which is the focus of this study. Hydrogen isotope effects predominantly emerge due to variations in atomic mass when moving from hydrogen (1.0073 u) to deuterium (2.0141 u) to tritium (3.0160 u). Thus, hydrogen isotope substitution leads to a change in the stretch vibrational frequencies (ν (H_2): 4161.2 cm^{-1}, ν (HD): 3632.2 cm^{-1} and ν (D_2): 2993 cm^{-1}) and consequently a change in ZPE [1], which is given as $E(ZPE) = \frac{1}{2} h \nu$. This means that isotope substitution directly impacts the strength of the bonding.

We studied hydrogen isotope effects (HIEs) on molecular geometries and chemical bonding in charge inverted hydrogen bonded (CIHB) and dihydrogen bonded (DHB) systems by substituting hydrogen (H) with deuterium (D) and tritium (T). We applied nuclear electronic orbital-density functional theory (NEO-DFT) [2] to capture nuclear quantum effects and energy decomposition analysis (EDA) methods to analyze the changes in electronic structure due to geometric isotope effects. For all complexes, the intermolecular as well as intramolecular distances gradually decrease with heavier hydrogen isotope substitution. In the case of boron clusters interacting with AlH_3, HF and NH_3 the major stabilizing contributions comes from the electrostatic interaction while in case of carbene it is the orbital contribution. In most of the complexes, isotope substitution enhances the electrostatic as well as orbital contribution but at the same time cause sufficient large increase in the Pauli term which overcompensate the above mentioned two stabilizing contributions resulting in the destabilization of the overall interaction energy. Natural orbital for chemical valence (NOCV) deformation densities show the charge depletion from the partially negative charge hydrogen side towards the vacant orbital on the neighboring molecule in CIHB systems which confirms the formation of CIHB.

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Effect of attosecond electronic coherences on conical-intersection dynamics in core-excited states

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We propose to exploit the novel $\omega - 2\omega$ X-ray attosecond pump-probe capabilities at X-ray free electron laser facilities [1] to explore the influence of electronic coherences on few-femtosecond conical-intersection dynamics of core-excited states in fluoroacetylene (FCCH). X-ray attosecond pulses will be used to excite coherent superpositions of carbon (1s)-excited resonances, and the ensuing dynamics will be probed by attosecond X-ray photoelectron spectroscopy using probe pulses. By preparing coherent superpositions of resonances, the effect of attosecond electronic coherences on conical-intersection dynamics will be studied. By shifting the photon energy of the pump pulse, electronic control over the branching ratios of the electronic relaxation processes will be investigated. Whereas conical-intersection dynamics have been probed over a broad range of time scales, the effects of electronic coherences and electronic coherent control have so far remained elusive. For this purpose, we make use of high-level *ab-initio* calculations together with a full quantum treatment of the non-adiabatic dynamics using the multi-configurational time-dependent Hartree (MCTDH) method [2] . This procedure opens new perspectives in controlling chemical dynamics on electronic time scales.

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Charge transfer mechanisms in singlet fission donor-acceptor complexes

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The spin-allowed photophysical process of singlet fission (SF) in organic materials has the ability to multiply charge carriers by transforming a singlet exciton to two triplet excitons [1]. Materials exhibiting SF are thus potential candidates to surpass the Shockley-Queisser limit and hence enhance the efficiency of solar cells [2,3]. To investigate future applications for energy harvesting, we analyse the charge and energy transfer processes in a model dimer system consisting of a SF active molecule based on two linked diazadiborine chromophore units [4] and a tetracyanoquinodimethane acceptor.

To characterise the charge and energy transfer processes in the donor-acceptor complex, we use a combined approach of ab-initio multireference perturbation theory techniques and quantum dynamics [5]. Specifically, we perform quantum dynamical simulations using a vibronic model Hamiltonian and investigate the charge transfer dynamics from the donor to the acceptor molecule. We analyse the influence of vibronic coupling on the dynamics as well as the competing transfer mechanisms from the initially prepared locally excited state in the donor molecule to the multiexciton or charge transfer states. Furthermore, the influence of particular vibrational modes on the dynamics is discussed.

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Ab Initio Nonadiabatic Dynamics for Photochemical Processes and Simulation of Time-Resolved Observables

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The investigation of photochemical dynamics requires quantum chemical methods that can accurately describe both ground state and electronically excited states, as well as a framework to enable radiative and nonradiative transitions between them. In our work, we employed the complete active space self-consistent field (CASSCF) method together with second-order perturbation theory (CASPT2) or spin-orbit multireference configuration interaction (CASSCF/SO-MRCI), combined with trajectory surface hopping for the inclusion of nonadiabatic effects to accurately simulate photo-isomerisation of *cis*-stilbene and photochemical dissociation of cyclobutanone. As the time-resolved observables, we predict the time-resolved photoelectron spectrum for the former and ultrafast electron diffraction patterns for the latter.

The *cis*-stilbene molecule was studied using the state-averaged extended multistate CASPT2 method. Our simulation reproduces the experimental time-resolved photoelectron spectrum (*cf.* Fig. 1) and identifies an ultrafast ring closure reaction of *cis*-stilbene, apart from the well-known *cis–trans* isomerisation. For the cyclobutanone molecule, which has been studied in the frame of the "Prediction Challenge: Cyclobutanone Photochemistry", the state-averaged CASSCF/MRCI method was employed. By including spin-orbit coupling and modifying the surface hopping equation to allow intersystem crossing, we demonstrate, contrary to the interpretation of some experimental results, a minimal impact of triplet states on the photodynamics of cyclobutanone excited to its 3s Rydberg state. To enable a direct comparison to future experiments, we simulate the gas phase ultrafast electron diffraction patterns (*cf.* Fig. 2).

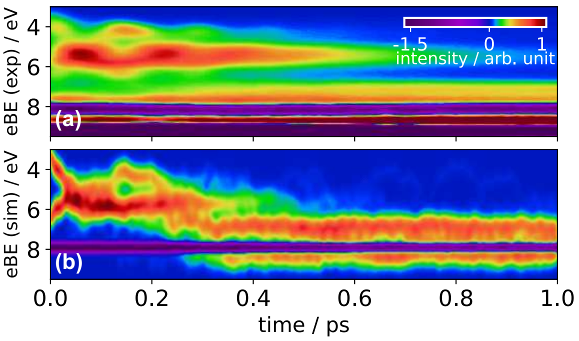

Fig. 1: (a) Experimental and (b) simulated time-resolved photoelectron spectrum of *cis*-stilbene.[1]

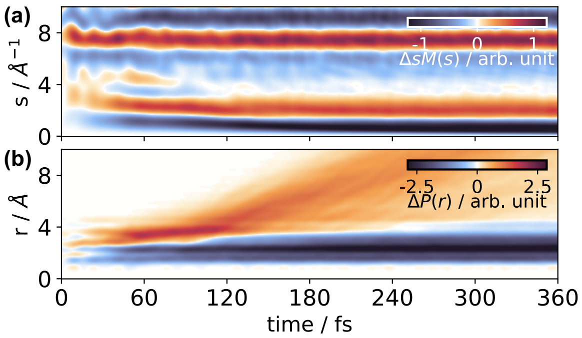

Fig. 2: (a) Ultrafast electron diffraction pattern and (b) difference pair distribution function of cyclobutanone.[2]

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Computing Accurate Enthalpies for the Efficient Modelling and Prediction of High-Entropy Materials

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The computational design of ionic materials such as ceramics relies on accurate enthalpies. While standard electronic structure approaches based on density functional theory can provide quantitatively accurate results for intermetallic compounds, they fail to yield a proper description of the thermodynamics of ionic materials such as oxides as the mean absolute errors for formation enthalpies are on the order of several hundred meV/atom [1]. This hinders the materials design of for instance high-entropy ceramics or lower dimensional systems such as 2D oxides.

To address this pressing issue, we have recently developed the coordination corrected enthalpies (CCE) method based on the number of cation-anion bonds and the cation oxidation states. This correction scheme founded on the bonding topology decreases the prediction errors by almost an order of magnitude down to the room temperature thermal energy scale of ~25 meV/atom for oxides, halides, and nitrides [1,2]. It is also capable of correcting the relative stability of crystal polymorphs. The efficient implementation of this scheme into the AFLOW framework for materials design in the form of the AFLOW-CCE module [3] enables now the correction of enthalpies in large materials databases as well as for the construction of convex hull phase diagrams.

These computational advances are an important enabler for the design of novel high-entropy materials. The reliable computational modelling of such systems can be realized by the partial occupation algorithm [4] by expanding the disordered system into a large set of ordered structures. For the actual design of these compositionally complex disordered high-entropy systems, predictive synthesizability descriptors such as the disordered enthalpy-entropy descriptor (DEED) [5] are crucial prerequisites. It critically relies on the accuracy of the enthalpies of all competing phases within the chemical space of interest as provided by the CCE method.

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Simulation of Open-Shell Organic Molecular Systems for Quantum Applications

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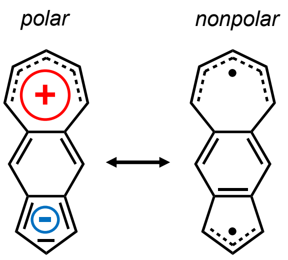
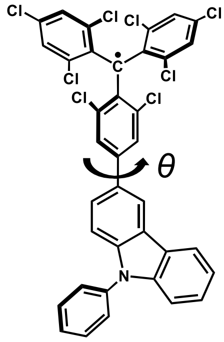
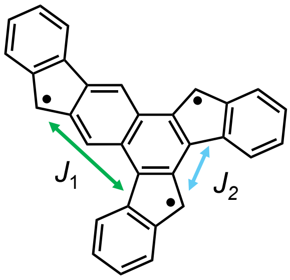
Chemical science offers unique possibilities for the introduction of new quantum devices as it facilitates control over molecular and material properties by structural design. Utilization of organic molecules for quantum applications is a promising approach due to readily available resources, ease of fabrication and structural flexibility. The complex nature of quantum processes and the vast number of possible structures necessitate computer-based simulations to elucidate underlying mechanisms and identify suitable molecular structures. This work involves application of high-level computational methods to study electronic structure and molecular properties of relevant systems as well as machine learning techniques to further augment *ab initio* methods. Undergoing computational investigations comprise the following topics: bistable molecular systems switchable by an external electric field [1], design of efficient luminescent radicals to provide an optical interface for quantum architectures and topological engineering of magnetic properties in molecular graphenoids.



Bistable Molecules



Luminescent Radicals



Topological Engineering

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Towards First-Principles Electron—Phonon Coupling in CISS

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Considering charge transport phenomena, a connection of the electronic spin and the chirality of the conducting medium can be observed. This leads to a preferred spin state of the electron in e. g. molecular conduction of helical molecules, and is known as the chiral induced spin selectivity (CISS) effect [1]. Although the underlying mechanism is not yet fully understood, some experiments show an increase in spin polarization with increasing temperature, indicating a contribution based on molecular vibrations [2, 3]. Their effect on molecular conduction can be e. g. studied via inelastic electron tunneling spectroscopy (IETS), and an approach of Troisi *et al.* [4] in combination with relativistic two-component density functional theory was used to simulate spin-resolved IETS intensities.

Using a carbon-based model helix, helicity-dependent IETS spin polarizations are visible with polarizations up to ten times higher compared to spin polarizations emerging from elastic tunneling, even though at lower transmission intensities. Both inelastic and elastic tunneling spin polarizations show a strong dependency on the imaginary part of the molecular effective single-particle Hamiltonian matrix, which is furthermore strongly influenced by the chosen gold electrodes. First indications of correlations of vibrational properties (like the vibrational frequency or the resulting change in chirality) and spin polarizations could be observed. However, further steps towards more realistic systems and the calculation of a wider range of vibrational frequencies is required for a more profound understanding.

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Analytical nuclear gradients with spin-pure state-averaged HCISCF wave functions

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Abstract

Accurate calculations on chemical systems that possess significant static electron correlation pose a notorious challenge to quantum chemists. The last two decades have witnessed significant efforts to overcome the steep computational cost of the conventional CASSCF approach.[1] This, in turn, has opened up the possibility of performing geometry optimizations with active spaces of unprecedented size.[2] In our previous work, we developed a heat-bath CI[3] algorithm that uses orbital configurations as the building blocks of the wave function (CFG-HCI).[4,5] In the spirit of common SCI approaches, the method bypasses CASSCF's exponential wall by choosing only the important contributions to the wave function. A useful aspect of the CFG-based implementation is spin-adaptation, which provides wave functions without spin contamination and allows the user to target specific spin states without any concerns of ending up with an unintended spin state. This presentation reports an extension of the previously mentioned work. We implemented the calculation of analytical nuclear gradients and the non-adiabatic couplings with state-averaged[6] CFG-HCISCF wave functions. The results presented here demonstrate the performance of the method in geometry optimizations of excited states with active space sizes of around 20 active orbitals. We focus on assessing the method's accuracy in relation to the time required to perform the geometry optimization.

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Simulation of Experimental NMR Signals from Charge Transfer Complexes Using Novel Quantum Chemistry Methods

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Electron donor acceptor (EDA) complexes of photocatalysts or substrates are essential for assembly controlled photocatalysis. As model system for the study, perylene diimide (PDI) and its derivatives, shown in Figure 1, are selected as electron acceptor while triethylamine (TEA) or tetrakis(dimethylamino)ethylene (TDAE) as electron donor. To establish universal and useful links to the experimental observations, both nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) related properties are computed and analyzed systematically involving a variety of approaches. Because experimentally observed chemical shifts in solution are generally a weighted average of all possible conformers during the NMR acquisition time, in theoretical investigations the statistical distribution of these conformers needs to be determined with the help of molecular dynamic simulations. We employ a newer variant of the extended-system adaptive biasing force (eABF) method [1] that enables enhanced sampling and furthermore better prediction of nuclear magnetic resonance shieldings. As an important part, this work aims to explore the solvent influences on the electronic distribution and molecular properties of the EDA complexes with different solvent models, ranging from implicit solvation models to explicit solvation models.

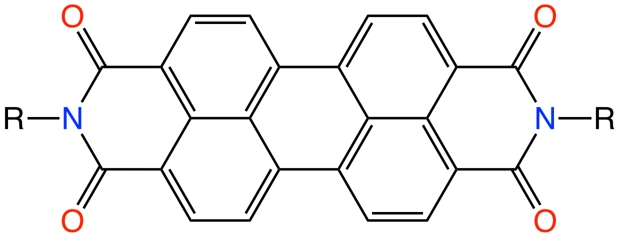

Figure 1: Structure of perylene diimide (PDI) molecule with potential substituents denoted with R

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SIMaL – Building custom Descriptors for Machine Learning Exchange Spin Coupling made easy

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Exchange coupling between unpaired electrons plays a crucial role in determining the magnetic properties of molecules, e.g., dinuclear copper(II) complexes, deciding their usability as molecular magnets in fields such as molecular spintronics or quantum technologies as well as for describing the catalytic reactions of actives sites within certain metalloenzymes [1,2]. Machine learning models based on Gaussian Process Regression have proven capable of predicting the strength of the exchange spin coupling, expressed via the Heisenberg exchange coupling constant J, within small subsets of dinuclear copper complexes [3,4].

Custom, property-tailored descriptors (numerical representations of chemical structures) can outperform off-the-shelf descriptors by capturing the essential correlations between the structure and the desired property in a low-dimensional and easy-to-compute feature vector [4,5]. However, creating custom descriptors can be difficult and time-consuming for datasets that exhibit a high degree of structural diversity, as the process of automatic feature extraction needs to be consistent across different structure types. Additionally, as with the prediction of exchange-spin coupling, the extent of feature-property correlation is different for different structure types (differently bridged complexes, different bridging ligands) with some structure types requiring different descriptors.

In this contribution, we will present the essential features of SIMaL (**S**tructural **I**nformation for **Ma**chine **L**earning) in the context of predicting exchange spin coupling. SIMaL is a python library that aims to streamline the construction of custom, structure-derived descriptors by making the process of feature extraction intuitive, user-friendly and applicable to a wide range of organic and inorganic compounds.

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At the Crossroads of Experiment and Theory: Revealing reaction mechanisms in molecular photodevices

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In the realm of photochemistry, light-sensitive molecular structures, with the ability to undergo reversible changes in structural and electronic properties upon exposure to light, have captivated the scientific community. Among them, photoswitches and -motors stand out as versatile agents, capable of transforming light energy into mechanical motion, which leads to numerous potential applications across a broad spectrum including nanotechnology,[1] catalysis,[2] and drug delivery.[3] The quest for precise control over these light-induced processes necessitates unraveling the complex pathways of excited-state phenomena, however to date, the mechanisms driving their functionality remain partially obscured. The challenging task of elucidating photoreaction mechanisms can rarely be accomplished solely through experiments *or* theory due to the weaknesses inherent in both approaches:

Experimental-spectroscopic studies of photoreaction mechanisms reveal information about electronics and can give hints on the structural changes involved, but owing to the ultrafast nature of light-induced processes and reactions, an experimental atomistic resolution of the structure of electronically excited states is in many cases unfeasible. Quantum chemical calculations have emerged as indispensable tools, yielding structural details at in principle every point of interest. Thus, they offer insights into molecular structure-property relationships, complementing experimental results. On the downside, they are typically limited to investigating the evolution of the system within a few picoseconds.

This results in a dynamic interplay where experiments and theory profoundly enhance each other. Therefore, the spotlight of this work is on how to expediently harness the potential that lies in intertwining computational and spectroscopic methods allowing to elucidate photoreaction mechanisms. Specifically, we showcase example molecules from the compound class of photoswitches[4] and photomotors[5] undergoing light-induced E/Z isomerization and directional rotation, respectively.

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Multi-Level Fragmentation Schemes for Proteins

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The accurate calculation of system properties like energetics, thermochemical and optical properties is a central objective in theoretical and computational chemistry. While these calculations can be achieved for small- to medium-sized molecules using *ab initio* quantum chemistry, supermolecular quantum-chemical calculations for big molecules are not computationally feasible.[1] Energy-based fragmentation methods offer an efficient way to achieve accurate quantum chemical calculations for even large biomolecules like proteins. Many of these schemes exist[1–4], though numeric comparisons are rare. To enable a flexible and simple application of different methods, some of us developed a novel general fragmentation formalism.[2] It incorporates most existing fragmentation expansions and allows for the formulation of novel schemes. It includes single- and multi-level schemes, as well as recently also an electrostatic embedding of the fragments in point charges of the whole system.

The aim of this study is to evaluate the energies of proteins using three fragmentation methods, namely the molecular fractionation with hydrogen caps[2], the pair-pair approximation to the generalized many-body expansion[3] and the molecules-in-molecules approach[4] within the common framework. We find that the molecular fractionation with hydrogen caps is the best compromise between accuracy and computational cost, while methods using electrostatic embedding lead to the most accurate results for all three fragmentation schemes.

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Assessment of local hybrid functionals with and without range-separation for organic dye-sensitized TiO_2 interfaces

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Reliable density functional theory (DFT) methods for the electronic structure at organic-semiconductor interfaces are crucial for the prediction of charge injection efficiencies in organic dye-sensitized solar cells (DSSCs). The main characteristic of metal-free organic sensitizers is their highly conjugated donor-π-acceptor (D-π-A) structure resulting in strong charge-transfer excited states.

We assess flexible hybrid functionals with special emphasis on local hybrids with and without additional range-separation for DSSC model systems. The central element of local hybrids is a local mixing function (LMF), which is introduced to control the amount of exact exchange at each point in space. The underlying idea of range-separation can be combined with local hybrids in different ways. In hybrids with local range-separation (LRS) the normally constant range-separation parameter ω is replaced by a density-dependent range-separation function.[1] The local mixing of short- and long-range exchange by an LMF leads to a range-separated local hybrid (RSLH).[2]

In this work, absorption spectra of free dyes and dyes adsorbed on a sizeable $(TiO_2)_{38}$ cluster were calculated with different exchange-correlation hybrid functionals. We highlight the importance to allow excitations from all occupied orbitals, instead of only the highest, to avoid artificial blue shifts and lower oscillator strengths. Energy level alignments for the ground- and excited state confirm previous findings of the reversed level alignment in the excited state with the CAM-B3LYP functional.[3] Comparison of the linear response time-dependent DFT (TDDFT) with the Tamm-Dancoff approximation (TDA) deliver comparable spectra and level alignments. Moreover, we calculate the fundamental band gap of various TiO_2 cluster sizes, using G_0W_0 calculations as a reference. Our results indicate that the band gap of the TiO_2 cluster is significantly larger than the anatase TiO_2 bulk gap of 3.2 eV and increases with decreasing cluster size. In conclusion, range-separated functionals perform well for D-A dyes and band gaps of TiO_2 clusters but show unphysical level alignment at the TDDFT level.

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Jumping between Layers - Vacancy Dynamics in Ceria Nanoparticles for CO2 and Beyond

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The recent increase in global greenhouse gas emissions and their impact on global warming necessitates the development of innovative solutions for greenhouse gas reduction.[1,2] Our poster focuses on the advancements of ceria-based catalysts for the electrochemical CO2 reduction into long-term stable products, beyond conventional short-term solutions such as fuels and solvents, to achieve effective and lasting Carbon Capture, Conversion, and Storage (CCCS). We demonstrate the potentials of ceria particles for the use in CCCS methods for CO2 reduction reactions (CO2RR). Although metal oxide materials are well studied the general theory on oxygen transport and vacancy dynamics on surfaces is still widely unexplored. Our work aims to provide deeper insights into the behavior of vacancies to address the critical questions of when, why, and how vacancy patterns form on surfaces. By utilizing kinetic Monte-Carlo simulations and nudged elastic band calculations in a large scale, we investigate the dynamics of vacancies on ceria surfaces over 50 hours of real-time to assess their potential in CO2RR for CO and post-CO products. The obtained data from our simulations are used for machine training to study general descriptors for vacancy dynamics in metal-oxides.

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Machine Learning Angular Overlap Model Parameters

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The Angular Overlap Model (AOM) is a conceptual framework within Ligand Field Theory (LFT), enhancing our understanding of the directional characteristics of metal-ligand interactions.[1,2] The AOM takes into consideration the degree of orbital overlap and hence the strength of these interactions. Originally, LFT was developed to analyze experimental electronic spectra, helping to correlate *d*-orbital splitting energies with observed transition energies. With the advent of the *ab initio* ligand field theory (aiLFT) module as implemented in the ORCA software package, a more detailed analysis is possible.[3,4] This module allows the fitting of an *ab initio* complete active space self-consistent field (CASSCF) wavefunction to the one- and two-electron ligand field matrices, the one-electron matrix of which is used for the AOM parameterization.[5,6]

However, a significant challenge in this parameterization is that, for most coordination compounds, the number of AOM parameters that need fitting exceeds the number of independent variables in the one-electron ligand field matrix. This results in an underdetermined system where the parameterization is not unique. Machine learning techniques can be employed to establish a relationship between local metal-ligand features and the AOM parameters. This approach promises to overcome the underdetermined fitting procedure, with another advantage being its applicability to various coordination geometries as it predominantly relies on metal-ligand-focused features. Once trained, the model can predict AOM parameters based solely on structural information, without requiring explicit high-level calculations beforehand.

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Graph Neural Network Models for Predicting the Yields of Cross-Coupling Reactions

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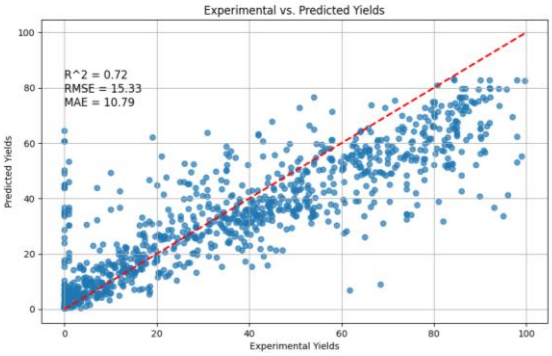
Abstract

Cross-coupling reactions constitute an important class of reactions in synthetic organic chemistry. However, the efficiency and cost of catalysts/reagents often represent critical impediments to the commercialization of these reactions. The conventional approach to catalyst discovery, based on empirical methods, makes the process both time-consuming and expensive. Henceforth, given the urgent need for developing more sustainable and economical methodologies, the integration of machine learning with advanced computational power has notably accelerated advancements in predictive modeling for organic reactions. This study explores the application of Graph Neural Networks (GNNs) for predicting the yield of transition metal-catalyzed cross-coupling reactions. We investigated several GNN architectures, including Graph Attention Networks (GATs), Graph Convolutional Networks (GCNs), Graph Isomorphism Networks (GINs), and GraphSAGE, to predict chemical reaction yields through graph-based representations of molecular structures. The dataset consists of 4825 diverse cross-coupling reactions, catalyzed by various transition metals like Mn, Fe, Co, Cu, Zn, Pd etc. This dataset was pre-processed and encoded using molecular descriptors from RDKit. For standardized input encoding, the chemical data was represented in SMILES format. The features were then scaled and transformed into graph structures using k-nearest neighbors (KNN). Each model was trained and evaluated to assess its predictive performance. The GraphSAGE architecture achieved the highest predictive accuracy among the tested models, with an R^2 value of 0.72 on the test set, outperforming other GNN models. This work demonstrates the effectiveness of GNNs, in predicting reaction yields of organic reactions which could thereby reduce the dependency on traditional experimental methods, offering a more efficient and reliable tool for reaction optimization.



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Determining the stability of nucleophile–CO_2 adducts

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CO_2 – being an inexpensive and inexhaustible carbon source – is a promising building block in organic synthesis [1] whose full potential has not yet been uncovered. C–H functionalization with CO_2 is a particularly interesting synthetic transformation in this context due its high step and atom economy. Different approaches for base-mediated carboxylation reactions under mild conditions have been presented in the last years [2,3]: After deprotonation of a carbon-centered nucleophile, the addition of CO_2 to the generated carbanion is performed under mild conditions. However, the thermodynamics of CO_2 often do not favor the formation of an adduct.
We present a data-driven approach based on multivariate linear regression for predicting the carbon dioxide affinity, which is defined as the thermodynamic stability of carboxylation adducts with carbanions. The three-parameter model takes quantum chemical descriptors based on electronic (two) as well as steric (one) properties as input. A validation set of nucleophiles not present in the training procedure has been designed. An automated prediction workflow sets the reaction up and a prefiltering is performed. Nucleophiles passing are subjected to calculations and the CO_2 affinities are predicted by the model. The best eight predictions in terms of highest adduct stability are currently under experimental validation by the group of Matthew S. Sigman at the University of Utah.

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Molecular Design of Azoles: From QSAR to QSPR

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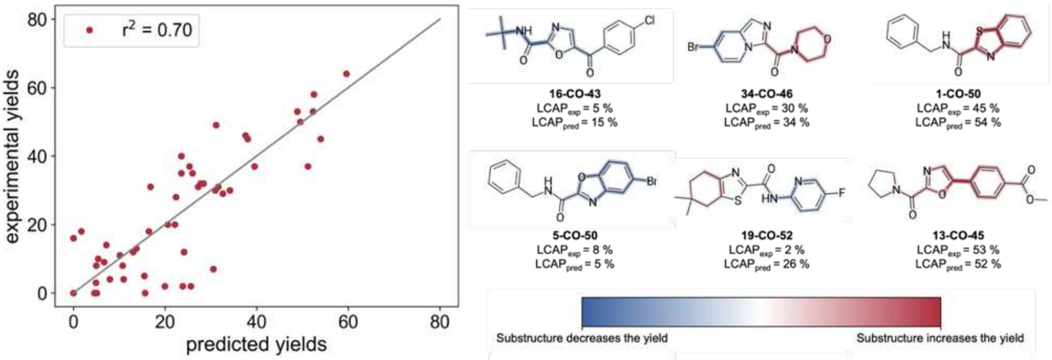
Carbon dioxide (CO_2) is a non-exhaustive waste product that can be transformed into functional building blocks for value-added chemicals or drugs [1] such as C2-carboxylated 1,3-azoles. Since only a fraction of the millions of available 1,3-azoles are carboxylated in C2-position, this leaves great potential for new research in this field by exploring the synthetic accessibility of those compounds and their applications as phar-maceuticals, cosmetics, and pesticides.[2]
Regarding synthetic accessibility, reaction yields are valuable experimental quantities. For a recent data set on amide-coupled azoles, we used supervised machine learning to build an interpretable quantitative structure–property relationship (QSPR) model to predict yields.



Experimental versus predicted yields of amide-coupled C2-carboxylated 1,3-azoles (left) and the results of the developed heat-mapping algorithm (right).

To explain the model's predictions and be able to use it as a tool for molecular design, a heat-mapping algorithm was created, which takes the feature importance of fingerprint bits as an input and visualizes the influence of the molecular substructures on the target values (here, the yield). This visualization can then be used by synthetic chemists to design molecules with desired reaction outcomes. In this way, we hope to contribute to expanding the chemical space of C2-carboxylated 1,3-azoles and therefore to the discovery of new drugs.
We performed a pharmacophore-based target prediction to give a perspective for C2-carboxylated 1,3-azoles in drug design.[2] This revealed, among others, the ATP-sensitive inward rectifier potassium channel 1 and Kinesin-like protein KIF18A as new, potential targets for these compounds. In the pursuit of identifying active molecules, the heat-mapping algorithm mentioned above can be a helpful tool for enhancing molecular design with QSAR models.

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Breit-Pauli Model Configuration Interaction Methodology for Relativistic Effects in Excitonic Molecular Aggregates

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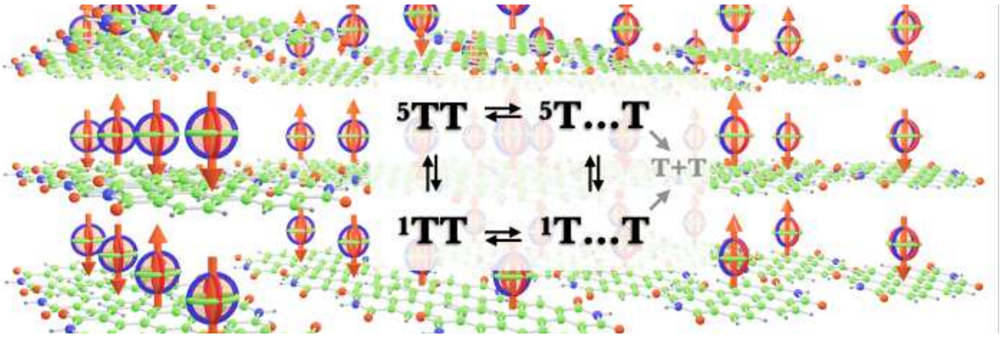
Relativistic effects are often neglected in photophysical processes of molecular aggregates. One such process, Singlet Fission[1], involves a singlet exciton generating two triplet excitons in a spin-allowed manner, forming a singlet-correlated triplet-state pair (^{1}TT). While the generation of the ^{1}TT state is well-studied, its subsequent evolution while retaining the correlation has often been overlooked. Recent experiments suggest the involvement of quintet states[2], necessitating the inclusion of relativistic effects like spin-orbit coupling (SOC) and spin-spin coupling (SSC) to accurately describe these interactions.

We have developed a model configuration interaction (CI) approach incorporating relativistic couplings from the Breit-Pauli Hamiltonian to study these effects in excitonic molecular aggregates. Using a generalized Michl-Model[1], we only consider the frontier orbitals (FO) of each fragment. Symbolic algebra and Jordan Wigner mapping generate diabatic states within this FO basis[3], which are then coupled to form a diabatic Hamiltonian. This Hamiltonian allows the selection of electronic states and multiplicities of interest.

To apply this model to real molecular fragments, we calculate the HOMO and LUMO of each fragment, evaluate Breit-Pauli-relativistic and non-relativistic integrals and construct the diabatic Hamiltonian for the aggregates. This method provides insights into the evolution of the ^{1}TT state and enables the construction of various states of interest, such as ^{1}TT, ^{5}TT, ^{5}T…T, ^{1}T…T, and T+T. Such interaction descriptions require studying at least a trimer system to include non-neighboring spin sites like ^{1}T…T.



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Hydroxide mobility in aqueous systems: Combining *ab initio* accuracy with millisecond timescales

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Based on the *ab initio* Molecular Dynamics method, an adapted combined Molecular Dynamics/Lattice Monte Carlo (cMD/LMC) approach, which models hydroxide ion transfer on significantly larger timescales and extended systems, was developed and employed. The algorithm was applied to a series of aqueous potassium hydroxide systems with different concentrations, reaching from 3 wt. % to 61 wt. %. The derived diffusion coefficients of the hydroxide ions were compared with those from first-principle molecular dynamics simulations. The cMD/LMC bridges the gap between highly detailed but computationally costly *ab initio* Molecular Dynamics simulations and more extensive but less detailed classical Molecular Dynamics simulations, combining their respective advantages and thus allowing for simulations of aqueous KOH solutions spanning timescales from nanoseconds to milliseconds and involving several thousand atoms, all with relatively low computational cost. With this approach, the dynamics of hydroxide ions in various complex systems can be characterized in greater detail. For instance, it can be used to study layered double hydroxides and anion exchange membranes, which constitute a critical component in fuel cells.

Predicting Thermodynamic Corrections via Machine Learning Hessians based on GFN2-xTB derived Features

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A machine learning (ML) model for predicting Hessian matrices based on GFN2-xTB derived features is proposed. This approach opens the possibility for a more cost-efficient routine to compute Hessians compared to the semi-numerical approach. Thus, quantities such as thermodynamic corrections of larger structures or for structures in high-throughput screening techniques may become more accessible.

For the ML model, the cartesian Hessian is decomposed in atom-pairwise block matrices. This allows for an ML model independent of the size of the molecule. The features are derived from a GFN2-xTB[1] single point calculation. They depend on the energy, density and geometric information of the involved atoms. The rotational variance of the Hessian is addressed by a rotation scheme to yield an invariant representation.

The approach is tested with different ML models on a variety of data sets.

The models are then benchmarked on the performance of predicting thermodynamic quantities, i.e. the Gibbs energy, enthalpy and entropy which are derived from the Hessian via a quasi-Rigid-Rotor-Harmonic-Oscillator[2] approach. A precision of the thermodynamic quantities within chemical accuracy (1 kcal/mol deviation) compared to the parent GFN2-xTB method can be achieved for the QM7[3,4] data set.

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Local Wave-Function Embedding: Correlation Regions in PNO-LCCSD(T)-F12 Calculations

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Modern explicitly correlated local coupled cluster methods using pair natural orbitals [PNO-LCCSD(T)-F12] allow to carry out accurate calculations of molecular energies for large molecules (up to 200 - 300 atoms).[1-4] However, despite formally asymptotic linear scaling and efficient parallelization, the required computational resources (CPU, memory, disk) for molecules with more than 100 atoms can be rather large. Many chemical reactions affect only a small number of bonds, leaving the largest part of the chemical and geometrical structure of the molecules unchanged. In this work we extended the previously proposed region method[5] to PNO-LCCSD(T)-F12. Using this method, we investigate whether accurate reaction energies for larger systems can be obtained by correlating only the electrons in a region of localized molecular orbitals close to the reaction center. The remainder is either treated at lower level (e.g., PNO-LMP2-F12) or left uncorrelated (Hartree-Fock frozen core). It is demonstrated that indeed the computed reaction energies converge rather quickly with the size of the correlation regions towards the results of the full calculations. Typically, 2-3 bonds from the reacting atoms need to be included to reproduce the full result to within ±0.2 kcal/mol. The approach may fail, however, if long-range intramolecular dispersion effects significantly affect the reaction energies, or if the geometrical structure of the molecules changes strongly. We also computed spin-state energy differences in transition metal complexes, where only a small region around the metal is correlated. This also works well and can in large complexes reduce the computation time by up to 2 orders of magnitude.

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A density functional benchmark for shielding anisotropies and the role of the density functional in the calculation of residual chemical shielding anisotropies in structural elucidation of natural compounds

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Nuclear magnetic resonance spectroscopy is an important tool for structural elucidation. About a decade ago, the investigation of residual chemical shielding anisotropies (RCSAs) induced by the application of alignment media proved valuable for determining the absolute configuration of small molecules in solution.[1] However, the method relies on the quantum chemical determination of the shielding tensors within the target compounds, and due to its unrivaled cost/performance ratio to date, studies in this field have typically employed density functional theory in the reformulation of Kohn and Sham. The KS-DFT is based on the approximation of the non-classical contributions to the electron energy by means of a so-called density functional approximation (DFA), for which a large number of different functionals have been proposed. However, in most applications, the famous B3LYP functional has been used, for which more accurate or cost efficient alternatives may exists considering various benchmarks in the field of magnetic resonance properties and shielding data in particular.[2,3] Moreover, a systematic investigation of the performance of DFAs for anisotropic shielding data and other tensor metrics, such as the tensor shapes and orientations, has not been performed.

We here present a comprehensive benchmark of carbon shielding anisotropies based on coupled cluster reference tensors taken from the NS372 benchmark data set. Furthermore, we investigate the representation of the shielding tensors by the DFAs by means of the reproduction of relevant tensor properties, such as the eigenvalues and eigenvectors. Finally, we study the influence of various DFAs in the determination of the relative configuration in a set of natural products with different scaffolds and functional groups on the basis of their predicted carbon shielding tensors, i.e. we investigate the role of the tensor description by the tested functionals in the configurational assignment on the basis of RCSAs.

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Active Learning for Chemical Space Exploration

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Machine learning models have been successfully developed for various applications, including different matters in chemistry. [1] While in many cases the efficiency of these models makes them more favorable than classical computational chemistry methods, their usage has a major constraint: the need for sufficient training data. This poses a serious limitation in contexts where labeled data is scarce or expensive to obtain. To overcome this issue, machine learning models can be trained with active participation. An active learning algorithm actively decides which training instance needs to be labeled next for the machine learning model to obtain the highest knowledge gain. [2] This process accelerates the convergence of model performance and therefore allows the use of less training data. A key performance factor of active learning is the criterion by which the next training instance to be labeled is chosen. Numerous different selection strategies are known. Selecting an active learning algorithm with superior convergence of model performance for a given dataset requires time for research, analysis and implementation. To bypass that obstacle, we present **regAL** (**A**ctive **L**earning for **reg**ression) [3], a Python package enabling active learning in various flavors and in a black-box fashion for arbitrary datasets.

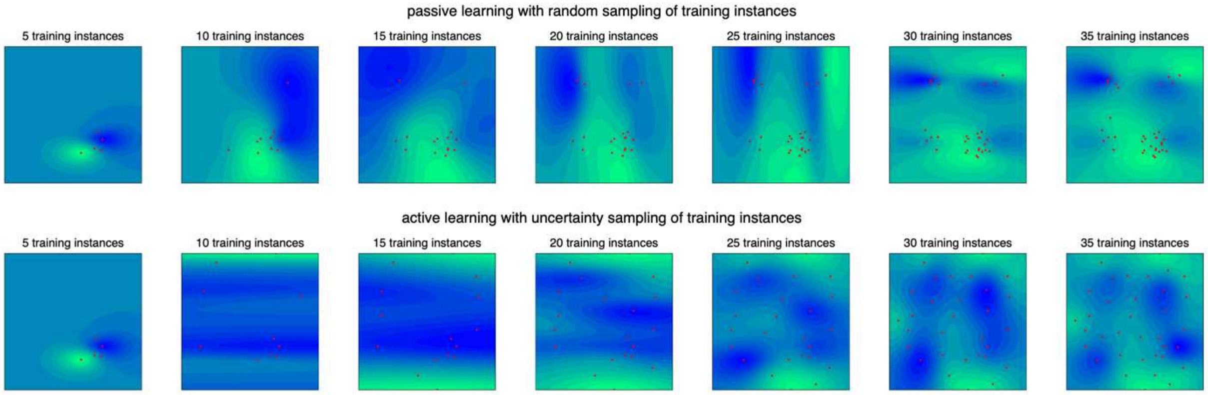

Fig.1. Performance comparison of active learning (uncertainty sampling method) and passive learning (random sampling method) on the Himmelblau function space.

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Computational Modeling of the Chemical Modifications in RNA

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RNA molecules are synthesized in cells primarily as polymers composed of four basic nucleotide residues: adenosine (A), uridine (U), cytidine (C), and guanosine (G). These residues can be further modified naturally by cellular enzymes, with the number of identified natural modifications continuously increasing. Additionally, researchers introduce numerous artificial chemical modifications for experimental purposes. Both natural and artificial chemical modifications can significantly impact RNA's structural integrity and its interactions within the cellular environment. Understanding these modifications is essential for understanding the molecular mechanisms of gene regulation, the mechanisms of various diseases including cancer and neurodegenerative disorders, and designing experiments involving RNA molecules.

We developed the MODOMICS database [1], which provides comprehensive information on RNA modifications, including both natural and synthetic residues identified in RNA structures. We also introduced the ModeRNA modeling method for the comparative modeling of RNA structures incorporating natural modifications.

Our current work focuses on developing a comprehensive computational modeling method that encompasses all possible chemical modifications of RNA molecules. This includes naturally occurring biological modifications and artificial modifications introduced by researchers for experimental purposes. Natural and artificially modified nucleotides are different from normal (A/U/G/C) nucleotides either in the sugar-phosphate backbone or nitrogenous base. We have developed a prototype of a new method, ModeRNA+, which facilitates the modeling of substitutions of any backbone or base moieties with corresponding chemical counterparts. Our ModeRNA+ program involves converting nucleotides in an RNA structure from one form to another. The process performs precise nucleotide mutations while preserving the parent overall RNA structure specially the backbone stereochemistry. This ModeRNA+ takes input and target sequences to guide the conversion process. In parallel, we are developing new knowledge-based statistical potentials for our SimRNA[2] method, incorporating quantum chemical calculations to estimate interactions mediated by modified nucleotides. This approach will enhance the computational folding simulations of RNA molecules with modified residues.

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Accurate and Efficient Computation of Nuclear Magnetic Resonance Chemical Shieldings within the Random Phase Approximation

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The development of quantum chemical methods for the accurate and efficient computation of nuclear magnetic resonance (NMR) shieldings is an important task to aid structure determination of chemical compounds. A suitable approach combining both accuracy and computational efficiency is the direct random phase approximation (RPA), which provides NMR shieldings comparable to coupled cluster singles and doubles (CCSD) in accuracy [1], while having a much lower computational cost.

Within the resolution-of-the-identity (RI) approximation, RPA – a fifth rung density functional method without any empirical parameters – has a formal scaling of $\mathrm{O}(M^4)$ [2] with the system size M, rendering it one of the formally lowest scaling correlation methods. In addition we have introduced asymptotically linear-scaling RPA implementations for the computation of ground-state energies [3-5].

Here, we present an efficient method for the computation of NMR shieldings within RPA, based on our recently introduced RI-RPA-NMR method in the atomic-orbital space [6]. Utilizing Cholesky-decomposed density matrices and an attenuated Coulomb RI metric, the introduced sparsity is efficiently exploited through sparse matrix algebra [7]. This allows for an efficient and low-scaling computation of RPA NMR shielding tensors. Additionally, by implementing a memory-efficient batching method [8] for computing memory-intensive intermediates, we can extend the applicability of the method to even larger systems such as a DNA strand with 260 atoms and 3408 atomic orbital basis functions. This allows for the efficient computation of NMR shieldings with CCSD accuracy for extended systems. The introduced analytical RPA NMR shieldings are expected to be a viable alternative for the accurate and efficient investigation of NMR chemical shieldings.

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Spin-Orbit Couplings for Linear-Response Density Functional Theory implying Periodic Boundary Conditions

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One major problem in fighting climate change is the production of a sufficient amount of energy while remaining at competitive cost without emitting CO_2 or other greenhouse gases. Therefore, more efficient ways to produce electricity using green technology are needed. One approach to increase the efficiency of solar panels is by introducing singlet fission materials into a single-junction to generate multiple low energy excitons from a single excitation, thus increasing the useable part of the electromagnetic spectrum.[1] To aid this development with quantum chemical calculations, efficient methods for calculating spin-orbit coupling and intersystem crossing within the condensed phase are needed.

We present an implementation of perturbational spin-orbit couplings for all-electron computations within the restricted closed-shell time-dependent density functional theory (TDDFT) module of the CP2K program package.[2-4] The perturbative ansatz enables the construction of both singlet and triplet contributions relying on an ”auxiliary” set of many-electron wavefunctions.[5] Our code within the TDDFT module is based on and checked against the related module for X-ray absorption spectroscopy.[6] The reported method utilizes the already established TDDFT implementation of CP2K together with the quasi-relatistic ”Zeroth Order Regular Approximation” (ZORA) Hamiltonian [7,8] or spin-orbit corrected pseudopotentials.[9]

The implementation was validated using benchmark of small molecules with overall mean error of 1.0 to 13.6 cm^{-1} compaired to density functional theory multi-reference configuration interaction results.[10] Computational timings are presented for a bithmuth-containing metal-organic framework.[11]

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Combining Classical MD and Coarse-Grained MC Simulations to Study Large Biomolecules

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An inverse coarse-graining protocol is presented for generating and validating atomistic structures of large (bio-) molecules from conformations obtained via a coarse-grained sampling method. Specifically, the protocol is implemented and tested based on the (coarse-grained) PRIME20 protein model, and the resulting all-atom conformations are simulated using conventional biomolecular force fields. Using this approach we combine good sampling from coarse-grained Stochastic Approximation Monte Carlo method and all-atom accuracy with explicit solvation from force-field Molecular Dynamics simulations. [1]

Additionally, we present a calibration scheme to determine the conversion factors from a coarse-grained stochastic approximation Monte Carlo approach using the PRIME20 peptide interaction model to atomistic force-field interaction energies. We provide a physical energy scale for both the backbone hydrogen bonding interactions and the sidechain interactions by correlating the dimensionless energy descriptors of the PRIME20 model with the energies averaged over molecular dynamics simulations. The conversion factor for these interactions turns out to be around 2kJ/mol for the backbone interactions, and zero for the sidechain interactions. [2]

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Two-photon absorptions from the Bethe-Salpeter equation

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Two-photon absorption strengths could be calculated with time-dependent density functional theory and Coupled-Cluster methods. In the beginning of the year, we published the *GW*-Bethe-Salpeter equation (*GW*-BSE) for non-linear light-matter interactions. With the implementation of this into the Turbomole program package, we can calculate two-photon absorptions and the first hyperpolarizabilities. Benchmark calculations on small molecular systems reveal that this approach is accurate for predicting both. Using *GW*-BSE with Kohn-Sham references as a starting point, the accuracy exceeds that of time-dependent density functional theory and CC2.

Gaussian Process Regression for ^{195}Pt Chemical Shift Prediction

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Platinum complexes are highly relevant in many areas of physical and medicinal chemistry, with applications in catalysis, pharmaceutics and usage in light emitting devices. While ^{195}Pt-NMR is an important tool in the elucidation of their structures and the determination of reaction mechanisms, the remarkably wide chemical shift range of more than 13000 ppm can render measurements tedious and thus establishing a correlation between structures and NMR signals challenging. Effectively narrowing down the shift range with suitable calculation or prediction methods can therefore assisst in the experimental measurement procedure.
Since quantum chemical methods can be quite expensive due to the need for relativistic corrections for magnetic shielding calculations of heavy nuclei, resorting to the use of machine-learning (ML) based prediction methods can be advisable. Especially for lighter nuclei such as ^{1}H and ^{13}C, ML methods have been proven to be useful for the accurate prediction of chemical shifts, but the ML assisted prediction of ^{195}Pt chemical shifts is less well studied.
In this work, we build on a previously proposed protocol by *Ondar et al.* [1] that was based on semiempirically calculated structures and properties. Using Gaussian Process Regression (GPR) and a dataset of 298 platinum complexes with experimental chemical shift values we explore different descriptors that are either exclusively based on atomic properties like the electronegativity and polarizability, the 3D structure, or a combination thereof. We find that, even without including structural information, the chemical shifts can be predicted with a mean absolute error of around 200 ppm. It is further shown that the most accurate predictions are obtained using the SOAP descriptor (*Smooth Overlap of Atomic Positions*) [2] as molecular representation that is easily accessible with established libraries. Moreover, the use of GPR enables a reliabe uncertainty quantification of each prediction and therefore can assist in specifying a shift range to be measured for a given Pt complex.

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The Berry curvature in finite magnetic fields and its relevance in rovibrational spectroscopy

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Rovibrational spectroscopy is a useful and well-established method for the characterization of molecules. It can be used to obtain structural data of the system and is, for example, of use in astrochemistry to identify molecules in the vicinity of interstellar objects. Certain celestial bodies such as White Dwarfs possess incredibly strong magnetic fields that are several orders of magnitude larger than fields that can be generated in experimental setups on earth. Thus theoretical calculations of these spectra are of great interest, not only to validate spectra obtained in laboratories but also to aid in the investigation of molecules in astrochemical applications.

The presence of both external and internal magnetic fields can give rise to additional interactions, one of which are Lorentz forces acting on moving charged particles in the system, namely electrons and atomic nuclei. Different wavefunction and density-based quantum chemical methods have already been adapted to describe the interaction of the electrons and the magnetic field. When studying the motion of the atomic nuclei, as it is the case in rovibrational spectroscopy, Lorentz forces acting on nuclei are modified by the presence of the electrons that screen the magnetic field experienced by the nuclei. This so-called Berry force can give a significant qualitative contribution in these cases and is calculated from the Berry curvature tensor.

We present an efficient implementation of the Berry curvature based on Hartree-Fock and density functional theory. The analytical calculation of the Berry curvature involves the solutions of the coupled perturbed Hartree-Fock or Kohn-Sham equations.[1] These equations have been implemented in a two-component framework for finite magnetic fields and within the exact two-component (X2C) theory for relativistic calculations involving spin-orbit coupling. The Berry curvature was calculated to investigate its effect on rovibrational spectra using the harmonic approximation and molecular dynamics simulations.[2] Additionally, the Berry tensor can be utilized to calculate atomic partial charges.[3] The screened Lorentz forces acting on the nuclei give an effective charge of each nucleus that would result in the same force in the absence of any screening. These so-called Berry charges show a close relation to population analyses based on the atomic polar tensor (APT). As the APT is also needed in the calculation of intensities in vibrational spectra this relation already suggests the high importance of the Berry curvature in this context.

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Compensation States Approach in the Hybrid Diabatization Scheme

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The diabatization of reactive systems for more than just a couple of states is a very demanding problem and generally requires advanced diabatization techniques. Especially for dissociative processes, the drastic changes in the adiabatic wave functions often would require large diabatic state bases, which quickly become impractical.

Recently, we addressed this problem by the compensation states approach developed in the context of our hybrid diabatization scheme. This scheme utilizes wave function as well as energy data in combination with a diabatic potential model. In regions where the initial diabatic state basis becomes insufficient for an appropriate representation of the adiabatic states, new model states are generated. The new model states compensate for the state space not spanned by the initial diabatic basis. Such a compensation state is obtained by projecting the initial diabatic state space out of the adiabatic wave function. This yields a very efficient basis representation of the electronic Hamiltonian.

The present work presents two new aspects. First, it is shown how other operators like the spin–orbit operator in the framework of the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) can be evaluated in this compact model state space without losing the correct wave function information and accuracy. Second, the extension of the approach to multidimensional potential energy surface models is presented for methyl iodide including the C–I dissociation coordinate and the angular H_3C–I bending coordinates. [1]

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The Limits of the Landau-Zener Surface Hopping Algorithm

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Ab initio molecular dynamics in the excited state requires solving the equations of motion on multiple potential energy hypersurfaces simultaneously. A fully quantum mechanical solution for the coupled motion of atoms and nuclei is possible only for the smallest molecules, and therefore, semi-classical approaches based on the concept of hopping between states are most commonly used in practice. This work focuses on an algorithm based on the Landau-Zener theory, which can describe transitions between two states using only the knowledge of the energies of these states. The limits of applicability of this pragmatic approach are not well known, and it is unclear how to proceed, for example, when crossing more than two states. This work tries to identify and describe the limits of applicability of this method and the behavior near the crossing of multiple states, and to develop stable procedures for simulations of this type. The approaches are studied on suitably designed low-dimensional model potentials in comparison with the exact solution where difficulties are expected.

Developing a full dimensional 2 state diabatic PES for CH_3F^+ using artificial neural networks

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Understanding the unique behavior of CH_3F^+ in the series of methyl halide cations and their photo detachment spectra from a quantum dynamics perspective, requires a potential energy surface (PES), which describes the vibronic coupling effects accurately. Thus, a 9 dimensional 2 state vibronic coupling PES model for the CH_3F^+ was constructed utilizing an optimized coordinate system and complete nuclear permutation inversion (CNPI) invariant artificial neural networks. [1–3] Because neural networks require a large amount of data, we used an algorithm to generate evenly distributed directions in the 9 dimensional space. Along these directions a large number of ab initio data was generated using MRCI/avtz calculations including points up to around 4 eV above the Franck-Condon point. Faulty data points were filtered out by blockdiabatization and linear fitting of wavefunction norm and diabatic matrix elements. The current model uses a combination of two multilayer feed forward neural networks seperating the training for diabatic diagonal and coupling elements. The model represents the ab initio data with a root mean square error below 150 cm^{-1}. In the future, a geometry dependent spin-orbit coupling model will be added.

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Quantum Chemical Estimation of the Electrophilicity of Carbon Dioxide

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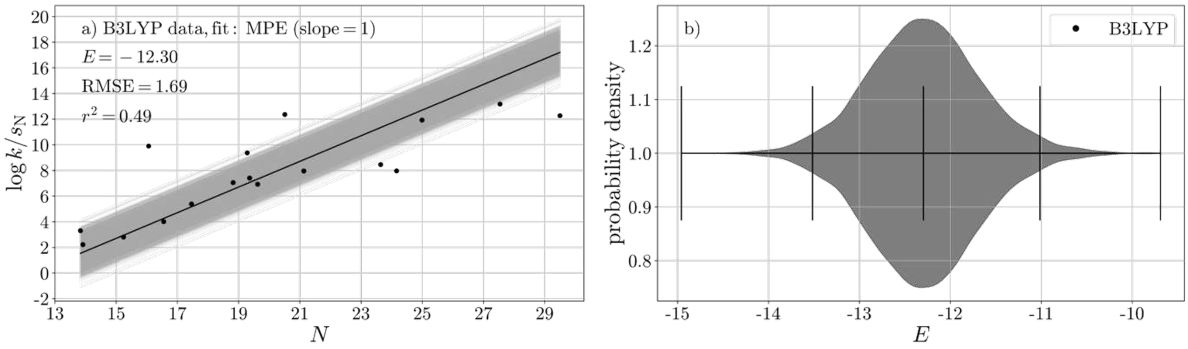
Carbon dioxide is an abundant carbon source that can be used as C1 building block in organic synthesis. To predict reaction outcomes and to identify suitable reaction partners for the creation of value-added chemicals and drugs, it is of great interest to know the reactivity of CO_2. Recent studies suggest two distinct values for Mayr's electrophilicity parameter E of CO_2 (experiment, $E = –16.3$; B3LYP, $E = –11.4$) [1], showing a discrepancy of up to five orders of magnitude for bimolecular rate constants of carboxylation reactions. To enable rate constant predictions for carboxylation reactions, this discrepancy needs to be resolved.

By means of quantum chemical calculations including transition state searches we determined the rate constants for carboxylation reactions of carbanions. To ensure the reliability of our results, different electronic-structure methods (based on B3LYP, DLPNO-B2PLYP and DLPNO-CCSD(T)) were benchmarked against experimental rate constants of similar reactions with CS_2.

Our final protocol is based on B3LYP-D3(BJ)/def2-TZVPD/SMD(DMSO)//B3LYP-D3(BJ)/def2-SVPD. Including uncertainty quantification, we were able to narrow down the electrophilicity of carbon dioxide to $–13.5 < E(CO_2) < –11.0$, reducing the aforementioned discrepancy from five to two orders of magnitude.



a) Calibration of E against $\log k$ values obtained from B3LYP calculations for 17 reactions of carbanions with CO_2 in DMSO with respect to the Mayr–Patz equation. b) Corresponding bootstrapped distribution of $E(CO_2)$.

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Accurate treatment of hyperfine coupling in the diabatic potential model of HI

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The accurate treatment of relativistic couplings like spin-orbit (SO) coupling into diabatic potential models is an important but very difficult task. To this end, the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) approach has been developed over the past years.[1] The central idea of ERCAR is the representation of the system's operators in an asymptotic diabatic basis consisting of direct products of atomic and fragment states. This allows to treat relativistic coupling operators like SO coupling analytically within the atomic basis states. This idea is extended to the incorporation of hyperfine coupling into the diabatic potential model.

Hyperfine coupling is due to the magnetic dipole and the contact interaction as well as the electric quadrupole interaction. The corresponding operators can be expressed in the angular moment operators $\hat{I}$ for nuclear spin and $\hat{J}$ for total angular momentum of the atomic fine structure states. The magnetic dipole and contact interactions both are proportional to $\hat{I} \cdot \hat{J}$ while the electric quadrupole operator is more complicated. The diabatic basis of an existing ERCAR model can be complemented by nuclear spinors and the hyperfine coupling operators are easily evaluated in that basis. Diagonalization of the resulting full diabatic ERCAR model yields the hyperfine structure energies and states for any molecular geometry of interest.

The new method is demonstrated using an existing accurate diabatic potential model for hydrogen iodide (HI)[2] to see the effects of hyperfine coupling. As a proof of principle study, the hyperfine coupling effect of the $^2P_{3/2}$ ground state and spin-orbit excited $^2P_{1/2}$ state of Iodine combined with the $^2S_{1/2}$ ground state of hydrogen are added to the ERCAR Hamiltonian and the effect of hyperfine coupling is investigated. Since both atoms have a non-vanishing nuclear spin, the hyperfine coupling needs to be treated in analogy to the multi-atom variant of the ERCAR approach.[3]

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Poster P169

Tuning Photochemistry in Diarylethenes Macrocycles

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Diarylethene (DAE) photoswitches hold significant potential for applications in materials science and biology due to their ability to undergo a reversible light-induced ring-closing/opening reaction.[1] This study investigates the effect of embedding them into a cyclic topology on their absorption properties in a series of synthesized DAE macrocycles (see Fig. 1).

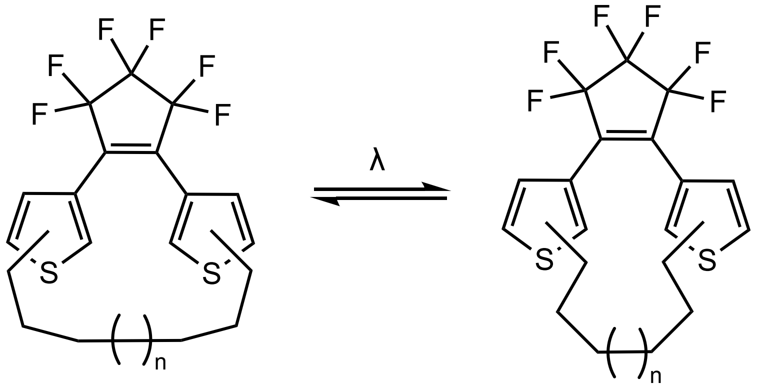

Figure 1: Photoswitching DAE macrocycles between their open to closed forms.

The photocyclization of the DAE generates the corresponding ring-closed isomer, which experiences some geometric perturbation due to the presence of the linker. By extending the linker, this perturbation can be adjusted, thus providing a means to control the DAEs' photophysical properties. The influence of the linker is clearly reflected in the absorption maxima of the closed form.

The absorption properties of the closed form were calculated and compared with experimentally determined spectra.

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Understanding binding modes of dinitrogen in dinuclear transition metal complexes with respect to reactivity and properties

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Dinitrogen is difficult to reduce, as it is thermodynamically stable and kinetically inert. Nevertheless, Nature and the Haber–Bosch process can split dinitrogen and produce ammonia using transition-metal based catalysts. Even though dinitrogen is poor σ-donor and π-acceptor, transition metal complexes can bind dinitrogen and further activate it for N–X functionalization (X = C, Si, B, O), *i.e.* going beyond ammonia as the target product. Several different binding modes have been reported in mono- and di-nuclear transition metal complexes, including linear end-on, bent end-on, and diamond coordination modes (Fig 1).

This work theoretically characterizes dinuclear transition metal complexes reported by Sita and coworkers with a detailed electronic structure analysis. The complexes are stabilized by a highly tunable cyclopentadienyl-amidinate (Cp-Am) ligand environment. Herein, we investigate the isomerization pathway of several dinuclear Tantalum complexes from a linear to a diamond core in isostructural ligand sets.[1-3] Our results suggest that unlike observed for other transition metal complexes capable of dinitrogen splitting, terminal nitrido complexes formed within the Cp-Am ligand framework are thermodynamically unstable. We will present an electronic structure rationale for this finding and present insights on the further reactivity towards nitrogen functionalization products.

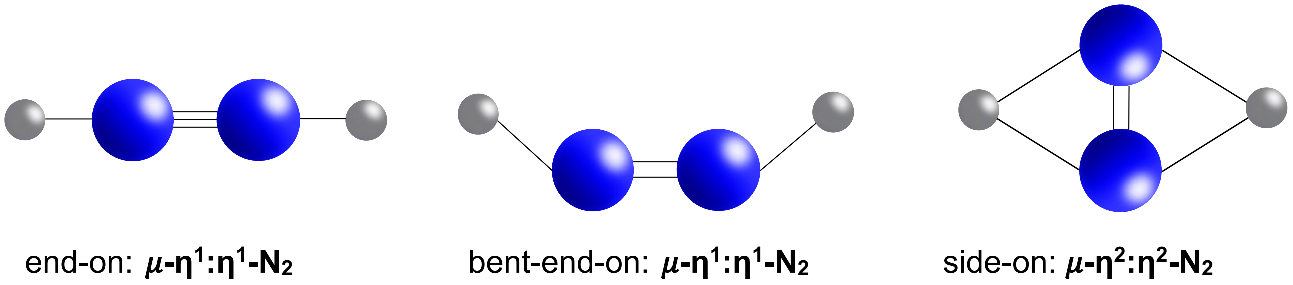

Fig 1: Selected coordination modes of dinitrogen in dinuclear transition metal complexes.

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Designing a Genetic Algorithm for Highly Compressed Spin-Adapted Wave Functions of Poly Nuclear Transition Metal Clusters

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Within the Configuration Interaction (CI) framework, advanced techniques exist for constructing spin-adapted wave functions and efficiently evaluating Hamiltonian matrix elements in that basis. Exemplary are the unitary group approach [1] and its graphical extension [2,3]. By construction, the spin-adapted basis functions are eigenfunctions of the cumulative partial spin operators. This property creates an important dependence of the structure of the CI Hamiltonian matrix and its eigenvectors on the orbital/site ordering when they are expressed in such spin-adapted bases. Crucially, some orbital/site orderings lead to extremely sparse matrices, with a unique (quasi) block-diagonal structure, and highly compact corresponding eigenvectors, [4,5,6,7] advantageous for approximate CI eigen solvers, such as Full-CI Quantum Monte Carlo (FCIQMC). FCIQMC optimizes the wave function through a stochastic sampling of the Hamiltonian matrix elements designed to mimic the imaginary-time Schrödinger equation. [8] The stochastic sampling of sparse Hamiltonian matrices, and the representation by stochastic particles (walkers) of compact wave functions, greatly reduces stochastic errors and the time to reach the minimum. The permutation space of the orbital/site orderings grows factorially; and, although symmetry considerations may reduce the size of the problem, [9] an exhaustive search of near-optimal orderings remain impractical.

In this work, we apply a genetic algorithm (GA) to identify near-optimal orbital orderings, leading to highly compact wave functions. Various metrics are compared as fitness functions, namely the energy or the weight of the dominant configuration, or the approximated estimate of the L4 norms. The successful metric will be chosen on the basis of its performance on small and exactly solvable problems. The predictive power of the GA strategy will be demonstrated on model poly nuclear transition metal clusters including Fe_8S_7, the P-cluster, and the FeMoCo cluster.

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Stochastic Perturbation Theory for Strongly Correlated Spin Systems

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The study of strongly correlated systems featuring many unpaired electrons, such as polynuclear transition metal clusters at the core of metalloproteins (e.g., FeS clusters in nitrogenases and $CaMn_3O_4$ cluster in photosystem II), is an important and challenging task in quantum chemistry. Accurate predictions of their electronic structures often require multireference methods, which are generally very expensive due to the exponential scaling of the electronic wave function with the number of correlated electrons and orbitals in the active space. Recently, this problem has been tackled with some success by Li Manni's Quantum Anamorphosis strategy. [1]

Yet, dynamic correlation effects beyond the active space are to be accounted for. Attempts in this direction have been made by combining large active space wave functions (Stochastic-CAS or DMRG-CAS) with multiconfiguration pair-density functional theory (MCPDFT). [2]

In this work we present a stochastic variant of SplitGAS, [3] a perturbation theory strategy based on Löwdin partitioning technique,[4] that could be efficiently coupled to large active space reference wave functions. Electronic configurations responsible for strong static correlation are kept in the principal space (P), while a much larger space of configurations responsible for dynamic correlation effects are listed in the perturber space (Q). Löwdin's working equations are carried out stochastically. This approach has been implemented both in Slater Determinant and GUGA spin-adapted bases, and differences will be discussed in this work.
Numerical applications are to prove the validity of the strategy.

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Computational Investigation of Plasmon-Induced Reactions

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Plasmon-induced chemical reactions on metal nanoparticles involve complex mechanisms, and unraveling this complexity is crucial for developing efficient and selective catalysts. This study delves into these complexities by computationally investigating plasmon-driven process, exemplified by protonation of 4-mercaptopyridine (4-MPY) on silver nanoparticles.[1] We extend our computational methodologies as established in several recent joint spectroscopic-theoretical studies in the frame of plasmonic-molecular hybrid systems, which aimed to assess structure-property relationships mainly within the context of the so-called chemical effect.[2-4] Our investigation covers the influence of molecular binding modes and molecule-molecule interactions on the thermodynamics and kinetics of these reactions, as well as on charge transfer processes.[5] We identified various potential reaction pathways and assessed their energy barriers as well as analyzed the impact of different molecular orientations and proton sources. In contrast to previous studies, we also explored near-field electromagnetic effects using a hybrid quantum/classical approach, examining the potential of near-field enhancement to alter reaction thermodynamics. Furthermore, we calculated 600 low-lying dipole-allowed excited states using the TDDFT method and meticulously analyzed these in terms of characteristics using charge-density differences (CDDs). We conducted an analysis of all charge-transfer excited states within the 532 to 632 nm range across various molecular binding modes, with and without dispersive interactions. This research sheds light on the protonation mechanisms on silver surfaces, emphasizing the critical role of molecular-surface and molecule-molecule-surface orientations in plasmon-induced reactions.

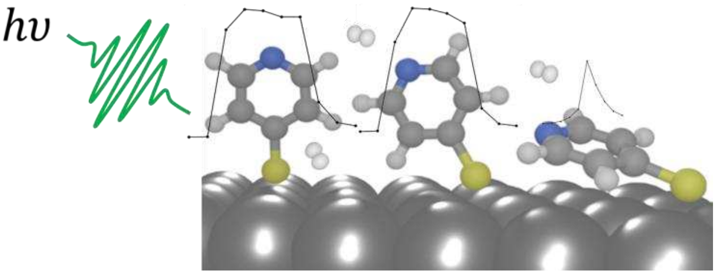

Figure 1. Schematic protonation pathways of different molecular binding modes.

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Finding suitable reaction partners for CO_2 by machine-learning the acidity of nucleophiles

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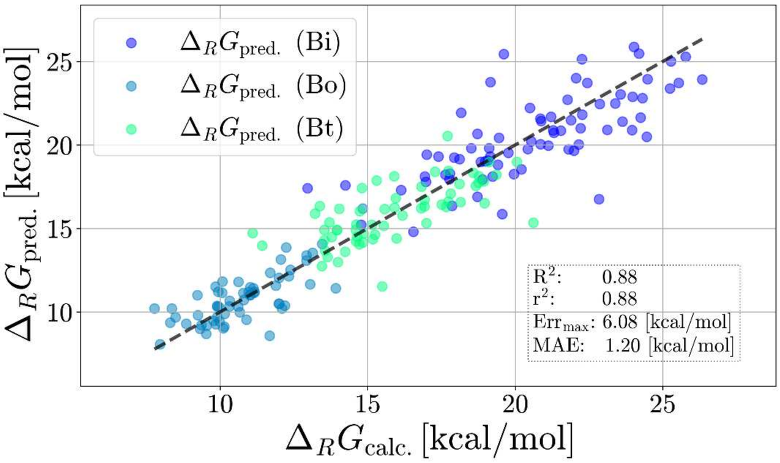
An increasingly popular and green path towards utilizing CO_2 is base-mediated C–H carboxylation. The first step of the underlying reaction sequence requires deprotonation of a nucleophile's reactive C–H site. The lower the acidity of this site, the more efficient the subsequent carboxylation step. 1,3-azoles are promising nucleophiles in this regard due to their high potential for pharmaceutical applications. [1]

This study explores the application of machine learning (ML) techniques to predict the acidity of 1,3-benzoazoles. For this purpose, a dataset of Gibbs reaction energies for 195 substituted 1,3-benzoazoles was established, enabling the training of ML models for accurate predictions. Various combinations of ML model and descriptor were evaluated, identifying Bayesian linear regression and RDKit descriptors as best-performing and well-interpretable setting.

This work highlights the potential of ML to reduce the computational cost associated with electronic-structure calculations while providing insights into the underlying structure–property relationship.



Predicted versus DFT-calculated Gibbs reaction energies for benzimidazoles (Bi), benzoxazoles (Bo), and benzothiazoles (Bt). The lower the Gibbs energy, the higher the acidity.

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Mechanophore activation in deformed polymer systems

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In mechanochemistry, forces are used to initiate chemical reactions. This approach can be used in the production of mechanochromic materials, which change their colour when a threshold stretching force is applied. In the case of polymers, for example, a molecular subunit, the so-called mechanophore, is embedded in the polymer backbone. Upon application of stretching forces, the mechanophore changes its structure, e.g. via bond-rupture or cis-/trans-isomerization, which can be accompanied by colour changes. The mechanophore activity can be tuned by using different polymer types as well as switching from entangled linear chains to a polymer network due to higher force transduction.[1]

In our work, we focus on spiropyran-doped polymethyl methacyrate (PMMA) polymers, where uniaxial deformations can induce a bond break into the mechanophores and spiropyran (SP) will be turned to its activated merocyanine (MC) form. We developed a multiscale simulation model and studied several bulk properties of PMMA doped with SP. By applying deformation along different directions, we were able to separately investigate the stress-strain behaviour under specific types of stress such as tensile and shear stress and their influence on mechanophore activation. We also observed enhanced mechanophore activity with increasing temperature.[2] Currently, we are working on establishing a hybrid all-atom/coarse-grained model to take our simulations up to a larger scale and enhance their comparability to experiments. We will compare mechanophore activation rates with mechanically induced polymer degradation. In particular, the role of defects will be investigated. Regarding crystalline materials the crack propagation due to elongation is already widely studied and it has been shown that the stress is especially concentrated near the crack tip.[3,4] We will take advantage of this phenomenon in order to tune the mechanophore activity in this region. Another objective is to restore the activated MC to its deactivated SP form by applying pressure to the stretched polymer system after tension. This so-called baromechanical cycle for repeated activation of SP and deactivation of MC by alternating mechanical stretching and hydrostatic compression has already been shown in the gas phase.[5] We will try to transfer it to our SP-doped polymer systems by subsequently performing alternating deformation and compression simulations.

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DFT- and Machine Learning-Supported Catalyst Design for the Ring-Opening Polymerization of Lactide

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Since the limited fossil resources to produce conventional plastics and the accompanying environmental pollution of non-recyclable plastics increased the awareness of the people regarding this topic, research highly focused on sustainable plastics such as polylactide (PLA).[1] As the catalyst for the industrial ring-opening catalyst is the toxic tin(II) 2-ethylhexanoate, the need for more active and less toxic alternatives emerged in the past years.[2] Herein, zinc-guanidine complexes showed promising potential due to their non-toxicity as well as their functionality as single site catalysts in the ring-opening polymerization (ROP) of lactide.[3]

With the help of computational studies, the design of novel highly active catalysts for this purpose is facilitated: Activation energy calculations are carried out using density functional theory (DFT) methods.[4] These give insights about the influence of the ligand design towards the catalyst activity. Although this approach is resource-intensive, it can be feasible if the applied method is chosen carefully and in accordance with various experimental data. This leads to a faster prediction of the activity as only a few stationary points of the mechanism may be sufficient. However, calculations of predictive quality involve conformational sampling and high-level electronic structure theory calculations and, thus, still come at a relatively high computational demand. To circumvent this issue, the existing collection of known zinc-guanidine systems is examined using Machine Learning (ML) approaches with the aid of multiple GFN2-xTB-based features[5] to train and compare various ML models and quickly determine the activity of new catalysts. In addition, the importance of the features leading to efficient catalyst design is analyzed.

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Second-order Møller–Plesset perturbation theory with pair natural orbitals for periodic systems

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To this day, the toolset for describing electron correlation in periodic systems remains DFT-centred. Despite its low cost and strengths, DFT lacks systematic improvability and is known to have difficulties with noncovalent interactions such as dispersion. Periodic methods are still largely missing the tremendous advancements that molecular quantum chemistry has experienced in the past two decades to reduce the steep polynomial scaling encountered in second-order Møller–Plesset perturbation theory (MP2) and coupled-cluster methods.

The Turbomole package is uniquely placed to address this. A periodic LCAO Hartree-Fock method is already available within the *riper* module [1], providing the necessary infrastructure for computing crystal orbital coefficients in terms of Bloch atomic orbitals for a set of *k*-points. Efficient molecular pair natural orbital (PNO) methods for MP2 and CCSD(T) are available in the *pnoccsd* module [2] and can readily be extended to a periodic setting.

This contribution will discuss recent developments in the implementation of a 3D-periodic LCAO PNO-MP2 method in the Turbomole environment. We outline the general framework of the PNO-MP2 approach and highlight some key adaptions for the periodic scheme, such as the generation of localised occupied Wannier functions, the imposition of periodic boundary conditions on virtual orbitals, and the use of translational invariance to reduce cost, and the treatment of the slow converging lattice sum of the Coulomb integrals. Preliminary results on non-conducting systems are presented.

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Parallel Implementation of Two-Photon Absorption Strengths Employing the Second-order Algebraic Diagrammatic Construction Scheme for the Polarization Propagator

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Due to the increasing popularity of non-linear optics in recent years, there is a growing interest in non-linear response properties, such as two-photon absorption strengths, circular dichroism, and second harmonic generation. The accurate theoretical description of these properties can be achieved either with numerical or analytical derivatives of the energy or by the evaluation of so-called sum-over-states expressions. The algebraic diagrammatic construction (ADC) schemes are accurate and reliable excited-state methods based on Møller-Plesset perturbation theory and provide an elegant way to calculate molecular response properties by redefining the sum-over-states expressions in the ADC formulation.[1] So far, the implementation in the HPC module of the Python package gator was concerned with excitation energies and linear response properties at ADC(2) level of theory. These extend the applicability from small molecules to molecules with up to 1000 basis functions.[2, 3]

Building upon these prerequisites, this work is concerned with the expansion of the Python package gator from calculation of excitation energies and linear optical properties to non-linear optical properties. As an example, we present the parallel implementation of two-photon absorption strengths at ADC(2) level of theory by reformulating the textbook sum-over-states expressions in terms of so-called Fock-like matrices, which are used in the HPC module of the Python package gator.

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Nonadiabatic Transition Path Sampling

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Molecular dynamics (MD) has become an indispensable tool for studying the dynamics of chemical reactions. However, the time scales of many processes are significantly slower than the time steps of all-atom MD simulations. To address this issue, various enhanced sampling methods have been developed, although nearly all are restricted to a single potential energy surface.

In the realm of electronic excited state phenomena, many chemical processes also occur on timescales much slower than a single MD time step. Nonadiabatic molecular dynamics (NAMD) further complicates this scenario due to the increased computational demands per time step, thereby intensifying the need for enhanced sampling techniques. Previously, we introduced one of the first enhanced sampling method for NAMD, based on forward flux sampling, known as Nonadiabatic Forward Flux Sampling (NAFFS) [1]. A major limitation to employing more efficient path sampling strategies has been the non-time-reversibility of the Fewest-Switches Surface Hopping (FSSH) algorithm, a widely used technique in NAMD.

In this work, we leverage the novel Mapping Approach to Surface Hopping (MASH) [2], which is inherently time-reversible, to present a robust non-adiabatic transition path sampling method. This approach significantly enhances the efficiency of probing slow dynamics in NAMD, paving the way for more accurate and comprehensive studies of complex chemical processes.

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Computational Study of the Methanol to Syngas Reaction by a Ru-Pincer Lewis Acid-Base Pair

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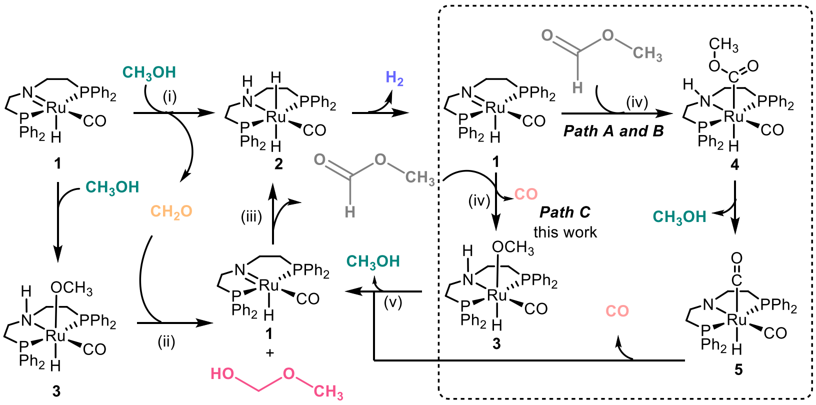
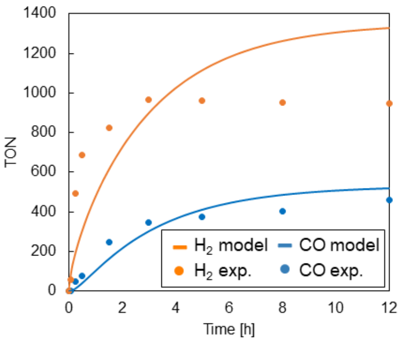
Methanol, particularly when produced from CO_2 and renewable H_2, is regarded as a viable alternative to fossil fuels for energy storage, transportation, and as a precursor to synthetic hydrocarbons. It can be used as a surrogate for H_2 and CO in the synthesis of alcohols, aldehydes, and amines. In 2021, Leitner's group reported the use of $RuH(CO)(BH_4)(HN(C_2H_4PPh_2)_2)$ and $MnBr(CO)_2(HN(C_2H_4P\textit{i}Pr_2)_2)$ as catalysts for the decomposition of methanol into syngas, achieving a ratio of $CO:H_2$ close to the stoichiometric 1:2. [1]





In this work, the methanol to syngas reaction mechanism catalyzed by Ru complex was studied using DFT calculations and analyzed using microkinetic models. Our results indicate that methylformate decarbonylation, contrary to previous studies of forming intermediate **4** via Path A or B, proceeds via CO release to yield intermediate **3** (Path C). This pathway is favored due to the greater stability of methylformate compared to formaldehyde. Furthermore, the reaction preferentially occurs in non-polar solvents such as toluene rather than protic methanol, as toluene promotes the formation of methylformate and suppresses the formation of intermediates **3**. After refining the reaction thermodynamics using CCSD(T)/cc-pVTZ method corrections, the proposed mechanism aligns well with experimental data. In addition, given the similar acid-base properties of the Ru-N in **1** with some heterogeneous catalysts, the mechanistic information presented in this work could also be applied to heterogeneous catalysis.

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Molecular-Level Modeling of NO_x -Precursor Release During Oxy-Fuel Combustion

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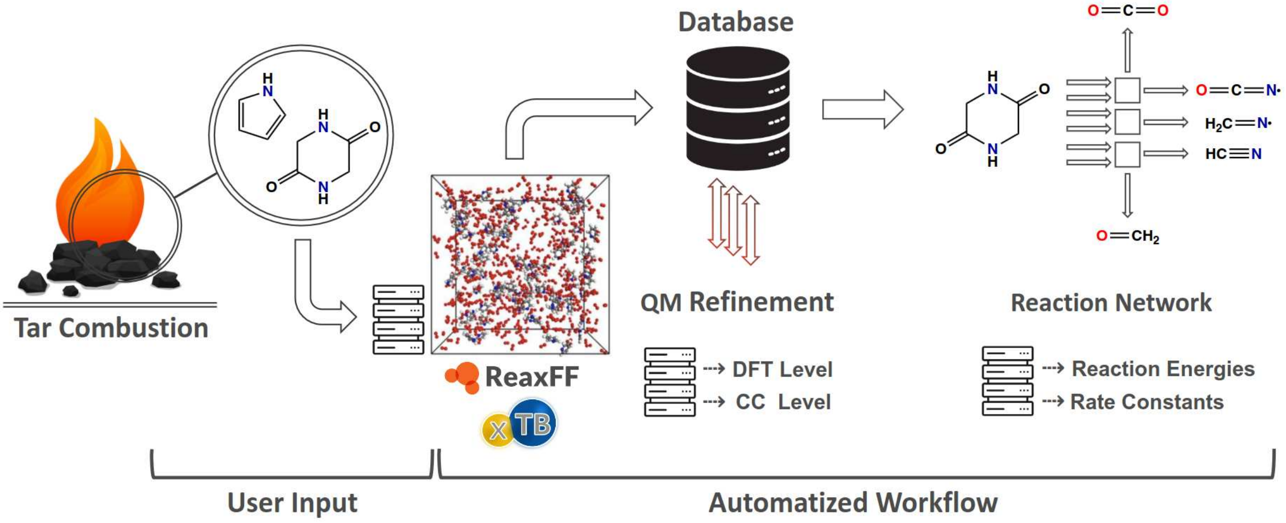
Atomistic models for the oxy-fuel combustion of tar molecules have been limited to direct pyrolysis reactions in recent decades. Molecular oxygen and OH• radicals are essential in the combustion process and yet have frequently been overlooked in earlier research. Here, we provide an automatized process [1] and techniques for combustion modeling using the example of tar that contains pyrrole and 2,5-piperazinediones. To sample the reaction space of these tar compounds in an oxy-fuel atmosphere, we use reactive MD simulations (ReaxFF, xTB). By applying our workflow, the user is able to refine automatically reaction events to Coupled Cluster (CC) level. Our approach and modeling strategies offer large-scale reaction networks for the formation of NO_x precursors from fuel-nitrogen including mechanisms, reaction energies, barriers, and rate constants. In perspective, a detailed mechanistic network is the basis for guiding emission control strategies during tar and char combustion.



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Targeting open-shell compounds within pCCD using spin-flip-type methods

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In its standard single-reference formulation, the coupled-cluster model is one of the most accurate tools for describing dynamical electron correlation, as the hierarchy of approximations rapidly converges to the full configuration interaction solution. In the presence of quasi-degeneracies, the higher-order excitation terms are indispensable since low-level approximations do not provide a qualitatively correct structure of the wave function. The hierarchy of approximations based on the excitation level breaks down for systems featuring many correlated electrons, as found in complexes containing elements from the d- and f-block of the periodic table. Possible remedies dedicated to capturing strong electron correlation effects are, for instance, tailored coupled cluster methods or simplified coupled-cluster approaches, where the cluster operator is restricted to electron-pair states. We will focus on a specific flavor of CC approaches where the amplitudes can be derived from geminal-based approaches like the pair coupled cluster doubles (pCCD) ansatz. Specifically, we will show how open-shell compounds can be modeled within pCCD-based approaches using spin-flip-style methods to describe the electronic structures of both closed- and open-shell molecules.

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Performance Estimation of Pool-Based Active Learning Algorithms for Regression Problems

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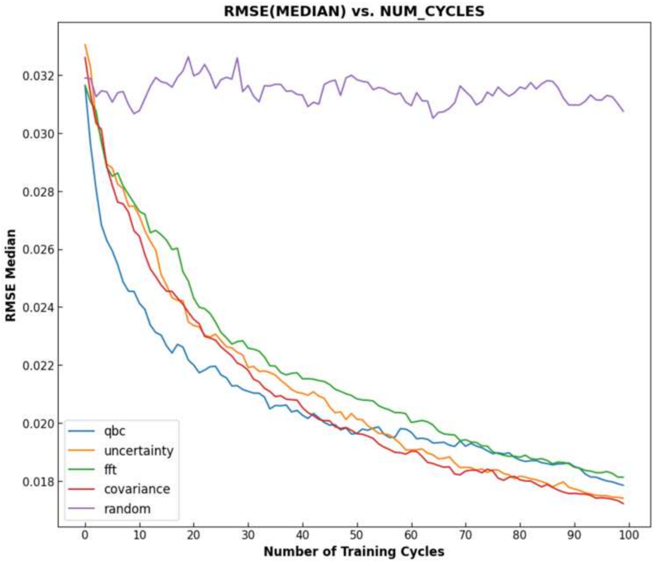
Active learning (AL) is a machine-learning approach where the algorithm selectively queries the most informative data points for labeling, thereby improving model performance with fewer labeled instances. [1] This technique is valuable in computational and experimental chemistry where labeling data is expensive or time-consuming. Our research investigates the performance of different AL algorithms as a function of the underlying data set.

To explore this hypothesis, several popular AL algorithms, including uncertainty sampling, query-by-committee, expected model change, and covariance sampling were compared along with random sampling by changing the labels of an otherwise constant data distribution. Using these results, we deduct the correlation between the performance of an AL method and the underlying label distribution.



Performance of different AL methods over multiple training iterations on the same dataset.

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Ab Initio Molecular Dynamics on Quantum Computers

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One of the most promising applications of quantum computing is the quantum-chemical calculation of molecular properties [1-3]. On near-term quantum computers, the electronic ground state wave function of a given molecule can be found by minimizing the expectation value of the molecular Hamiltonian. One common algorithm to perform this minimization is called the variational quantum eigensolver [4]. Arbitrary operators can then be evaluated on the electronic wavefunction on the quantum computer to determine molecular properties like energy, electric dipole moment or magnetization.

The molecular forces can thus be obtained by evaluating the corresponding operators on the quantum computer [5]. Based on this, a hybrid quantum-classical algorithm can be formulated for the simulation of ground-state Born-Oppenheimer dynamics [5,6]. The algorithm consists of three repeating steps: firstly, on the quantum computer, obtain the ground state wavefunction of a molecule in a given nuclear configuration. Secondly, on the quantum computer, evaluate the nuclear force operators. Thirdly, on a classical computer, integrate Newtons equation of motion for the nuclei.

We implemented the proposed algorithm and applied molecular dynamics simulations for single lithium hydride, hydrogen and water molecules. The quantum computation is performed on a noiseless statevector simulator. The infrared spectra derived from the simulations achieve a good agreement with experimental data.

Our results demonstrate the viability of hybrid quantum-classical simulation of accurate Born-Oppenheimer dynamics. While current quantum computers are too limited to demonstrate an advantage compared to classical methods, in the future they may become a powerful tool for molecular dynamics.

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Phase-Cycling Two-Dimensional Infrared Spectra from Anharmonic Calculations

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Two-dimensional infrared (2D IR) spectroscopy is a versatile experimental method to probe molecular structures and dynamics on various time scales. 2D IR experiments use multiple laser pulses in an advanced pump-probe setup studying vibrational couplings, energy transfer and relaxation or dynamics like protein folding mechanisms or the formation of hydrogen bonds. The complexity of spectra necessitates computational methods to analyze the results.[1]

Recently published experiments use a phase-cycling scheme to measure 2D IR spectra of isolated molecular ions showing waiting time dependent intensity variations of coupling vibrational modes.[3] Here, we set out a computational approach to calculate collinear phase-cycling spectra similar to our lately developed simulation method VIBRATIONS 2D for standard non-collinear 2D IR spectroscopy [2], presenting first quantum chemical results.

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Pushing the Limits of First Principle-Based Approaches to Characterize Organic Semiconductor Thin Films: Modelling Photo Physical Effects of Complex Crystal Packings and Blends

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Organic semiconductor thin films are of fundamental importance as active layers in various optoelectronic devices, including light-emitting diodes, organic photovoltaic cells, and field-effect transistors [1,2]. Unlike their inorganic counterparts, optoelectronic properties can be tuned by chemical design, a complex task that requires band-structure engineering. Consequently, the photophysics of these layers has received significant attention in recent years. A comprehensive theoretical understanding of the various processes involved in photoexcitation is necessary to evaluate the effectiveness of organic semiconductor materials.

Therefore, the subject of our study is to accurately describe a total and polarization-resolved absorption spectra of thin films with an optimally tuned, range-separated time-dependent density functional theory approach. Several theoretical studies on organic semiconductors [3,4] reveal that our approach has excellent agreement with experimental data when combined with the utilization of clusters comprising multiple monomers and a standard polarizable continuum model to simulate the thin film environment.

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Understanding Radicals via Orbital Parities

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We introduce analysis of orbital parities as a concept and a tool for understanding radicals. Based on reduced one- and two-electron density matrices, a fundamental quantity, our approach allows us to evaluate a total measure of radical character and provides spin-like orbitals to visualize real excess spin or odd electron distribution of singlet polyradicals. Finding spin-like orbitals aumotically results in their localization in the case of disjoint (zwitterionic) radicals and so enables radical classification based on spin-site separability. We demonstrate capabilities of the parity analysis by applying it to a number of polyradicals and to prototypical covalent bond breaking. [1]

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High-dimensional neural networks (HDNNs) as reactive potentials for ML/MM simulations in environments

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In order to describe biochemical processes a hybrid quantum mechanical/molecular mechanical (QM/MM) approach can be applied. Typically, semi-empirical methods, such as density functional tight-binding (DFTB), are used as the QM method due to the computational cost of numerous calculations. While DFTB is 2-3 orders of magnitudes faster than DFT, their approximations lead to deviations from higher level methods [1].

In our ongoing research we are dedicated to training a 4th generation High-Dimensional Neural Network Potential [2] incorporating environmental effects during QM/MM-calculations. This involves including the electrostatic potential caused by MM-zone in order to calculate the electrostatic interaction between QM- and MM-zone within the electrostatic embedding scheme. While the training takes place using established Python libraries TensorFlow and PyTorch, the ML/MM simulation is handeled by Gromacs. The network is trained using structures of the thiol-disulfide exchange reaction and the Alanindipeptide dihedral rotation, two processes known for their strong dependence on the surrounding environment [3,4].

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Quantum chemical study of a Co-catalyzed carbon dioxide reduction

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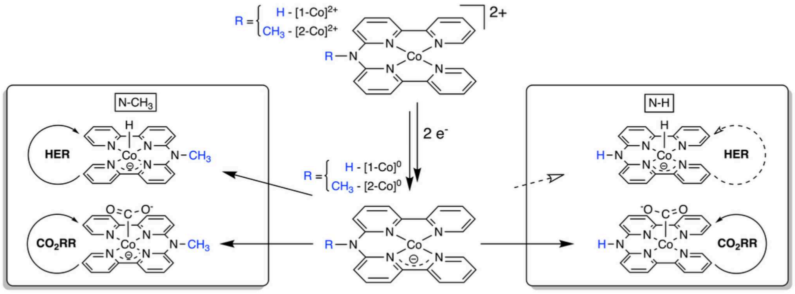
The transformation of carbon dioxide (CO_2) into valuable carbon-based fuels presents a compelling avenue for addressing both the growing global energy demand and the pressing issue of climate change. However, the development of catalysts capable of selectively and efficiently reducing CO_2 to desired products while outcompeting the kinetically and thermodynamically competitive hydrogen evolution reaction (HER) remains challenging.[1] Homogeneous molecular catalysts provide a unique platform to dissect the electron and proton transfer mechanisms underlying CO_2 reduction reaction (CO2RR) due to their precise tunability. While significant progress has been made in designing molecular catalysts with tailored ligand systems, an understanding of the key determinants for efficient and selective CO_2 conversion remains elusive, although understanding the role of supporting ligands is crucial, as redox-active ligands can potentially divert electron density away from the metal center, thereby hindering hydride formation and potentially suppressing the undesired hydrogen evolution reaction.[2] This work investigates the electrocatalytic CO_2 reduction of two structurally similar cobalt complexes, $[1\text{-Co}]^{2+}$ and $[2\text{-Co}]^{2+}$, based on N,N-bis(2,2'-bipyrid-6-yl)amine ligand (see figure below). Despite their structural similarity, these catalysts exhibit distinctly different product selectivity. While $[2\text{-Co}]^{2+}$ undergoes both HER and CO2RR (54:46 ratio after 8 h), $[1\text{-Co}]^{2+}$ demonstrates a pronounced preference for the CO2RR (~97% after 8 h). To elucidate the origin of this selectivity disparity, the reaction mechanisms for both HER and CO2RR were investigated utilizing different DFT-functionals. These calculations revealed the well-known issue of functional-bias, with varying computational results. Notably, however, all tested functionals predict a negligible difference in selectivity for $[1\text{-Co}]^{2+}$ and $[2\text{-Co}]^{2+}$. Moreover, analysis of the electronic structure of $[1\text{-Co}]^{2+}$, $[2\text{-Co}]^{2+}$, $[1\text{-Co}]^{0}$ and $[2\text{-Co}]^{0}$, displayed signs of strong static correlation, as previously observed for similar cobalt complexes.[3] To address these challenges and gain deeper insights into the underlying factors governing selectivity, multi-reference computational methods are currently being employed.



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Reaction Path Search for MC/MD Hybrid Simulation of Carbon Fiber Production

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Industrial-scale carbon fiber production with polyacrylonitrile (PAN) as precursors consists of several stages, among which a flame-proofing process involves complex multiple chemical reactions, such as cyclization, dehydrogenation, and oxidaton. Structural improvement requires a detailed understanding of the reaction mechanism at this stage, and molecular simulations would provide useful information. Howver, it generally takes long time (typically 10^3 s) to complete the process and thus conventional molecular simulations using molecular dynamics (MD) are hard to apply. To address this issue, we have proposed a novel MC (Monte Carlo) / MD hybrid scheme with a simple stochastic reaction model, which makes it possible to deal with the evoluation of the target system on a much larger time scale.

It is crucial to appropriately set the parameters for the MC part which stochastically changes the molecular structure using templates. We have picked up seven relevant reactions for the flame-proofing process. When we assumed a simple reaction path a priori for each reaction and empirically give MC parameters (e.g., atomic distance criterion and reaction rate), we successfully traced the structural change for 10^3 s with this MC/MD hybrid simulations.

As a next step, we aim to establish a method for determining MC parameters more reasonably based on quantum chemical calculations. As an example for cyclization of a copolymer of acrylonitrile and acrylic acid, two atomic distances (d_{OC} and d_{HN}, Fig. 1) are chosen as the reaction coordinates, and the potential energy surface is evaluated by quantum chemical calculation using DFTB+[1]. A preliminary result is shown in Fig. 2, which clearly indicates a saddle point. This approach allows us to have theoretically more appropriate MC parameters.

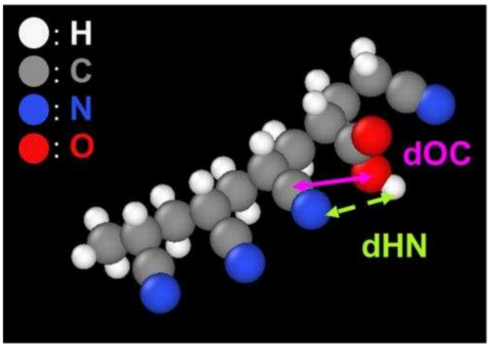

Figure 1. PAN-IA copolymer model and two types of distance as the reaction coordinates for cyclization.

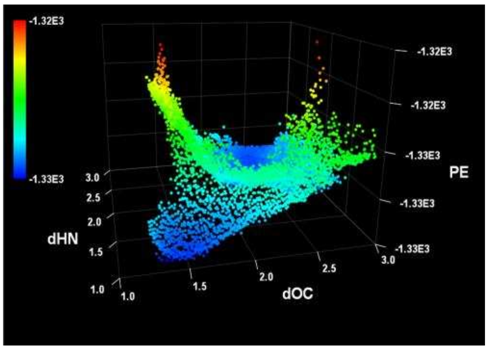

Figure 2. Example of obtained potential surface.

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A QM/MM Approach to Investigate the Photophysical Properties of Zinc-Based TADF Emitters in Crystal Environment

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Organic Light-Emitting Diodes (OLEDs) are of significant interest due to their potential in creating efficient, flexible displays and lighting, widely used in smartphones, televisions, and portable devices. Recent advancements have focused on enhancing their performance, lifespan, and color purity, driving the development of new materials and technologies.

One such advancement is Thermally Activated Delayed Fluorescence (TADF), which boosts OLED performance by utilizing both singlet and triplet excitons. Through reverse intersystem crossing non-emissive triplet states are converted into emissive singlet states, resulting in delayed fluorescence. This all-exciton-harvesting mechanism allows TADF-based OLEDs to achieve high quantum efficiency.

Quantum chemical calculations are crucial for a detailed understanding of the photophysical processes undergoing in such systems. The consideration of environmental effects is particularly important, as these have a major influence on the photophysics of the molecules.

In this work, we introduce a QM/MM approach for investigating the photophysical properties of zinc-based TADF emitters in crystalline environment. Starting from an experimentally determined unit cell, a super cell is created via expansion into all spatial directions. The central molecule of the supercell is treated at quantum mechanical (QM) level using the combined density functional theory/multi-reference configuration interaction (DFT/MRCI) method. The surrounding is modeled using molecular mechanics (MM) with the AMBER software package and the General Amber Force Field (GAFF).

Explaining machine learning to understand the influence of DFT methods on chemical bonding

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Decomposition methods are essential for understanding chemical bonding by breaking down the interaction energy into interpretable terms. However, when using density functional theory (DFT)-based methods, like energy decomposition analysis (EDA), the results often vary dramatically with the chosen density functional, raising concerns about consistency in bonding interpretations.

To address this issue, we benchmarked molecules that are representative of the four distinct bonding types often compared in EDA, namely, covalent, main group donor-acceptor, transition metal donor-acceptor, and weakly bound complexes, using a total number of 28 combinations of functionals and dispersion corrections. We employed statistical analysis along with supervised and unsupervised machine learning (ML) to assess how the choice of density functional affects the bonding interpretation. Explainable artificial intelligence was further used to identify the most influential energy decomposition terms in classifying the four bonding categories.

Our study found that, despite significant variations in individual EDA terms, bonding classes can be effectively distinguished using a combination of interaction energy and the relative electrostatic energy term. [1]

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Controlling Nonlinear Optical Properties in Functionalized 2D TMDC Heterostructures

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Transition metal dichalcogenides (TMDCs) are promising candidates for applications in ultra-small, low-power optoelectronic devices.

However, for successful development, the nonlinear optical properties of these compounds, including MoX_2 and WX_2 (X = S, Se, Te), need to be understood theoretically and tailored by functionalization with dye molecules. This project investigates these properties in functionalized 2D heterostructures, combined with graphene and boron nitride (BN).

To achieve this, we first study the TMDC layers and the dye independently. The TMDC layers are investigated periodically to understand their electronic properties. [1] The dye, a rylene derivative, is analyzed using time-dependent density functional theory (TD-DFT) to simulate its excitations and understand its electronic properties, including the frontier orbitals, which are crucial for determining light absorption and charge transfer characteristics. Next, we explore the functionalization of TMDC surfaces with the dye to study the resulting changes in electronic properties and optical responses. By adsorbing the dye onto the TMDC surfaces, we aim to enhance and tailor the nonlinear optical behavior of the heterostructures. These simulations utilize a combination of local basis set methods and periodic calculations with Turbomole's riper module. [2]

Our goal is to obtain a fundamental mechanistic understanding and achieve precise control over the nonlinear optical properties of these 2D TMDC heterostructures, paving the way for innovative applications in optoelectronics.

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Charge Storing Mechanisms in Polyheptazine Imide based COFs

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Covalent organic frameworks (COFs) [1] relying on heptazine imide building blocks are a class of porous materials that consist of abundant elements such as C, N and H. Polyheptazine Imide (PHI) based COFs can be synthesized as highly ordered structures where the heptazine units linked by imide moieties form a 2D planar graphene-like (g-C_3N_4) porous material. The design flexibility furnishes them with tuneable pore size, shapes, and functionalities, making them appealing materials in recent years. PHI based COFs thus feature as promising candidates for a wide range of applications like photocatalytic water splitting or materials for solar batteries. [2]

Here, we focus on charge storing properties of hydrogen polyheptazine imide (HPHI), and potassium polyheptazine imide (KPHI), an essential property for their use in solar batteries. We use force-field-based and ab initio molecular dynamics (AIMD) simulations to develop a structural model of PHI in aqueous environment subject to stochastic interactions with K^+ counter ions. The model allows to explore the radical anionic dynamics and equilibration of excess electrons, i.e., the active species for catalysis in PHI and their interactions with the aqueous environment. Moreover, the effect of GGA and hybrid-GGA functionals on the equilibration dynamics is explored.

From our simulations we find that the excess electron spin density shows varying degrees of localization in the heptazine moieties of PHI, even extending partially into the aqueous environment in the pore structure, indicating partial charge transfer between PHI layers or/and PHI-solvent molecules. Further analysis shows the formation of polaronic structures via structural distortion of the KPHI lattice and a reorientation of solvent molecules.

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Deep equivariant neural networks for time-dependent spectroscopic properties

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Vibrational spectroscopy, particularly infrared (IR) and vibrational circular dichroism (VCD) spectroscopy, is a powerful technique for elucidating the structural and stereochemical properties of molecules and materials. However, interpreting experimental data often requires computationally intensive quantum chemical calculations that limit their interpretation. In this study, we develop deep equivariant neural networks to predict molecular properties, aiming to improve the simulation of IR and VCD spectra using time autocorrelation and cross-correlation functions of the electric and magnetic dipole moments, respectively. Given that the latter is a time-dependent property, this presents significant challenges for machine learning. We evaluate various methods to incorporate time-dependency into the learning process and assess their effectiveness using *(R)*-propylene oxide in both gas and condensed phases, advancing the application of vibrational spectroscopy.

Investigations of a PLATICT system

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A PLATICT system undergoes an intramolecular charge transfer through electronic excitation during that it experiences a planarization of one and a twist of another single bond.[1] After electronic relaxation the original geometry is retained through another PLATICT rotation.

In this studies, a PLATICT system is investigated to gain insight into the pathway.

In a first step, minima on the ground state and the first excitated state have been optimized and their spectra have been investigated in vacuum and in 1-chlorobutane using COSMO as implicit solvation model. The studies of spectra, intrinsic reaction coordinates and potential energy surface scans of the PLATICT system with the continuum solvation model COSMO and in vacuum gave rise to the assumption that one can start further studies of the molecule in vacuum and could still compare them with experimental results in aprotic weakly polar solvents like 1-chlorobutane.

With this assumption, the excitation and dynamics of the vibrational relaxation on the excited potential energy surfaces S_1-S_3 have been studied using the surface hopping method SHARC.[2]

The investigation with SHARC have lead to the assumption, that there are two main pathways how the PLATICT system can vibrationally relax. These different pathways lead to different minima on the S_1 potential energy surface.

After the analysis of the excited state surface hopping dynamics, the dynamics on the ground state should be exploided. Hereby, the excited state minima have been optimized and their frequencies have been calculated. Upon this frequency calculations, a Wigner distribution for all S_1 minima can be performed.[3] Upon this Wigner distribution, the emission spectra of this minima have be calculated and ground state dynamics have been performed.

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The Fluoride Ion Affinity and the Anchor Point Approach

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Although Lewis acidity is a fundamental concept in chemistry, there is no unique method to quantify it. An often used possibility is to employ the fluoride ion affinity (FIA) as a measure. When calculating this property with DFT methods, one usually uses an isodesmic reaction with fluorophosgene or the trimethyl silyl cation for which the FIA is known experimentally or at a high theoretical level. That is done to avoid the treatment of the naked fluoride ion which is often stated as problematic.[1] The latter statement is rarely explained or proven. Therefore, the question arises whether it is actually necessary to take the path via the isodesmic reaction. To answer this, we generated a high-level benchmark set based on CCSD(T) data and used it to evaluate different density functionals for the calculation of the FIA of different main group Lewis acids. This was done with the anchor point method as well as with direct computations. The results shed new light on the applicability of DFT for calculating FIA and the necessity of an anchor point approach.

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Computational modeling of the electrocatalytic oxygen evolution reaction in transition metal oxides

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Transition metal oxides constitute prototype catalysts for the oxygen evolution reaction (OER) in alkaline conditions,1. In order to improve the fundamental understanding behind its catalytic efficiency, numerous studies attempted to derive structure activity relationships.[2,3]These are complex,[4] as the atomistic and electronic structure of the interface is strongly dependent on the electrochemical potential and pH. Computer simulation based methods are an important auxiliary tool for the rationalization of the factors affecting electrocatalyst stability and activity[5]. Theoretical studies recently devised models for the structure of transition metal oxide based electrocatalysts, and computed OER energy landscapes, with the inclusion of implicit solvation, and potential/pH effects, by explicitly varying the system charge and the protonation state.[6,7] Nevertheless, the explicit atomistic description of the electrolyte/catalyst interface has proven to be important,but also a huge challenge.[8,9]

In the present work, the protocol implemented by our group is employed for the determination of the pH/potential dependent surface structure of nickel oxide/nickel-iron oxide materials, using $Ni_7O_{24}/Ni_{(7-x)}Fe_xO_{24}$ model nanoparticles. Incorporation of the iron atom in the metal oxide nanoparticle changes the redox properties of the entire structure, which in turn determines also acid-base properties of the oxygen in the whole structure. Our calculations suggest that the electrons in the Fe d-orbitals are most likely to be removed first, upon oxidation, generating species with different oxidation states in the catalyst, and also oxygen-based species with different degrees of protonation. As a consequence, remarkable changes are seen in the nature of the reaction intermediates,which ultimately determines the OER energy landscape and the rate-determining steps.

Born-Oppenheimer DFT based ab initio molecular dynamics (AIMD) is employed,as a first attempt to include explicit solvation in the current pH/potential model. For this purpose,transition metal hexa-aqua complexes, with Fe, Ni, Cu, Co and Ir as the central ion are studied,with three explicit water solvation shells, along with polarizable continuum solvation. The AIMD trajectory averaged total free energy changes upon oxidation/protonation are compared with pKa/redox potential experimental values. In the picosecond scale, single trajectories already sample many relevant configurations. Differences in the water mobility between different DFT functionals are observed, which affects average energies from AIMD. Moreover, it is possible to build an pH/redox scale in which acidic/alkaline or reduced/oxidized species are within 0.2-0.3V and 2-3 pH units of experimental values. The ultimate objective is to develop a computationally feasible method to identify and rationalize rate determining steps of electrocatalytic processes on different materials with explicit inclusion of the electrochemical potential, pH and the dynamics of the catalyst/electrolyte interface[9].

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TTConf: Achieving low scaling systematic conformer sampling through tensor train representation of torsion angle combinations

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Identifying the thermodynamically accessible conformers of a molecule is of utmost importance for quantum chemical predictions.[1] The fundamental relevance of conformational sampling has led to the development of numerous approaches over the past decades. Systematic grid search approaches reduce the search space to bond rotations only and sample every possible combination of the associated torsion angles. The resulting exponential scaling with the number of bond rotations, limits the approach to small molecules. However, introducing heuristic rules, like utilizing a database of favorable molecular fragments, allows for exploring the conformational space of drug-like molecules in the matter of seconds.[2] To extend the search space beyond simple torsional modes metadynamics (MTD) simulations using the atomic RMSD as collective variable have been established as a reliable and broadly applicable method. However, the simulation itself and, particularly, the large number of subsequent geometry optimizations come at a high computational cost, restricting the treatable system size to about 200 atoms.[3] In order to match accuracy to state-of-the-art MTD based methods at a significantly reduced computational effort, a systematic grid search in combination with an efficient dimensionality reduction strategy is presented. For this purpose, a tensor train-based global optimization algorithm is used in combination with local gradient optimizations.[4] For typical drug-like molecules, a relative acceleration of one order of magnitude is achieved over the MTD-based reference and in addition the polynomial scaling algorithm allows to extend conformational sampling to significantly larger molecules at the same electronic structure theory level.

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Tailored calculation of anharmonic infrared signatures of protonated flavins

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Infrared spectroscopy is a versatile tool for the elucidation of subtle structural changes in biomolecular systems.[1] For example, difference infrared spectroscopy can capture the subtle structural changes occurring in the hydrogen-bonding network in the center of the blue light sensor using flavin (BLUF) upon illumination.[2] Still, the interpretation of the spectra requires computational assistance. At the same time, accurate anharmonic calculations of vibrational spectra affected by hydrogen bonds are computationally only in reach for small molecules. Fortunately, often only certain spectral signatures are of interest, as in the case of BLUF the spectral region is dominated by C=O stretching vibrations in the flavin.

Recently, we have developed a protocol for tailored potential energy surfaces that enable accurate calculation of certain infrared signatures by vibrational structure methods and validated this protocol on small molecules.[3] Here, we show that this protocol enables accurate calculation of infrared C=O signatures in (protonated) flavins using vibrational wave function methods, which is out of reach for non-tailored methodologies. This study is, hence, a first step towards the description of vibrational signatures of large biomolecular systems using tailored vibrational-structure methods.

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Investigations on the Spin States of the Fully Oxidized Glutamate-Coordinated O_2-Tolerant [NiFe]-Hydrogenase

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Hydrogenases are metalloenzymes facilitating the conversion between molecular hydrogen and protons and electrons. They are categorized into three types based on their active site compositions: [FeFe]-, [NiFe]-, and [Fe]-hydrogenases. [NiFe]-hydrogenases primarily catalyze the oxidation of molecular hydrogen, whereas [FeFe]- and [Fe]-hydrogenases are more inclined towards the production of molecular hydrogen.[1-2] Shomura et al. reported the structure of the oxygen-tolerant [NiFe]-hydrogenase from *H. thermoluteolus* and proposed an unusual coordination of the active site nickel atom.[3] In the oxidized state of the active site, a terminal cysteine residue is displaced to a µ-cysteine bridging position by the bidentate coordination of a nearby Glu32. Recently, Kulka-Peschke *et al.* suggested an uncommon closed-shell Ni(IV)/Fe(II) state based on the spectral features observed.[4] In biological systems, such a high oxidation state of nickel coordinated with soft ligands was unprecedented, prompting further investigation. Here, we present arguments for why we consider the assignment of the Ni(IV) oxidation state in the soluble hydrogenase (SH) to be ambiguous and not fully plausible.[5] An energetically low-lying broken-symmetry Ni(III)/Fe(III) state at the active site is a more likely scenario. This state also accurately replicates the spectral properties and coordination sphere observed in the oxidized state of the [NiFe]-hydrogenase.[5] The Ni(III)/Fe(III) open-shell singlet ($S = 0$) is formed through antiferromagnetic spin-coupling between Ni-d^7 and Fe-d^5, resulting in evenly distributed spin densities across both metal atoms. Finally, we offer some suggestions for experimental chemists to help clarify the definitive assignment of redox states.[5]

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Uncertainty Quantification for Thermodynamic Properties and Frequencies for Molecules with Torsional Modes

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An important source of error in *ab initio* calculated thermodynamic properties is the harmonic treatment of vibrational modes that represent hindered internal rotations. Various methods have been developed to address this problem. Widely used are uncoupled approaches employing the one-dimensional hindered rotor (1D HR) model, many of which are based on the work of Pitzer and Gwinn [1].

Our objective is to develop a method that quantifies the uncertainty caused by the harmonic treatment of torsional modes for each vibrational frequency obtained in a frequency calculation, as well as the resulting uncertainty of the thermodynamic properties of a molecule.

To this end, we implemented a 1D HR model within a python package. Within this model, the torsional barrier height V_0 and the reduced moment of inertia I_{red} of the rotating top are the variables defining the 1D HR correction to the thermodynamic functions.

We used the implemented model to realize an approach that quantifies the differences between the 1D HR-corrected thermodynamic functions and those obtained for a harmonic potential corresponding to the torsional potential used in the 1D HR model, both defined by V_0 and I_{red}.

This approach was tested on a range of V_0 and I_{red}, that was selected to cover typical values for internal rotations of methyl groups.

The poster presents the obtained results and the employed methodology.

The idealized approach reflects errors introduced by the use of a harmonic potential function to describe hindered internal rotation, but thereby assumes pure torsional motion in a normal mode. Presently, we are working on the incorporation of the mixing of torsional and other vibrational motions through internal coordinate analysis.

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Research Data Management in Theoretical Chemistry

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Effective data management has emerged as a critical component for scientific advancement and collaboration. While a detailed manual record-keeping of all parameters seems to be the standard in experimental disciplines, researchers in theoretical chemistry often simply rely on their folder structures and the saved input and output files. Arguably, this can lead to massive problems in reproduction of simulation results when things out of the scope of these files change.

In the first funding phase NFDI4Chem developed an Electronic Lab Notebook (ELN), extended data and meta-data formats, and ontologies to digitalize experimental data. In our ongoing work, we took the fist steps of making the Chemotion ELN[1] fit for use in theoretical chemistry. In order to do this, new functions had to be implemented in the ELN (e.g. reading general data formats like json and an API to interact with the ELN).

To make this integration of quantum-chemical data even more seamless an ontology for theoretical chemistry is absolutely essential. From this, the universal data (and metadata) format and even the structure of quantum-chemical code can be derived. The barriers of integration into already existing solutions (e.g. NOMAD[2]) and even on-site solutions are reduced to an absolute minimum. An adoption of these data-formats as standard output formats of quantum-chemical software will improve data handling not only in conjunction with ELNs. In the mean time, already established frameworks for quantum-chemical workflows (e.g. pyADF[3]) are able to fill this gap.

Once established and sufficently automated, this framework will enable real-time data capture, organization, and annotation. Researchers can effortlessly navigate, interpret, and reproduce computational results within the context of their electronic lab journals. By enhancing Findability, Accessibility, Interoperability, and Reusability[4], it not only facilitates effective collaboration but also strengthens the integrity and longevity of quantum-chemical research data.

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Vibrational Dynamics of $H_3O^+ \cdot He_n$ Clusters

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The investigation of $H_3O^+ \cdot He_n$ clusters can provide insights relevant in different areas of research. First, He-tagging is used in action spectroscopy to investigate molecular vibrations. Second, the investigation of hydronium in Helium-droplets offers insights into solvation processes in quantum fluids.

The present project focusses on detailed quantum dynamics calculations H3O+*He_n clusters of increasing size. Simulations employing the multi-layer multi-configurational time-dependent Hartree (MCTDH) approach were performed to study the coupling of the floppy hydronium molecule with the surrounding helium atoms. First results will be presented.

Teaching quantum chemistry with Jupyter Notebooks

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The threshold to learn programming is naturally lower for computational chemists than for experimentalists, but still it is often a skill that is developed along the way. Among experimentalists, programming is often completely neglected in their training, although data analysis is an important field and the work load could be reduced in the long run, if programming skills were developed early.
Recently, Jupyter Notebooks have gained increasing attention in university teaching. They are for example used as interactive textbooks,[1] or to teach programming for data analysis and presentation.[2] Their advantage is the possibility to write small portions of code and see the result after execution, which makes it easier for beginners to understand what is happening with the bits and pieces of larger programs.

We want to present our approach of incorporating Jupyter Notebooks in our quantum chemistry bachelor course, where we use the interactivity to improve the problem presentation, and the integrated coding environment to let the students solve quantum chemistry tasks directly in the notebook. It was tested this summer in the computational chemistry bachelor course at the TU Darmstadt and has received mainly positive responses by the students. Students see more directly were they can employ their new programming skills to solve problems, helping them not only with quantum chemistry, but with data acquisition and analysis in general.

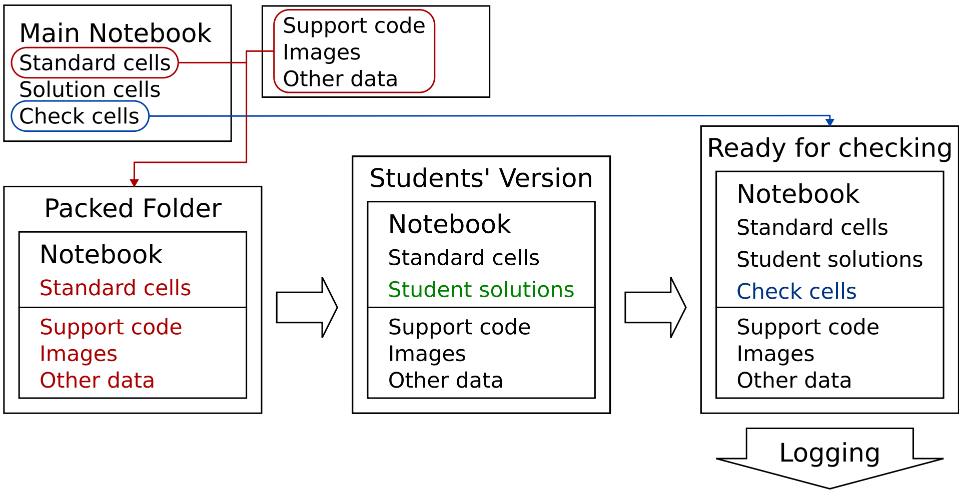

Figure: Flow scheme of the exercise process with a main notebook as reference.

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Computational approaches to find the hidden phosphate hydrolysis intermediate in ATPase p97

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Phosphate ester hydrolysis is fundamental to various cellular processes, and has been the topic of many experimental and computational studies. Many NTPases have similar active sites, and yet small but subtle differences can be enough to result in substantially different catalytic efficiencies. Reaction intermediates in various NTPases were postulated by several QM/MM free energy studies and the question of whether the reaction follows an associative, dissociative, or concerted pathway has sparked controversial debates in the literature [1].

Recently, evidence from real-time NMR and single-particle cryo-electron microscopy led to the observation of a long-lived reaction intermediate in p97 [2, 3]. Motivated by these findings, the focus of our QM/MM based approach was to create a robust and computationally cost-efficient framework for computing 31P NMR chemical shifts of nucleotides [4]. When applying our methodology to different stages of the ATP hydrolysis process at the active site, many questions arise about the catalytic mechanism of p97. What is the nature of the experimentally observed stable intermediate? What is the associated reaction mechanism and does it take place via a general base or the substrate itself? Our current work aims to provide a carefully calibrated QM/MM-MD study to answer these questions with a combination of reaction profile sampling and direct comparison of associated NMR chemical shifts to experiment.

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Multidimensional Hubbard models in the MCTDH framework

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The Bose-Hubbard model facilitates a simplified description of superfluid behavior. In the present work, the perspective of describing the quantum dynamics of superfluid systems by MCTDH calculations is investigated. Interesting examples would be, e.g., molecules solvated in He-droplets.

While the simulation of the quantum dynamics on one-dimensional lattices can be routinely performed using tensor contraction schemes as, e.g., DMRG, simulations on two and three-dimensional lattices pose a challenge. The present work addresses the problem by employing the tree structure of the multi-layer MCTDH approach and a self-similar mapping of the lattice structure onto a one-dimensional sequence.

Specifically, the multi-layer MCTDH approach in second quantization representation is used to study two-dimensional Bose-Hubbard models with up to 64x64 sites. The free energy and the condensate fraction are studied as a function of temperature. A statistical sampling approach specifically designed for application in the MCTDH framework facilitates these calculations.

In addition, available results for the the fermionic Hubbard model will be presented.

Relativistic Quantum Chemistry in Finite Magnetic Fields

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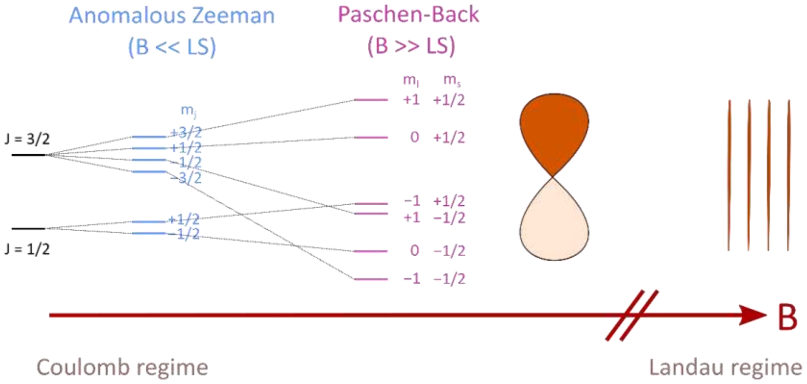
Recent years have seen a rapid increase in quantum chemical calculations performed with the finite magnetic field approach. Applications include molecular spectroscopy in weak magnetic fields, such as those typically produced in laboratories on earth,[1] as well as the investigation of astrochemical conditions, in which magnetic fields of considerable strength can be present.[2] Through the finite magnetic field approach, the seamless transition from the perturbative regime to the rich and fascinating world of non-linear magnetic interactions can be examined.[3] Beyond the *Coulomb regime*, in which the chemical bond is primarily dictated by the Coulomb interaction between electrons and nuclei, strange phenomena such as an entirely new type of chemical bonding can be observed.[4] Finally, within the *Landau regime*, magnetic fields are strong enough to dominate molecular interactions, making the formation of a chemical bond as we know it impossible.

While magnetic effects have successfully been included perturbatively in quantum chemical calculations with relativistic Hamiltonians for decades, only a few works have been concerned with the finite magnetic field approach.[5,6] This is somewhat surprising, as magnetism and relativistic effects are intimately connected with spin-orbit (LS) coupling inducing internal magnetic fields. Like the nonrelativistic case, the finite field approach can be used within relativistic quantum chemistry to describe non-linear effects. From the perturbative limit (*anomalous Zeeman effect*, B << LS) to the regime in which a magnetic field can effectively decouple spin and angular momentum again (*Paschen–Back effect*, B >> LS), a rich world of non-linear properties is waiting to be revealed.



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Microstructure of [EMIm][OAc]/DMSO/Water Mixtures Leading to Cellulose Solvation

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Cellulose, the most abundant biopolymer on earth, has many potential applications, including packaging materials, writing surfaces, biofuels, bioplastics, antifungal membranes, laminates and phosphorescent materials, among other innovative uses. Some processes require cellulose to be dissolved. However, dissolving cellulose is challenging due to its insolubility in most common solvents. Ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) are effective solvents for cellulose. The addition of aprotic co-solvents such as DMSO enhances dissolution, while protic anti-solvents such as water reduce solubility. The mechanism of cellulose dissolution in IL, and exactly how DMSO increases cellulose solubility while water decreases it, is not yet fully understood. However, the interplay of IL, co-solvent and anti-solvent in a system has been little addressed. [1][2]

In order to better understand the dissolution process of cellulose, force field molecular dynamic simulations of [EMIm][OAc] mixtures with different concentrations of DMSO and DMSO/water were performed as a first step. They provide a first insight into the microstructure of the two solvent systems in order to determine possible effects of the co-solvent DMSO on the IL and of the interplay of water and DMSO together on the IL. For this purpose, different radial distribution functions (RDF) were analysed. In a second step, cellulose was added to the mixtures to investigate the influence of different solvent compositions and concentrations on solvent-cellulose hydrogen bonding. The results provide an interesting perspective on the microstructure of the pure solvent systems, which gives insight into the effect of the co-solvent DMSO on [EMIm][OAc] and the effect of the co-solvent and anti-solvent together on the IL. Furthermore, the results show the impact of different solvent systems on cellulose hydrogen bonding.

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Insights into the Proton Transfer Dynamics in Liquid Water from Ab initio Molecular Dynamics Simulations

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The dynamics of an excess proton has been studied extensively due to its importance in biological and chemical processes but conflicting pictures persist from experiment and theory regarding the nature and abundance of solvation species in the so-called Zundel- and Eigen structures [1,2]. Here, we present our results of ab-initio molecular dynamics (AIMD) simulations using state of the art dispersion corrected hybrid-GGA and hybrid meta-GGA exchange-correlation functionals (rev-PBE0-D3, PW6B95-D3) that both provide an excellent description of bulk water, to track the temporal evolution of an excess proton in liquid water. Unprecedented long time molecular dynamics simulations extending into the 250 ps timescale assure a statistically converged description of proton transfer dynamics for which we have approached the ergodic limit of the dynamics.

Employing a newly developed distance-based model to follow the time evolution of the excess proton through the hydrogen bond network of liquid water, we provide an unbiased description of the excess proton structural diffusion. We find that transport of the proton occurs via uncorrelated hopping events and a characteristic correlation timescale of 200-300 fs. Moreover, the strong interaction of three water molecules with the excess proton induces an asymmetry along the proton transfer coordinate that is reflected in the diffusion dynamics observed in recent nonlinear two-dimensional infrared spectroscopy [3]. Such complex reorganization of the Hydrogen bond network are unambiguously connected to experimental structural observables via differential pair distribution functions.

Finally, the dynamics of the Hydrogen bond network is correlated with proton transfer events. We observe that the large-angular jump mechanism of Hydrogen bond exchange in bulk water [4] is instrumental in causing in the translocation of excess protons. In particular, H-bond cleavage of overcoordinated water species drives the transfer of excess proton in liquid water.

Keywords
Solvated Proton Dynamics, Ab Initio Molecular Dynamics, Density Functional Theory.

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Quantum chemical study of possible reaction pathways between IO and CH_3OO

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The chemistry of iodine plays a major role in the complex chemistry of the marine boundary layer, especially in the unpolluted atmosphere. A particularly important molecule in this context is the IO radical. Experimental studies already proved the possibility of IO being a factor in the depletion of ozone.[1]

Due to the high reactivity of the IO radical, it is involved in many other important reactions. The reaction with peroxy hydrocarbons, especially CH_3OO, is of particular interest because of the lack or reliable experimental reaction rates.[2] Even the reaction products are not known for sure, yet. For that reason, the focus of the present work is on the quantum chemical calculation of possible reaction pathways of IO with CH_3OO.

The aim of this work is to untangle some of the discrepancies between the different existing studies, experimental and theoretical. The computed reaction energies suggest the initial formation of stable adducts. The reaction energies and free enthalpies suggest that several other product channels seem thermodynamically possible. Especially for the adduct formation, thermochemical effects in terms of Gibbs-energy and enthalpy at finite temperature may be relevant. Less influence of temperature is found for other reaction channels. It turns out in general that the computed reaction energies are rather sensitive to the treatment of electron correlation, effective core potential, AO basis, and multi-reference effects.

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Configurational Entropy of Mixing in Molecular Dynamics Simulations

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Phase transitions such as solution and nucleation processes occur in a wide variety of chemical systems and therefore also cover a broad range of time scales. An easily accessible method to study and understand them are Molecular Dynamics (MD) simulations, which allow for analysis at both microscopic and macroscopic scale.
However, the simple question of how far the mixing or phase separation of the components has progressed at any given moment in a MD simulation cannot be answered by most common analysis methods, as they are limited to equilibrium states, where the entropy of mixing of a multi-component system is a simple expression of the molar fractions. To the best of our knowledge, its intermediate values for transient (non-equilibrium) states can not be calculated directly from the particle coordinates so far.

We propose a simple scheme to gain quantitative information also from non-equilibrium states by computing the configurational entropy of mixing ΔS based solely on the set of atomic coordinates [1]. This enables a more detailed and on the fly analysis of mixing and demixing processes and their dynamics. We demonstrate the potential of our approach on different molecular mixtures representing both different molecule sizes and fast and slow mixing and demixing processes.

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Electron force field: electronic stopping power and beyond

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Interactions of charged particles with condensed media present a significant challenge for theoretical modeling. The large number of particles, high density of states, and coupling of nuclear and electronic degrees of freedom make *ab initio* methods impractical due to the insurmountable computational cost. A pragmatic and unconventional solution is provided by the electron force field (eFF), which partially captures the quantum behavior of electrons at the cost of standard molecular dynamics simulations. [1,2] Modifications of the eFF potential are now being developed to overcome the limitations of the original version, such as the poor description of *p* electrons. [3, 4] These "second generation" eFF potentials have been applied to study materials under extreme conditions. Surprisingly little attention has been, however, paid to the applicability of the eFF in the context of radiation chemistry of liquids.

In this work, molecular dynamics simulations with the eFF potential are employed to calculate the electronic stopping power of water clusters for various charged particles (electron, proton, α particle, and carbon ion) at different kinetic energies. The model provides a qualitatively correct dependence, even at lower kinetic energies where standard analytical models (such as Bethe's formula) fail. However, the quantitative values of mass stopping power are somewhat underestimated compared to experimental results. Additionally, the integral cross sections for different proton-initiated events (charge transfer, fragmentation) are calculated within the framework of classical collision theory. The results suggest that further modification of the potential may be necessary to achieve quantitative agreement with experimental observations, paving the way for further development of the eFF as an exploratory tool for the radiation chemistry of water.

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Development and Implementation of fully variational CASSCF-DFT Methods

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In this contribution, we report on the development and implementation of fully variational versions of the hybrid CASSCF-DFT methods long-range CASSCF / short-range DFT[1] and multi-configurational pair-density functional theory (MCPDFT).[2,3] In contrast to a previous implementation [4], a full second-order energy minimisation algorithm[5] is employed to achieve robust convergence of variational MCPDFT calculations.

We investigate the accuracy of both hybrid CASSCF-DFT methods for potential curves and typical open-shell molecules and transition-metal complexes.

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Li^+ Diffusion at Interfaces of Graphyne and Amorphous Silicon

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Silicon is widely studied as an anode material for lithium-ion batteries due to its significantly higher Li storage capacity than the commercially used graphite, but it lacks good cyclability. To overcome this problem, composites of silicon and different carbon allotropes are experimentally investigated, raising the question of the influence of Si/C interfaces on overall Li diffusivity in the material. We study Li^+ diffusion at interfaces of graphyne and amorphous silicon by means of ab initio molecular dynamics simulations, and we characterize the diffusive behavior of lithium in the bulk materials as well as through the interface on an atomistic level. For this purpose, we identify elementary diffusion paths in our simulation trajectories and perform nudged elastic band calculations to obtain their migration barriers, which we link to atomic charges and coordination geometries of Li along the pathways. In this way, we explain different Li mobilities in graphyne, amorphous silicon and through the interface, and highlight implications for material design.

Machine Learning to predict anharmonic frequencies and their effect in thermochemical properties of fluid hydrogen fluoride

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An accurate description of anharmonicity has been a long-standing problem of physical chemistry. Anharmonic effects play an important role in infrared (IR) spectroscopic and thermochemical measurements.

However, it is very challenging to model such behaviour due to the absence of an explicit theoretical/analytical framework. One of the most widely used computational techniques to obtain anharmonic frequencies is based on the vibrational self-consistent method (VSCF). Unfortunately, VSCF is only applicable to the systems of limited sizes typically less than 12 atoms and it is computationally very demanding.

On the other hand, statistical data analysis and machine learning (ML) are gaining momentum and are proving to be useful in many fields of science and technology.

In our recent study gradient boosting regression (GBR) and multilinear regression (MLR) algorithms were utilized to predict VSCF frequencies of various hydrogen-halides and halogenated hydrocarbon molecular clusters. Critically our descriptor set consists of a few simple harmonic-based descriptors. It is shown that GBR predicts anharmonic frequencies quite reliably and even simple MLR can improve over harmonic frequencies when mode-to-mode couplings are taken into account. Additionally, transferability to unseen systems is assessed using specific cross-validation and it is confirmed that the ML models are applicable to larger, unseen molecules.[1]

In another study we applied our ML model to predict anharmonic frequencies of large clusters (pentamers up to dodecamers) of hydrogen fluoride whereas anharmonic frequencies of smaller clusters were calculated using the VSCF method. The resulting anharmonic frequencies were used in thermochemical calculations to obtain fluid phase cluster populations and isobaric heat capacities. It was observed that the dominating structural motifs are sensitive to anharmonicity in IR frequencies.[2]

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First principles modeling of materials for optical applications

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Research in nanophotonics deals with the development of plasmonic and dielectric nanostructured materials. These so-called metasurfaces and metamaterials allow unprecedented control of light leading to revolutionary solutions in fields like beam structuring and beam steering, or coloring [1 3]. The realization of such metasurfaces and metamaterials is enabled by advances in nanofabrication techniques allowing a high design complexity at the nanoscale [4]. To design nanophotonic systems efficiently, new photonic optimization methods are required [5]. Additionally, the precise knowledge of the optical properties and especially the frequency-dependent responses of the underlying materials are of fundamental importance.

To facilitate the design of novel nanophotonic systems, we aim at the efficient calculation of the optical properties of established and novel materials from first principles. Starting from the atomistic structure of materials, we apply density functional theory (DFT) methods to calculate the optical properties (see Fig. 1). Typically, this requires the use of periodic boundary conditions (PBC) resulting in computationally demanding methods [6]. To overcome this high computational effort, we examine alternative simulation approaches without PBC to calculate the optical properties of materials efficiently [7].

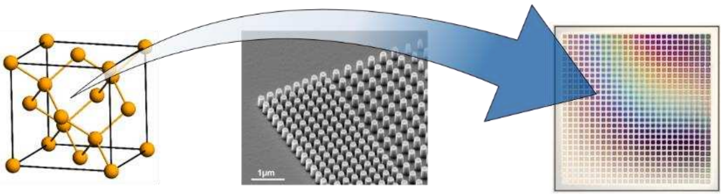

Figure 1: Starting from atomistic structures, optical properties of materials can be calculated from first principles. On this basis, the optical properties of nanophotonic systems can be calculated in subsequent studies. (Images taken from [3,8])

Acknowledgements:

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Parity-violating shifts in NMR spectra of chiral molecules containing heavy atoms

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The uniformity of chirality (homochirality) is a phenomenon found in nature for example in the prominent selection of L-amino acids in biological systems. One of many hypotheses [1] to explain this phenomenon are parity violating (PV) effects in chiral molecules, caused by the fundamental weak force that can induce an energy difference ΔE_{pv} between enantiomers [2]. PV effects should be in principle measurable in nuclear magnetic resonance (NMR) spectra of enantiomers [2,3,4] but has not yet been observed. Therefore, a chiral model system must be found, with PV effects large enough to be measurable, preferable in a typical laboratory setting. Fortunately, the PV energy shifts increases with increasing nuclear charge number [2]. Thus, we report on predicted PV effects in NMR chemical shifts and indirect nuclear spin-spin coupling constants (J-couplings) for chiral molecules containing heavy atoms. Calculations were performed within a quasi-relativistic framework using the zeroth order regular approximation (ZORA) [5] with a model potential [6] proposed by VAN WÜLLEN implemented in a modified version [4,7,8] of TURBOMOLE [9]. To estimate the quality of the chosen prediction, the calculations use quasi-relativistic two-component density functional theory, employing various exchange-correlation functionals, as well as generalised HATREE-FOCK (GHF) for reference. The parity conserving NMR chemical shifts and J-couplings are compared to experimental data.

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Aconitase: An Iron-sulfur Cluster as Redox Sensor

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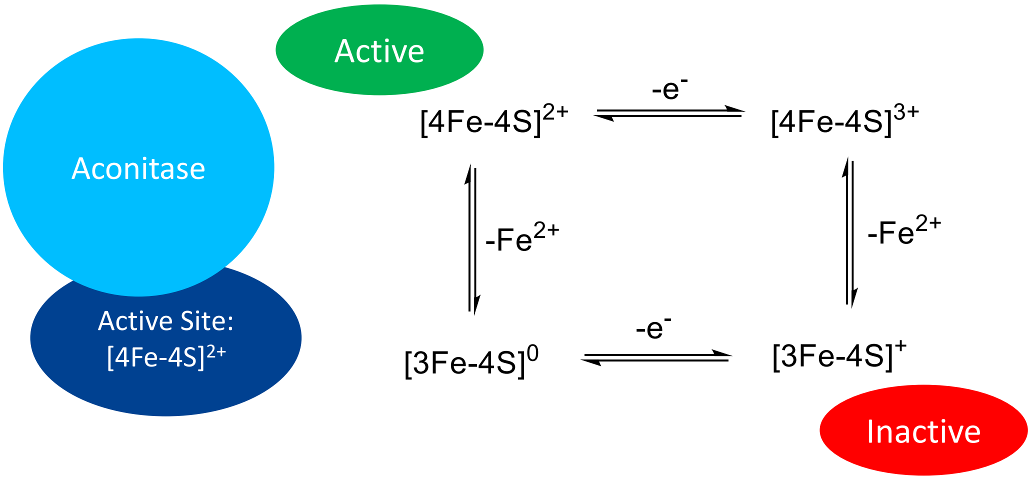
Iron-sulfur clusters play an essential role in biochemistry, participating in various tasks including the sensing of signaling molecules. One notable example is the enzyme aconitase, which contains a cubane [4Fe-4S] cluster at its active center and catalyzes the conversion of citrate to isocitrate within the citric acid cycle. Recent studies have revealed that aconitase also functions as a sensor for reactive oxygen species (ROS) to break the citric acid cycle. ROS can oxidize the [4Fe-4S] cluster, leading to the loss of one iron(II) center. This oxidation process is reversible, allowing the [3Fe-4S] cluster to be reduced and regain the iron(II) center.

To date, this process has been primarily studied experimentally. Theoretical insights could enhance our understanding of this system. While QM/MM methods are typically used to describe enzymes, these approaches often yield unsatisfactory results for the calculation of redox potentials due to the non-polarizable nature of most protein force fields. Additionally, accurately describing the electronic structure of the cluster poses a challenge. The iron centers are usually antiferromagnetically coupled, meaning that the cluster can not be described by single reference methods. However, multireference methods are really costly due to the large number of unpaired electrons at the iron atoms.

Previous calculations of redox properties using broken-symmetry DFT for [2Fe-2S] and [4Fe-4S] clusters have shown accurate results. However, the oxidized [3Fe-4S] cluster is a frustrated spin system, and no broken-symmetry state adequately describes this condition. A potentially suitable approach involves parameterizing the empirical Heisenberg-Dirac-van Vleck Hamiltonian. Diagonalization gives then the corresponding spin ground state.



Configuration Interaction in Frontier Molecular Orbital Basis for Screening the Spin-Correlated, Spatially Separated Triplet Pair State ^{1}(T...T) Formation

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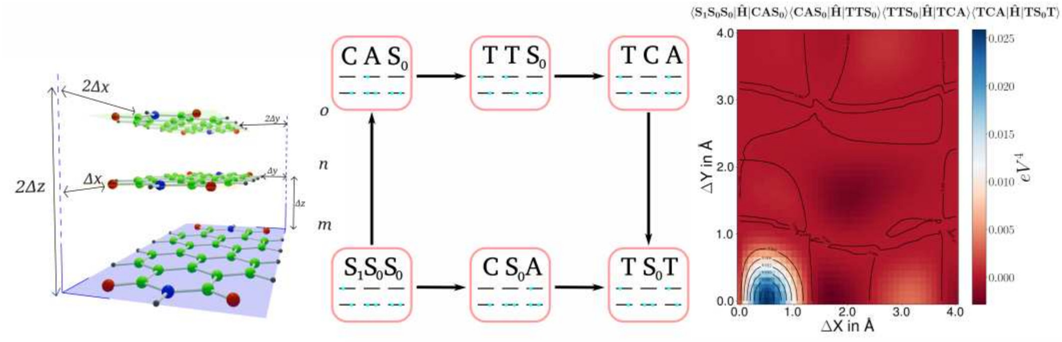
In the theoretical screening of Singlet Fission (SF) rates in molecular aggregates, the frontier molecular orbital model for dimers is commonly employed.[1] However, this dimer approach fails to account for recent experimental findings suggesting that SF progresses through an intermediate state featuring two spatially separated, spin-correlated triplets, specifically a ^{1}(T...T) state. To address this limitation, we generalize the frontier molecular orbital model for SF by incorporating separated Charge Transfer (C...T) and ^{1}(T...T) states, as well as mixed triplet-charge transfer states, thus delivering a Configuration Interaction (CI) methodology for describing SF processes in larger molecular aggregates.



The increased size of molecular aggregates necessitates the automated generation of analytic expressions for matrix elements, which we achieve using symbolic algebra. We combine second quantization techniques with the Jordan-Wigner representation of fermionic creation and annihilation operators, employing symbolic algebra to evaluate these operators as Kronecker products of Pauli spin matrices.[2][3] Spin-adapted combinations of fermionic operators are represented using branching diagrams. This method facilitates the symbolic generation of spin-adapted Slater determinants and Hamiltonian matrix elements for one- and two-electron operators, allowing the treatment of molecular aggregates with up to 10 monomer units. We demonstrate the application of this method by studying the packing dependence of competing formation pathways of the ^{1}(T...T) state in perylene bisimides, evaluating diabatic matrix elements.

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Computational Analysis of Non-Covalent Interactions in $[Ru(bpy)_3]^{2+}$ Aggregates

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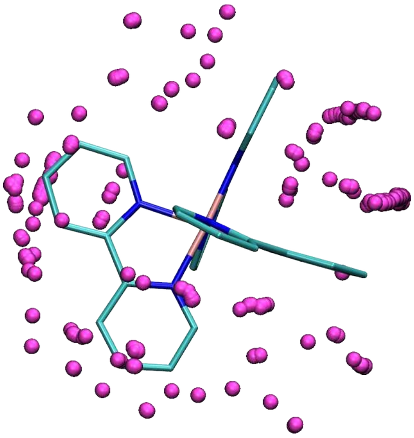
Photocatalysis represents a groundbreaking approach with vast potential applications in energy conversion, environmental remediation, and organic synthesis. By harnessing solar energy, photocatalytic processes can initiate and accelerate reactions that would otherwise require significant thermal or electrochemical energy [1]. Over the past decade, several studies have highlighted the excellent photophysical properties of the ruthenium(II) tris(bipyridine) complex, $[Ru(bpy)_3]^{2+}$, including strong absorption in the visible spectrum and efficient excited-state generation [2]. These attributes make [Ru(bpy)3]2+ a versatile and highly effective photocatalyst, particularly in processes such as carbon dioxide reduction reactions [3].

In this study, we conducted a detailed computational investigation into the conformational behavior of non-covalent aggregates involving $[Ru(bpy)_3]^{2+}$ and a series of organic substrates. Extensive conformational sampling was performed using the metadynamics non-covalent complexes and aggregates algorithm (NCI). The spatial distribution analysis of the conformers around the $[Ru(bpy)_3]^{2+}$ complex elucidated the preferred coordination sites and interaction patterns, such as π-π stacking and n-π interactions. Further TD-DFT calculations assessed the optical properties of the aggregates, revealing significant insights into the electron transfer between $[Ru(bpy)_3]^{2+}$ and the substrates, that occurs after light absorption. This comprehensive analysis provides a deeper understanding of the structural and energetic factors influencing the stability of non-covalent complexes involving $[Ru(bpy)_3]^{2+}$.



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Non–Radiative Excited–State Deactivation of Iridium Complexes

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Cyclometalated Ir(III) complexes are promising candidates for applications like photocatalysis and photodynamic therapy due to their unique photophysical properties.[1] However, understanding the factors that govern the photoluminescence efficiency and lifetime is challenging due to the involved excited–state deactivation processes. Recent research on a Ru(II) complex[2] has highlighted the importance of having a complete picture of all possible non–radiative deactivation pathways through different ^{3}MC states to correctly interpret temperature–dependent emission lifetimes. In this work, we conducted a computational study on four Ir(III) complexes, i.e., *fac*−Ir(R_2ppy)(ppz)$_2$ (R = H, F, CN or NH_2, ppy = 2–phenylpyridine and ppz = phenylpyrazole). The extensive experimental[3] and theoretical[4] data available for the *fac*−Ir(F_2ppy)(ppz)$_2$ complex allowed us to validate our protocol. The effect of electron–withdrawing (CN) and electron–donating (NH_2) substituents on the deactivation pathways have also been taken into account.[5] We provided a reaction mechanism for the non–radiative ground state recovery by characterizing the main stationary points (minima and transition states) on the triplet excited–state potential energy surfaces. Furthermore, we performed a kinetic analysis of the prominent events following photoexcitation by calculating the radiative rate constant (k_r) of the emissive state, the intersystem crossing (ISC) rate (k_ISC) from the emissive state to the ground state (S_0), and the thermally–activated non–radiative rate (k_nr). Our findings revealed that, beyond the two reported ^{3}MC minima,[4] four additional ^{3}MC structures could be potentially populated. This complexity provides opportunities to manipulate these structures to enhance or quench the lifetimes of the ^{3}MLCT state. The CN substitution leads to an enlargement of the ^{3}MLCT–^{3}MC gap by stabilizing the ligand π^* manifold but also diminishes the S_0–^{3}MLCT gap, resulting in high intersystem crossing rates and negligible emission lifetimes. In contrast, with the NH_2 substitution a balance between increasing the ^{3}MLCT–^{3}MC gap and promoting radiative deactivation is achieved, leading to higher emission lifetimes. This work offers insights into the strategic design of cyclometalated Ir(III) complexes, facilitating the rational manipulation of their photophysical properties through targeted ligand substituion.

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Problem-Specific Descriptors for Machine Learning in Quantum Chemistry

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The field of quantum chemistry has witnessed a paradigm shift with the advent of machine learning (ML) approaches, which have accelerated the exploration and understanding of molecular properties. Traditional quantum mechanical calculations, while precise, often demand extensive computational resources and time. Machine learning, by leveraging vast datasets and advanced algorithms, offers a promising alternative for predicting molecular properties with remarkable efficiency and accuracy. Especially for molecular dynamic simulations, machine-learned potentials have gained interest and are implemented in various computer codes.

Central to this success are molecular descriptors, which encode structural or topological information about the molecule in a way that is advantageous for a ML algorithm. Several established off-the-shelf descriptors such as ACSF or SOAP [1,2] are available. For specific situations however, we have found that problem-specific descriptors can outperform these descriptors while yielding smaller feature vectors and being easier to interpret [3,4].

Here, we will look into some insights and challenges encountered when designing such problem-specific descriptors. We discuss some implications of feature selection or active learning approaches when used in conjunction with these custom descriptors. We aim to provide some guidelines for studies in this area, which have the potential of enabling either more efficient calculations or insights into structure–property relationships.

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Non-covalent binding of a flexible ruthenium polypyridyl complex to DNA: A molecular dynamics study

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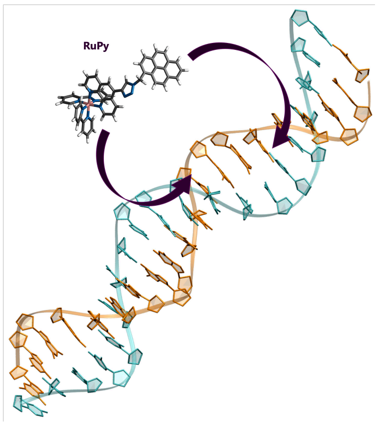
Ruthenium (II) polypyridyl complexes are attractive binders to DNA. Modifying the hydrophobicity, shape, or size of the ancillary ligands around the central ruthenium atom can induce changes in the binding mode to the DNA double helix.[1,2] We investigated the binding modes of [Ru(2,2′-bipyridine)$_2$(5-{4-[(pyren-1-yl)methyl]-1H-1,2,3-triazol-4-yl}-1,10-phenanthroline)]$^{2+}$ (RuPy for short), a metal complex featuring a flexible pyrene moiety known for its intercalative properties.[3,4,5] Classical molecular dynamics simulations were employed to gain insight into the non-covalent binding interactions of RuPy with two different 20 base pair DNA sequences, poly(dA)poly(dT) (AT) and poly(dC)poly(dG) (CG). In addition to examining the intercalation of the pyrene moiety from the major groove, the stability of RuPy–DNA adducts was investigated when the metal complex interacts externally with the DNA and with the major and minor groove pockets. The results indicate that external and major groove binding are not stable binding modes. Instead, RuPy preferably intercalates and binds in the minor groove. Unbiased MD simulations show that intercalation is enabled not only through the pyrene moiety but also via one of the bipyridine (bpy) ligands, though relative binding free energies predict intercalation of the pyrene moiety as the most stable binding mode.



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Growing Solid para-Hydrogen Matrices using Path Integrals

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Solid parahydrogen matrices have been successfully used in matrix isolation spectroscopy experiments[1,2] at low temperatures (3-5 K) to host molecular impurities. These matrices provide a gentle environment, allowing for studies of exotic molecules or labile intermediates hardly accessible by conventional spectroscopic tools. However, not much is known about how small molecules get embedded in these matrices. In order to facilitate better understanding of their quantum solvation, we use quantum simulation techniques like Path Integral Molecular Dynamics (PIMD)[3] and Ring Polymer Molecular Dynamics (RPMD)[4] to simulate this quantum solid. A crucial foundational step here is to accurately generate a pure solid para-hydrogen matrix with a realistic structure. To this end, we replicate the experimental deposition of the matrix within the simulation as accurately as possible. A new parahydrogen molecule is inserted with a random velocity towards an equilibrated, 4-layered slab of parahydrogen molecules and allowed to settle on it. This process is repeated until the desired size of the deposited matrix has been attained.

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The Role of Disulfide Bonds in Structural Stability and Dynamics of Human TFF1

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Trefoil factor (TFF) peptides are characteristic secretory peptides of mucous epithelia, having crucial roles in maintaining gastrointestinal mucosal homeostasis. These peptides possess a well-defined TFF domain stabilized by six conserved cysteine residues forming three intramolecular disulfide bonds. [1] The distinctive conformation of the TFF domain is associated with enabling the TFF peptides to adapt to different conditions in the gastrointestinal tract and making them resistant to degradation. [1,2] Despite their known resilience, the stability of disulfide bonds in the TFF peptides under reductive conditions and their relevance to the structural stability and integrity of TFF peptides remain elusive.

In this study, we examined the stability of the disulfide bonds in human TFF1 through reductive stability experiments and explored the impact of disulfide bond reduction on the domain structure and dynamics using microsecond-long molecular dynamics (MD) simulations. Our experiments revealed that the TFF1 domain is highly resistant to reduction, with complete disulfide bond reduction occurring only under the condition of an excess reducing agent. For further investigations, all atom MD simulations were performed for all possible redox states of the disulfide bonds in TFF1 (i.e., all-intact, mono-, di-, and fully-reduced states). Our results showed that, despite minor structural and conformational changes upon reduction, the overall compactness and integrity of the domain were retained in the all-intact and mono- and di-reduced states. Most disulfide bonds stayed buried within the domain, which may explain the high resistance of disulfide bonds to reduction as observed in our experiments. Only in the fully-reduced state structural changes, including a shift towards a less ordered protein fold, become obvious. Our study provides new insights into the notable stability of the TFF1 domain under reductive conditions, supporting its ability to maintain functionality in the harsh environment of the gastrointestinal tract.

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Unveiling the Catalytic Mechanism of Cezanne-2: Insights from MD and QM/MM Simulations

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Deubiquitinating enzymes (DUBs) catalyze the removal of ubiquitin (Ub) from ubiquitinated proteins, thereby regulating numerous cellular processes. The DUB Cezanne-2 (Cez2), a cysteine protease (CP), selectively cleaves K11-linked polyUb chains [1]. Dysfunctions of Cez2 have been associated with cancer and neurological disorders, underscoring the importance of elucidating its catalytic mechanism to facilitate the rational development of inhibitors [2]. In this context, molecular dynamics (MD) simulations are a powerful tool to explore the catalytical mechanism of DUBs [3].

In this study, we employed a combination of computational methods to investigate the catalytic mechanism of Cez2. AlphaFold2 and comparative structural analysis were used to predict 3D structures of both the substrate-free (apo) and diUb-bound (substrate-bound) states of Cez2. Based on the generally accepted reaction mechanism of CPs, we modelled apo Cez2 in the neutral charge state of the catalytic Cys210^0/His367^0 dyad, while diUb-bound Cez2 was modelled in both the neutral and zwitterionic charge (Cys210$^-$/His367$^+$) states of the catalytic dyad. We then performed MD simulations using the explicit TIP3P water model for 1 μs for four independent replicates for each system using the CHARMM36m force field.

Trajectory analysis revealed that substrate binding favoured the proton transfer from neutral Cys210 to His367, thus forming the zwitterionic state. This state positioned and stabilized the substrate near the catalytic center. We also identified substrate configurations likely to undergo enzymatic hydrolysis, suggesting a reaction mechanism similar to other CPs. Notably, we detected at least one water bridge between catalytic center residues Glu173 and His367 in the majority of the potential productive configurations. QM/MM (B3LYP/TZVP//CHARMM36) optimizations confirmed the reliability of these configurations and our proposed mechanism. Unlike most CPs, these configurations suggest that Cez2 performs catalysis via a Cys210-His367-water-Glu173 catalytic network. These insights support structure-based drug discovery efforts, enabling the design of selective Cez2 inhibitors.

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Moving with the Times: Electronic Decay Process Spectra Including Nuclear Degrees of Freedom

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Experimental breakthroughs have allowed for time-resolved measurements down to the femto- and attosecond scale [1], targeting the very heart of chemistry: nuclear and electronic motion. We can now directly observe how photoinduced rearrangements of electrons can significantly change nuclear degrees of freedom in atoms and molecules, up to dissociation events, as for example in Auger–Meitner decay or Interparticle Coulombic Decay (ICD) [2]. Interpreting such observations, though, requires reliable theoretical models for these ultrafast processes.

Having already established an analytical framework for the calculation and analysis of spectra for electrons which are emitted during electronic decay processes [3] focussing solely on the electronic states, we now significantly advance our approach by the inclusion of nuclear dynamics [4]. The combination of Fano's theory of resonances [5], the Born–Oppenheimer approximation and time-dependent perturbation theory yields improved analytical expressions. These permit a deeper understanding of the interaction between electronic and nuclear motion in these processes and enable us to extract characteristic energy spacings and lifetimes from complex spectral features.

To illustrate the merits of our improved description, we examine several systems with known eigenstates by calculating time-resolved kinetic-energy spectra and analyzing signal distributions, peak shapes and oscillation patterns. The selected cases encompass different bound states and also final states with a repulsive potential, which are important for ICD processes that result in a Coulomb explosion. More extensive investigations take into account both the electron emitted as a result of the decay and additionally the photoelectron the creation of which initiates the decay process [6].

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Palmatine's DNA Binding Mechanisms

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This study investigates the DNA-binding mechanisms of Palmatine, a protoberberine alkaloid, with an emphasis on its potential for photodynamic therapy (PDT) and DNA-targeted therapeutics [1]. Our research focuses on understanding the specific interactions of Palmatine with DNA, which are crucial for tuning its photophysical behavior and therapeutic potential. Previous experimental and theoretical studies have attempted to elucidate Palmatine's binding mechanisms, but the precise mode of interaction remained unclear [2,3]. In this study, we fill this knowledge gap by demonstrating that intercalation is the dominant binding mode of Palmatine to DNA. This binding mode is characterized by the insertion of planar, aromatic moieties between adjacent DNA base pairs, resulting in significant structural deformations of the DNA helix, such as elongation and unwinding.

The methodologies employed in this study include equilibrium molecular dynamics simulations to explore the conformational space of the Palmatine-DNA complex, and we utilized Umbrella sampling to generate free energy profiles, offering insights into the potential of mean force the binding process.

Our findings indicate that intercalative binding is not only thermodynamically favorable but also kinetically accessible, as evidenced by the absence of significant free energy barriers in the potential of mean force profiles. The free energy gain for intercalation is notably higher compared to other binding modes, such as minor groove binding, underscoring the enhanced stability and specificity of this interaction. This stability is attributed to strong π-π stacking interactions, van der Waals forces, and hydrogen bonding, which collectively contribute to the free energy preference for intercalation.

The comprehensive analysis provided by this study not only advances our understanding of Palmatine's DNA binding mechanisms but also highlights its potential as a therapeutic agent in PDT. By elucidating the specific interactions and stability of Palmatine when intercalated with DNA, we pave the way for optimizing its therapeutic applications, including selective generation of singlet oxygen and enhanced efficacy in cancer treatment.

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Performance of CASSCF Linear Response in ORCA 6 and Implementation of Gauge-Including Atomic Orbitals

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Many static molecular properties can be described by derivatives of the energy with respect to perturbations to the system. Accurate modelling of these derivatives presents challenges for systems whose underlying electronic structure is difficult to model. With systems such as transition metal complexes (TMCs), one often turns to multireference (MR) methods, such as the complete active space self-consistent field (CASSCF) method.

This contribution focuses on the performance of the CASSCF linear response (LR) method, first developed by Vahtras *et al.* [1] and now available in ORCA 6 [2]. Results of the LR method applied to several well-studied prototypical 3d TMCs show a similar accuracy for the EPR **g**-tensor (a second-order property in non-relativistic wavefunction theory) compared to alternative approaches for property calculations in ORCA at the CASSCF level—the effective Hamiltonian (EH) and quasi-degenerate perturbation theory (QDPT) approaches. A notable advantage of LR is that the wavefunction response implicitly includes the (untruncated) infinite sum-over-states, whereas other approaches must truncate this summation. Explicit consideration of the low-lying excited states is therefore avoided with LR, removing the decision of the number of roots to include in the summation when calculating CASSCF properties without sacrificing on accuracy. However, despite comparable accuracy of the different approaches, the deviation from experiment remains significant in many cases. This implementation in ORCA serves as the infrastructure upon which further developments in MR LR theories will be built. These methods, such as NEVPT2 LR, aim for higher accuracy by including dynamic correlation effects.

Currently, magnetic properties are only available in CASSCF without gauge-including atomic orbitals (GIAOs). Although this is not of large importance for the EPR **g**-tensor, this has a significant effect on properties such as NMR shieldings. As such, GIAOs are currently being implemented and we present here a formalism for the efficient handling of GIAO right-hand side terms in CASSCF LR.

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On the Predictability of Parity Violating Energy Differences in Unsatured Chiral Molecules

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The weak interaction violates parity, which is otherwise preserved by the other known fundamental interactions in nature. In chiral molecules, the effects induced by parity violation are quite pronounced, leading to a small albeit non-negligible energy difference between the corresponding enantiomers. While it remains an experimental challenge to quantify the influence of parity violation in such molecules, the expected effect sizes can be predicted theoretically within the framework of electroweak quantum chemistry [1,2]. One can yet wonder if there is a scope to develop a simplified theoretical model that predicts the energy difference between two enantiomers without explicit calculations. To investigate the same, we focused on few different unsaturated chiral compounds as our candidates. This presentation encapsulates the progress and the conclusions we have attained thus far.

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Quantum chemical studies on nitrogen reduction and hydrogen evolution reactions on porous C-N containing compounds

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In this work, the electrochemical Nitrogen Reduction Reaction (NRR) to NH_3 on a so-called single Atom catalyst (SAC) is investigated. To catalysts, namely C_2N and H-PHI, are chosen, and combined with different transition metals, Ag, Au and Fe, and the alkali metal K. For each of the systems, the reaction mechanisms of the NRR are investigated with the help of periodic density functional theory and Nørskov's Computaional Hydrogen Elektrode Model [1]. The thermodynamics of the different reaction steps, charge transfer and finite pH are considered to compute overpotentials for the reaction. Further, the Hydrogen Evolution reaction (HER), which is considered to be a competitive reaction to NRR, is investigated. The Faraday Efficiency for the NRR on the studied catalysts was estimated. The results are compared to experiment findings[2].

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Projection-Based Subsystem TDDFT for Bridge-Mediated TEET Couplings

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Subsystem time-dependent density-functional theory (sTDDFT) combined with projection-based embedding (PbE) has proven to be an effective fragment-based approach for the calculation of linear-response properties [1]. It is capable of both reproducing supermolecular excitation energies and providing electronic couplings for local and charge-transfer excitations [2]. We have recently extended this formalism to the description of triplet excitation-energy transfer (TEET) couplings in multichromophoric systems [3]. This includes analyses of environmental effects, such as explicit solvent molecules surrounding the interacting chromophores for short inter-molecular distances, and the role of bridging solvent molecules in longer-range TEET.

Building on these insights, this study aims at performing an in-depth analysis of TEET mediated by organic molecular bridges. Leveraging the ability of PbE-sTDDFT to describe strongly interacting subsystems, including those connected by covalent bonds [4], we explore intra-molecular bridge-mediated TEET processes in covalently bonded systems, such as the benzophenone–fluorene–naphthalene (Bp–F–Nap) system [5] or π-stacked polyfluorenes [6, 7]. Our focus is on calculating bridge-mediated couplings of solvated dimers and polychromophoric systems, considering different subsystem partitioning strategies to capture the two transfer channels of TEET for bridged chromophores: the single-step tunneling (superexchange) and multistep hopping pathways, in systems such as Bp–F–Nap molecules [5].

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Automatic orbital pair selection for multi-level local coupled-cluster based on orbital maps

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The domain-based local pair natural orbital method with coupled-cluster single, doubles (DLPNO-CCSD) with perturbative triples (T_0) is one of the successful local approximations to the "gold standard" [1, 2] of quantum chemistry, i.e., the CCSD(T) method. It significantly reduces computational costs while maintaining high accuracy [3, 4]. In this work, the DLPNO-(T_0) method is extended to a multi-level approach for studying proton transfer reactions [5], incorporating a fully-automatized orbital mapping which is enabled by a newly developed atom mapping algorithm. Building on the DLPNO-CCSD framework, where the orbital pair energies for strongly correlated orbital pairs are calculated and prescreened using semi-canonical Møller–Plesset (MP2), multi-level DLPNO-(T_0) only employees orbital pairs energies that exhibit significant changes along the reaction coordinate. Therefore, a pair-selection algorithm is applied in which the energy of specific orbital energies are compared to a predefined threshold. The orbital triples are then mapped along the reaction coordinate to the different structures A and B (like reactant and product), as in the previously work from our group, similar to the multi-level method with DLPNO-CCSD [6]. For the DLPNO-CCSD energies in the multi-level case, care is taken to ensure that the orbital pairs between two structures along a reaction coordinate are approximately the same by mapping, likewise for DLPNO-(T_0) for orbital triples. The aim of these approximations is to calculate only strongly correlated triples for all structures and to neglect triple energies which do not significantly change between different structures. In other words, this approximation focuses on contributions relevant for changes in relative energies. An advantage of this method is the computational effort in terms of computational time and memory usage.

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CAAC-4 as acceptors in TADF-exhibiting coinage metal complexes? Theoretically feasible!

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In the realm of thermally activated delayed fluorescence (TADF)-exhibiting coinage metal complexes, the CAAC-5—Cu/Au—carbazolate complexes shine as an exemplary beacon. [1] Key features are small energy gaps of the lowest singlet and triplet excited states ($\Delta E_{(S\text{-}T)}$), efficient spin–orbit coupling and large fluorescence rates. Comparative studies assessed the steric demand and the rigidity of the acceptor NHC as crucial in suppressing the nonradiative decay and achieving 100 % luminescence quantum yield. [2] Here, we computationally examine a series of carbene coinage metal amide complexes containing a novel CAAC-4 as potential TADF candidates.

To this end, we employ the combined DFT/MRCI method [3] to investigate the energy landscapes. It performs well in describing the sought charge transfer (CT) states due to a balanced description of dynamic correlation from DFT orbitals and static correlation from a CI treatment. Together with the spockCI and VIBES program, fluorescence, phosphorescence and intersystem crossing (ISC) rate constants can be quantified.

The desired ligand-to-ligand CT (LLCT) states [4] are found as the lowest excited states, with metal-to-ligand CT (MLCT) states lying closely above. All examined complex display potential for TADF-emission due to small $\Delta E_{(S\text{-}T)}$ values and substantial ISC rates. Despite emission in the red and infrared region, the fluorescence rate constants remain high (10^7 s^{-1}). The trends within the series of the donor ligands and the metal atoms allow to determine a best-performing candidate. Synthetic work is in progress to assess the theoretical predictions.

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Electronic and magnetic structure of two-dimensional transition metal dihalides

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Two-dimensional materials with unique electronic properties have been the focus of intense research due to their large potential for nanoelectronic devices. Magnetic ordering in such systems increases the range of possible applications and, consequently, has attracted increased attention [1]. A particularly promising class of materials are transition metal halides. In particular, MnI_2 is a multiferroic material, in which electric polarization and magnetization are coupled [2]. Understanding the atomic scale structure and its effect on electronic and magnetic properties is vital to optimize such materials for future applications.

Combining several microscopy experiments with density functional theory (DFT) calculations (in particular, PBE+U), we investigate the growth of MnI_2 on a Ag(111) surface. Calculated structural parameters agree with those obtained from Kelvin probe force microscopy. The MnI_2 islands grow in a truncated hexagonal shape with alternating short and long edges, which also vary in their contact potential differences. The calculated local work function and relative stabilities of different edge terminations suggest that the islands are zigzag-terminated. These results demonstrate the electronic properties of the MnI_2 layers and are the foundation for further experimental and theoretical work on their magnetic structure.

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COMPUTATIONAL INSIGHTS IN EXPLORING LIGAND AND SOLVENT EFFECTS ON THE REACTIVITY OF NON-HEME IRON-OXO BIO-MIMETIC CATALYSIS

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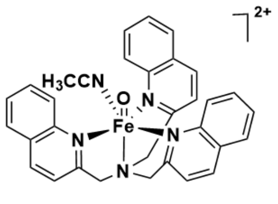
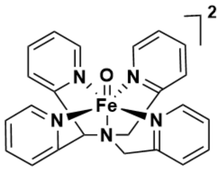
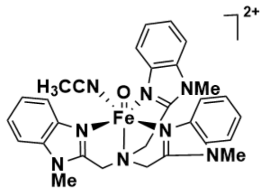
Non-heme iron-oxo bio-mimetic catalysts have emerged as promising bio-inspired candidates for various reactions, including oxidation, hydroxylation (specifically hydrogen atom transfer or HAT), and epoxidation. Besides the experiment, computational studies have recently become a vital tool in designing and optimizing such catalysts. It has been shown that the reactivity of non-heme iron-oxo bio-mimetic catalysts is strongly dependent on the electronic structure of the iron centre, which can be tuned by modifying the ligands. Additionally, solvent effects may significantly impact the reaction rate and selectivity of these catalysts [1,2]. Detailed information on the reactivity of such bio-mimetic complexes is required for the development of more efficient and sustainable catalysts for industrial and environmental applications. In this work, we present our computational results on the investigation of the electronic structure and reaction mechanisms of three non-heme iron-oxo bio-mimetic catalysts. To do so, we use different computational approaches, including ab initio single- and multireference methods (e.g., LUCCSD(T), DLPNO-CCSD(T), PNO-CCSD(T), and DMRG-CASPT2) to explore the catalytic activity of these systems and to elucidate the role of the ligands and solvent on their reactivity.



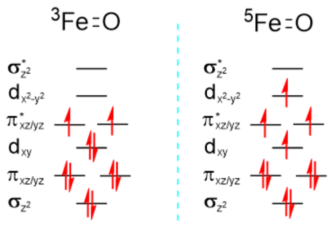
$[Fe^{IV}O(TQA)(CH_3CN)]^{2+}$



$[Fe^{IV}O(N_4Py)]^{2+}$



$[Fe^{IV}O(Me_3NTB)(CH_3CN)]^{2+}$



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Versatile Algorithm for Protein Bond Discovery: NOS Linkages as a Case Study

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Characterizing and unveiling new chemical bonds and interactions in proteins are essential due to their impact on deepening our understanding of these systems and their accompanying applications, e.g., in drug design and protein engineering. Despite the considerable impact of such investigations, to the best of our knowledge, no systematic framework is available to carry out such studies.

In this paper, we propose a machine-learning-based roadmap to automate discovering chemical bonds and interactions in proteins. Our method comprises (i) the construction of targeted datasets for specific chemical bonds, employing rigorous criteria including atom types, interatomic distances, and protein structure resolution, and (ii) exploration of this high-dimensional data using machine learning techniques to identify effective descriptors and predict candidates hosting certain chemical bonds in their structures.

To demonstrate the applicability of our approach, we integrate our predictive modeling method with experimental observations for covalent nitrogen-oxygen-sulfur (NOS) linkages between lysine and cysteine (Lys-NOS-Cys). Particularly, we have unveiled 78 new NOS linkages beyond the previously known lysine-cysteine cases [1, 2] for lysine-cysteine, glycine-cysteine and arginine-cysteine pairs from an analysis of 170,127 X-ray determined protein structures. Although we focus on exploring NOS linkages, our proposed method can characterize any chemical bond or interaction, which paves the way for discovering various chemical connections within protein structures.

This systematic, machine learning-driven framework represents a significant step forward in automating the discovery and characterization of chemical bonds in proteins, offering new insights and opportunities for innovation in structural biology and related fields.

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Protein Environment Design by Combining Equivariant Neural Networks and Generative Models

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Protein design via noncanonical amino acids (NCAAs) holds potential for improving specific interactions that is useful, for instance, in cancer therapy, but the vast chemical space of NCAAs and the computational demands associated with their investigation significantly limits any design. In this work, we leverage deep learning, in particular a MACE model (Message Passing Neural Network for Atomic Cluster Expansion) [1], trained on da dataset that contains density functional theory-based interaction energies of two million amino acid - NCAA pairs. These NCAAs were designed using generative learning. By using the MACE model to subsequently screen the interaction energies between each NCAA and the rest of the protein-side chains, it is possible to bias the generative model to improve the design [2,3]. The best candidates are analyzed with statistical tools tested against classical bioninformatics tools.

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Expanding the Clip-and-Cleave Concept: Approaching Enantioselective C–H Hydroxylations by Copper Imine Complexes using O_2 and H_2O_2 as Oxidants

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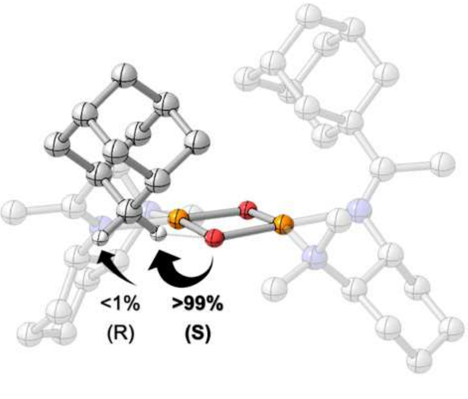
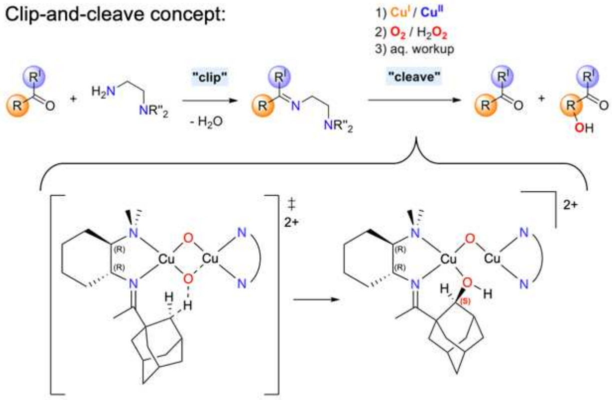
The regio- and stereoselective copper-mediated hydroxylation of non-activated aliphatic C–H bonds, initially reported by Schönecker, [1] has evolved into an enormously useful synthetic tool. [2,3] Continued research along these lines has led to the development of the so-called clip-and-cleave concept [4,5] that enables aerobic regioselective oxygenations of substrate ketones and aldehydes in a broader fashion. Recently, Schindler expanded this concept towards enantioselective transformations and showcases the regio- and enantioselective hydroxylation of 1-acetyladamantane to afford (S)-1-acetyl-2-adamantol with enantiomeric excess exceeding 98%. Experimental UV-Vis measurements suggest the presence of a transient bis-μ-oxo $[Cu_2O_2]^{2+}$ entity. [6] We present a comprehensive quantum chemical study exploring the underlying reaction mechanism and electronic structures of key species involved via broken-symmetry density functional theory. Analysis of Intrinsic Bond Orbitals and Natural Localized Molecular Orbitals along the reaction trajectory suggest a sequence of Hydrogen Atom Transfer, intramolecular electron transfer and OH^- rebound during the key reaction step. The results align well with experimental data and provide a detailed rationale for the observed selectivity.





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Spin-Forbidden Chemistry: The Case of Azobenzene

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Chemical reactions in excited states are typically initiated by photons and the field is well-developed due to the fast development of laser technologies. Little is known about electron-induced chemical reactions. Electron impact can excite molecules into spin-forbidden states, potentially altering their reactivity in an unusual manner. We chose the prototypal photosensitive molecule azobenzene as a model system for a theoretical study of electron reactivity. We describe azobenzene transformations in electron-induced excited states, investigate the effect of the solvent (methanol) on the processes, and compare the results with those obtained from light-induced phenomena. The excitation processes were described by calculating the electron energy loss spectra [1] and the characterization of molecular orbitals was conducted with density functional theory. Non-adiabatic QM/MM simulations with Landau–Zener surface hopping technique were used to study the relaxation processes after excitation into (i) the two lowest triplet states (T1, T2), directly available after the electron interaction, and the simulations with Tully surface hopping technique [2] were used to study (ii) the two lowest singlet states (S1, S2), primarily available after photochemical activation. Surprisingly, while the light-induced excitation led to the isomerization reaction as expected, electron interaction caused the molecule to dissociate into two phenyl radicals and a nitrogen molecule.

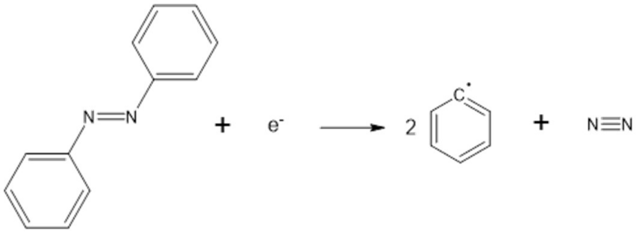

Figure 1: Electron-induced dissociation reaction

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Toward the improvement of vibronic spectra and non-radiative rate constants using the vertical Hessian method

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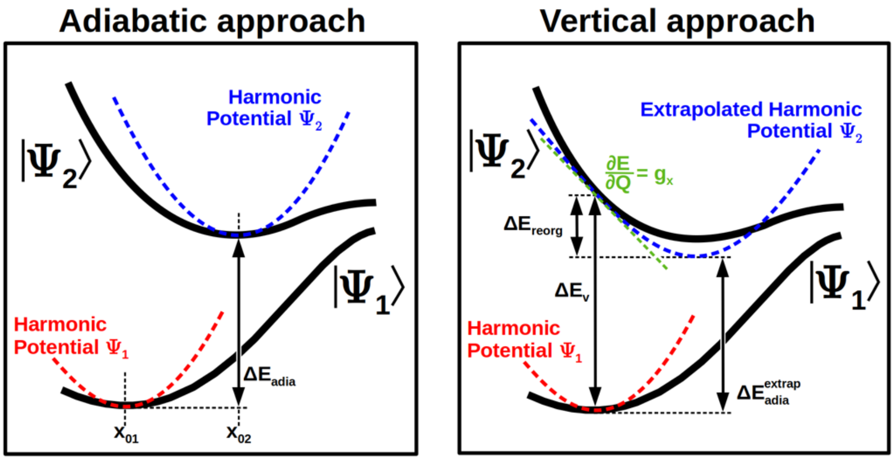
For the computation of vibrationally resolved electronic spectra, various approaches can be employed. Adiabatic approaches simulate vibronic transitions using harmonic potentials of the initial and final states, while vertical approaches extrapolate the final state potential from the gradients and Hessian at the Franck–Condon (FC) point, avoiding a full exploration of the potential energy surface (PES) of the final state. Our implementation of the vertical Hessian (VH) method has been validated with a benchmark set of four small molecules, each presenting unique challenges such as complex topologies, problematic low-frequency vibrations or significant geometrical changes upon electronic excitation. We assess the quality of both adiabatic and vertical approaches for simulating vibronic transitions. For two types of donor–acceptor compounds with promising thermally activated delayed fluorescence (TADF) properties, our computations confirm that the vertical approaches outperform the adiabatic ones. The VH method significantly reduces computational costs and yields meaningful emission spectra, where adiabatic models fail. More importantly, we pioneer the use of the VH method for the computation of rate constants for non-radiative processes, such as intersystem crossing (ISC) and reverse intersystem crossing (rISC) along a relaxed interpolated pathway of a donor–acceptor compound.



Adiabatic approach

Vertical approach

On the poster I will highlight the potential of the VH method to advance computational vibronic spectroscopy by providing meaningful simulations of intricate decay pathway mechanisms in complex molecular systems. I will compare the computational results of various different approaches and show advantages and disadvantages. [1]

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[1] Böhmer, T., Kleinschmidt, M., Marian, C. M. Toward the improvement of vibronic spectra and non-radiative rate constants using the vertical Hessian method. *J. Chem. Phys.* 2024, submitted.

Incorrect dynamics near through-bond QM/MM boundaries is rescued by respecting force field Coulomb exclusions

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QM/MM simulations have been established as a major method in computational enzymology. They are used to model chemical rearrangements within enzymatic active sites at the quantum mechanical level of theory, while keeping most of the simulated system under much simpler classical treatment to achieve reasonable computational speed. In the community, it is common to tie the reliability of the QM/MM-powered inference about real biomolecules to the level and intrinsic accuracy of the QM method used. However, we have recently demonstrated that the QM/MM covalent coupling itself may invalidate any QM/MM molecular dynamics experiment irrespective of QM description. [1] We presented concrete examples of cases where incorrect treatment of boundary electrostatics results in qualitatively different inference.

Here, we expand on the issue by addressing incorrect descriptions of near-boundary dynamics. We showcase that the use of the “amber” force field term retainment scheme dramatically and qualitatively distorts bond rotations. For the “classical” scheme, we report systematic shifts in distributions of angles and dihedrals involving one or two QM atoms. We uncover that the unifying reason for this artifact is the neglect of excluding covalently neighboring atoms from calculating non-bonded electrostatic interactions, a notion along which all modern force fields are parameterized. This results in 1-2 and 1-3 interactions between QM and MM atoms that should be absent, and in 1-4 interactions that are not properly scaled down, as is common in some force fields including the widely used Amber family. We then show how supplementing the calculations with counteracting potentials restores the correct near-boundary dynamics and structure, and provide direct recipes and code for creating such.

Our results highlight a universal critical issue in all additive-type QM/MM simulations with a profound negative impact on the quality of scientific inference. The guidelines we provide help to minimize the disruptive effect of such artifacts to power up more accurate and better interpretable computational experiments.

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Photochemical ring-closure reaction: Mechanism and product configuration

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A photochemical organic reaction mechanism is investigated with regard to a five-membered ring-closure and the absolute configuration of the chiral centers in the product. As a start, a qualitative Hückel Molecular Orbital analysis of the associated π-systems is performed and an orbital correlation diagram constructed. Subsequently, density functional theory is applied to obtain a state correlation diagram and more detailed information on the mechanism of the ring-closure, since intermediates of the proposed mechanism can not be isolated in the laboratory. Finally, the configuration of the chiral centers in the product molecules is determined. Results from the computational study are compared to experimental observations.

Towards Battery Simulations on a Quantum Computer using Quantum Embedding

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[3] University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm/DE

Advances in quantum computing hold the potential to revolutionize the simulation of complex materials, including those critical for next-generation batteries. However, the complexity of typical battery materials is still prohibitive for exact simulations on current or near-term quantum hardware.

One promising approach is the use of quantum embedding techniques, which enable the treatment of correlated electronic states in large systems by partitioning them into manageable subproblems. We explore the application of Density Matrix Embedding Theory (DMET) [1,2] as a quantum embedding method to bridge classical and quantum computational resources [3]. Within DMET, few correlated degrees of freedom can be solved on the quantum computer, while the remaining part is solved with classical methodology, self-consistently connected to the quantum part. This approach paves the way for real-world problems from battery simulation to profit from near-term quantum computers.

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Investigation of Thermodynamic Properties of Molecular Crystal Polymorphs

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Polymorphic stability is one of the critical considerations in drug development, which requires accurate energy estimations to determine the most stable structure. Molecular crystal polymorphs exhibit very small energy differences, often less than 1 kcal/mol. In addition to the electronic energy, relative polymorphic stabilities are influenced by thermodynamic conditions. Therefore, a comprehensive understanding of relative thermodynamic stability is essential for the successful description of crystalline compounds. Consequently, to determine the most stable polymorph, zero-point and thermal effects should be incorporated in the calculations. To grasp the change of the unit cell volume with temperature we use the quasi-harmonic approximation (QHA) [1,2], where vibrational free energies are calculated at several unit cell volumes around the equilibrium geometry, allowing to track the impact of thermodynamic conditions on the relative stabilities of polymorphs. From the electronic structure side, hybrid density functionals with large basis sets are usually preferred to get more reliable results, however, for periodic systems such calculations are often not feasible. Therefore, we use a multimer embedding approach [3], where multimer energies, calculated with a hybrid functional up to trimers (PBE0+MBD), are embedded into a cheaper GGA functional (PBE+MBD). Combining all the above methods, we finally arrive at the best possible polymorph stability rankings, including their phase diagrams.

As part of the COST action CA22107 (BEST-CSP), we compare our state-of-the-art theory with several experimental results. In this particular case, we computed phase diagrams for the orthorhombic (α) and monoclinic (β) polymorphs of benzophenone. Moreover, we showcase the relative lattice energies of five other compounds calculated via multimer embedding: 4-hydroxyacetophenone, metacetamol, picolinamide, phenylpiracetam, and sulfamerazine.

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Assessing Solid Catalysts with Ionic Liquid Layers (SCILL) from Molecular Dynamics Simulations: On the Role of Local Charge Polarization

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To enhance heterogeneous catalysis on metal surfaces, the addition of ionic liquids (IL) provides additional tuning options - which led to the increasingly prominent SCILL (solid catalysts with ionic liquid layer) concept. Our atomistic scale understanding of SCILL systems benefits from modelling and simulation in multiple ways. While small (sub-)systems may be characterized by quantum approaches, molecular mechanics (MM) models offer the evaluation of large and complex systems. This includes dynamic aspects such as the self-organiztion of the entire IL layer on the catalyst. While conventional MM readily describes IL arrangements on flat metal surfaces,[1] the assessment of IL deposition on substrate-supported metal nanoparticles calls for careful analyses of the locally induced charges. For this purpose, we demonstrate the application of the QEq model for unravelling i) metal polarization upon IL association, ii) charge transfer between substrate and supported nanoparticle species because of contact voltage and iii) externally applied voltage.[2] On this basis, up to 100 nm scale simulation models offer the assessment of complex SCILL systems used for state-of-the-art (electro-)catalyses.

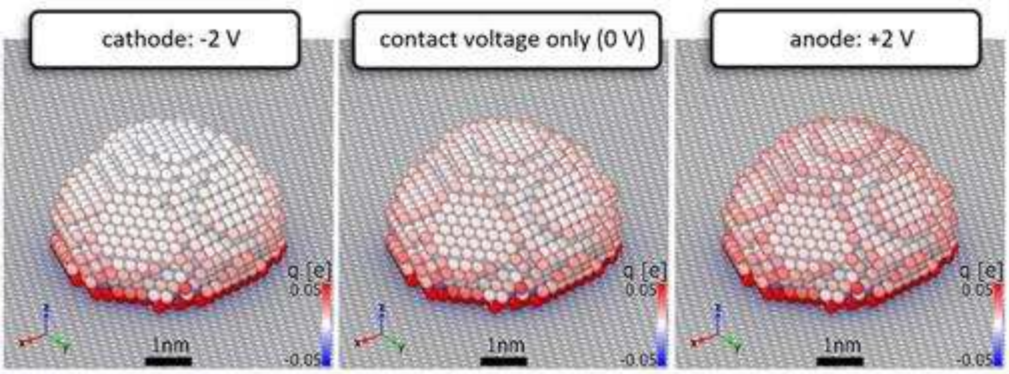

Fig. 1: Pd nanoparticle supported on a graphite electrode before IL association. Local charge is illustrated by a color code.[2]

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Model Reduction in Quantum Dynamics of Photoactive Transition Metal Complexes

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Photodynamical simulations of transition metal complexes are often challenging due to the high density of electron-vibrational states with numerous non-negligible nonadiabatic and spin-orbit couplings. Overall, the dynamics after photoexcitation is characterized by rapid transitions between states of different character and multiplicity. The kinetic rates may be deduced from transient absorption experiments, however, a more detailed analysis is prevented by the complexity of the systems. Quantum dynamics simulations based on a pre-computed model Hamiltonian may provide such insights. To reduce the complexity, one is tempted to identify couplings or vibrational modes most relevant to the dynamics. Here, we address challenges beyond such model reduction for an exemplary transition metal complex.

Using multi-layer multiconfigurational TDH with a model LVC Hamiltonian, we have studied the laser-driven dynamics [1] of the exemplary Fe(II) homoleptic complex which was previously studied spectroscopically and theoretically including surface-hopping simulations [2]. The reduction of the number of electronic coupling parameters was explored, followed by a reduction of the number of vibrational modes. The structureless linear absorption spectrum was not useful in this respect, and, therefore, the TDH dynamics results were analyzed instead. Quantum dynamics is influenced by a large number of small couplings, which prevents the identification of a representative model with just a few degrees of freedom. For the thus established model, still containing 70 vibrational modes and thousands of coupling terms, the effect of correlations on the dynamics was investigated. Here one would have expected that given the nature of the model, effects beyond the mean-field description play a minor role only. Surprisingly, only the inclusion of correlations brings the dynamics in good agreement with previously reported TSH simulations and experiments. We expect that the challenges for model reduction discussed here for an exemplary case are typical for similar TM complexes.

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Assessment of post-SCF Methods with Localized Basis Sets for Periodic Systems using FCI-QMC

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Periodic systems require a special treatment of the Coulomb operator for the description of electron-electron-interactions. In CP2K[1], Hartree-Fock energies are calculated with a truncated operator[2] affecting the accuracy of post-Hartree-Fock calculations. We benchmarked the different available post-SCF schemes (RPA-AXK[3], rPT2[4], MP2[5]) with accurate FCI-QMC[6,7] calculations to investigate the effect of these approximations. Our results confirm that in the given regime, post-SCF methods lead to too low energies, artificially stabilizing periodic systems.

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Spin Dynamics in the Basis of Irreducible Spherical Tensors

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The past decade heralds the gradual change of the ultrafast paradigm in physics and chemistry from the femtosecond to subfemtosecond and even a few tens of attoseconds domain. The fascinating growth in the number of ultrafast phenomena studies is due to the establishment of new sources such as X-ray free-electron lasers and high harmonic generation setups that give access to dynamics at electronic time scales. To keep apace with experiments, accurate and efficient theoretical methods need to be developed.

In my contribution, I will present recent developments of the density-matrix-based time-dependent restricted active space configuration interaction method (ρ-TD-RASCI) to compute the ultrafast electron dynamics [1,2] which is implemented in the form of the RhoDyn module in OpenMolcas. In particular, the use of irreducible spherical tensors (state multipoles) will be demonstrated for the ultrafast spin dynamics in the core-excited transition metal complexes, and a possible reduction of the computational complexity will be discussed [3].

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Effective Potentials for DFT-Studies of Photoacids

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We explore the proton dynamics of photoacids, which are molecules that become acidic when they are electronically excited. Since AIMD simulations require extensive sampling in the excited state, applying an optimized effective potential to the T1 state, so that it mimics the S1 state, could increase computational efficiency for these simulations. We investigate the changes in orbitals/densities for the T1 and S1 transitions for phenol and naphthol derivatives, in order to direct the way the effective potentials are applied.

Machine Learning Potentials for Molecular Dynamics Simulations of Water in Confinement

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The dielectric constant of water in nanoconfinement becomes anomalously low compared to bulk water due to structural order and reduced motion of the confined water molecules. [1] Theoretical investigations are usually carried out with empirical potential-based molecular dynamics simulations [2], which give qualitative results in agreement with experiments, but the results cannot fully explain the origin of the low dielectric constant. Ab initio molecular dynamics (AIMD) simulations, based on first-principles calculations like density-functional theory, provide accurate simulations but have a drawback of high computational cost. Machine learning potentials (MLPs), trained on AIMD simulations, have gained popularity recently, producing simulations with AIMD-like accuracy and with only a fraction of the computational cost. Neural Network Potentials are generally the model of choice in the literature to simulate (confined) water systems [3,4], while other models are seldom used.

In this work, MLPs trained on-the-fly with a Bayesian linear regression-based model, implemented in the Vienna ab initio simulation package VASP [5-7], are used to generate trajectories for bulk water and for 2D confined water with various graphene sheet distances. The trained MLP can simulate water densities and graphene sheet distances not included in training with good accuracy. Structural properties, like radial distribution functions and density profiles, of the generated trajectories match with AIMD reference simulations. The long-term goal of this work is to train a MLP which can generate trajectories for larger sheet distances with high accuracy and low cost to investigate the dielectric properties of nanoconfined water.

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Conformational Profile of α-Gal and Structural Basis of its Immunological Response

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Created by linking different monosaccharides through glycosidic bonds, oligosaccharides have a rich and complex conformational landscape, controlled by the glycosidic linkage, each ring's shape, and the orientations of the hydroxyl groups.[1] Disaccharides are the smallest member of this family. Understanding their conformational profiles is essential for understanding physicochemical behavior as well as biological functions. In this study we explore the conformational profile of galactose-α-1,3-galactose (α-Gal), which is responsible for tick bite induced mammalian meat allergy (i.e., Alpha-gal syndrome), cetuximab-induced anaphylaxis, and a possible risk factor for coronary artery disease.[2] Using classical MD simulations with explicit water, we found *three* distinct population regions in the Φ vs. Ψ plot. On the other hand, the Ψ dihedrals of conformers generated by CREST[3] (Conformer–Rotamer Ensemble Sampling Tool) are more flexible, forming *two* islands after optimizations with the R^2SCAN0-D4[4] functional. The difference between MD and CREST/R^2SCAN0-D4 conformer ensembles may be due to the use of an implicit solvation model with the latter method. However, the largest population of the structures from both methods belong to the same region in Φ vs. Ψ plot. To explore the interaction of α-Gal with the antibody, we started from the crystal structure of α-Gal bound to the M86 antibody[5] and constructed three QM/MM models. For all three models the Φ, Ψ, and the glycosidic bonds and angles agree well with the reported crystal structure. Intermolecular NCI analysis[6] reveals multiple stabilizing van der Waals interactions and hydrogen bonds of varying strength between α-Gal and its binding pocket. The DLPNO-CCSD(T)[7] level local energy decomposition (LED) shows that hydrogen bond interactions play a much more significant role than CH-π interactions in binding α-Gal to the M86 antibody. Further quantitative analysis of hydrogen bonds using QTAIM[8] and other methods[9] indicates that these bonds between α-Gal and the protein matrix or surrounding water vary a lot in strength, from –11.48 to –1.44 kcal/mol.

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Uncovering molecular secrets of deep eutectic solvents

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Deep eutectic solvents are mixtures of two compounds characterized by a melting point significantly below the predicted ideal eutectic melting point. Among the most used components for the preparation of deep eutectic solvents is choline chloride, which is produced on the megaton scale and has applications as an animal food supplement. Choline chloride can form eutectic mixtures with a wide range of organic compounds close to room temperature.

We studied the capabilities of polarizable force fields to model these systems.[1] Introducing an additional damping function was essential during force field development to screen the charge interactions between the chloride anion and the hydroxyl group of the cation in our developed approach. However, parameters of the non-bonded Thole screening function must be fitted against the first-principles molecular dynamics simulations. Therefore, invariant and equivariant machine learning interatomic potentials were studied next.[2,3] The equivariant Allegro model in combination with an active learning scheme requests solely few thousand DFT calculations of a small system to simulate systems with several thousand atoms on the ns-time scale on a single GPU-node within one day. This facilitates reliable investigation of dynamical properties since at least five simulations are recommended to obtain a well converged average value.[2] Thus, machine learning interatomic potentials provide reliable structural and dynamical properties at a fraction of cost of first-principles molecular dynamics simulations.

Our studies on the unique nature of deep eutectic solvents revealed that the incorporation of the chloride anion into the hydrogen bond network of the urea derivative is strongly correlated to the non-ideal mixing behaviour of choline chloride systems.[4] Furthermore, we observe close contacts between two lithium atoms bridged by oxygen atoms of the organic compound in lithium bistriflimide systems.[3] Please note, the close Li-Li-contacts play a minor role in classical force field simulations, even with scaled charges. This highlights limitations of common classical force fields compared to approaches with forces on the accuracy of density functional theory calculations.

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Spicy – A Functional Computational Framework for Multilayer Fragment Methods

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Modern ab initio methods provide unprecedented accuracy for a variety of chemical problems. However, their steep scaling with system size often limits their applicability to relatively small molecules. Even though the rise of linear scaling ab initio methods allows their application to systems with thousands of atoms, important aspects remain unsolved. First, a suitable computational method for both the desired physical property and the type of chemical system needs to be chosen. Not all of them are linearly scalable. Second, the crossover, where linear scaling methods become more efficient than their conventional counterparts, can arise at already too high computational costs to study dynamic phenomena.

In this contribution, we present our program *Spicy*, a computational framework for multilayer fragment methods. Combining the concepts of multilayer methods, where each layer is treated at a different, suitable level of theory, and fragment methods, breaking down large systems into smaller parts and combining their results, Spicy implements the multilayer fragment combination range (ML-FCR) formalism. Without altering the underlying computational methods, a flexible partitioning of the system and assignment of suitable methods to each fragment is possible, enabling a tailored and efficient treatment of systems with chemically diverse components.

An important advantage of fragment methods is their inherit ability to utilise network-based parallelism and distribute calculations over many computer nodes. Currently, the individual components for heavily parallel calculations are being developed and implemented in Spicy, namely a Nix-inspired content addressable storage to manage persistent data, a scheduling system based in MPI for distributed quantum and molecular mechanical calculations, as well as an interface to the DBCSR library for distributed block sparse array computations, enabling efficient response tensor and wave function transformations.[1]

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Spectral and Structural Sensitivity of the mCherry Chromophore

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For each molecular configuration, a direct mapping between the structure and different types of computable spectra exists. We developed a Monte Carlo method for inverse mapping, where molecular geometries are sampled with a restrain given by a reference spectrum (XAS, XES, UV/Vis) [1]. The acceptance criterion of the Metropolis Monte Carlo is modified for a bias towards the reference spectrum with an uncertainty factor, which limits how much the ensemble of spectra can diverge from the reference. The resulting ensemble of structures with corresponding spectra can be used to understand the sensitivity of atomic positions on a spectrum, i.e. which functional groups are important for spectral features.

mCherry is a fluorescent protein commonly used in biophysical experiments both in cellulo and in vitro, as it can be easily fused to a to protein of interest through genome editing. [2,3] This fluorescence protein is part of a group of similar proteins called mFruit, which show different spectral properties depending on the chromophore structure and the surrounding β-barrel environment. [2] In this class of chromophores, the UV/Vis adsorption and fluorescence emission spectra are closely related and follow the mirror image rule, making predictions on the emission behaviour based on adsorption spectra possible.

We present the application of our previously developed method using the UV/Vis absorption spectrum of the mCherry chromophore. In this first step, the sensitivity of the spectrum towards the structure of the chromophore is analysed in vacuo in the absence of a protein environment. To assess the influence of the protein on the structure sensitivity, amino acid residues proximal to the chromophore are added and the difference in the ensembles analysed.

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Unveiling the Novel Mechanistic insights into Zinc Catalyzed Sonogashira Cross - Coupling Reaction: A DFT Study

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Sonogashira coupling reactions are considered to be one of the most widely employed transition metal-catalyzed coupling reactions for the synthesis of carbon-carbon bonds. Among the multifarious carbon-carbon bond-forming reactions, those that involve the formation of aryl acetylenes have gained considerable attention in recent times. These reactions are deemed to be versatile tools for the fabrication of molecules having biological and pharmaceutical importance. The high cost, low abundance, and toxicity created a strong demand to search for an alternative to the traditional palladium metal catalyst. Zinc-catalyzed cross-coupling reactions have gathered momentum nowadays owing to the cost-effective and eco-friendly properties of zinc metal. In this presentation, we discuss a detailed quantum chemical study of the Zn (II) catalyzed Sonogashira coupling reaction between aryl halides and terminal alkynes employing DMEDA (*Dimethyl ethelene diamine*) as ligand. All calculations discussed in this presentation are performed at the Density Functional Theory (DFT) level, using the hybrid Becke3LYP functional. We have identified that the active catalyst species is a base-coordinated neutral 4-coordinate DMEDA Zn (II)-alkyne complex. The proposed mechanism proceeds through a concerted oxidative addition-reductive elimination pathway, which involves a single transition state. This is owing to the ease of reductive elimination involving the coupling of Csp^2-Csp carbon atoms and the less stable Zn (IV) intermediate. This shows that the mechanism of Zinc-catalyzed Sonogashira coupling reactions is quite different from those catalyzed by palladium. Furthermore, our study revealed an alternative mechanistic route to Zn-catalyzed Sonogahira coupling reaction, which was expected to proceed via an initial oxidative addition pathway. The activation barrier 31.0 kcal/mol concords well with the experimental temperature requirement (125°C). This work elucidates the relevance of a combined theoretical and experimental approach for rationally improving the cross-coupling reaction mechanisms.

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Computational Study on the Biocatalytic Ether Lipid Synthesis by an Archaeal Glycerolprenylase

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In nature, comparably few enzymes are capable of constructing ether bonds in a general fashion. Such enzymes are interesting for synthetic applications as they typically offer higher regioselectivity and operate under milder conditions than traditional organochemical approaches. Our overall study provides insight into the fundamental understanding of the archaeal prenyltransferase *Af*G$_3$PS as a representative member of the geranylgeranylglyceryl phosphate synthases family, thereby expanding the toolbox of ether synthases. Experimental evidences show that *Af*G$_3$PS makes various (E)- and (Z)- configured prenyl glycerol ethers from corresponding pyrophosphates. [1]

A mechanism is proposed which involves an intermediary prenyl carbocation equivalent and essential magnesium ions. This poster focuses on the computational investigation, including molecular dynamics simulations using GROMACS and quantum mechanical calculations using the Amsterdam Modeling Suite. The computational calculations are based on and support the experimental findings, offering valuable insights into the enzyme's behavior and mechanism. Simulation results show that the (E)- and (Z)- substrates adopt similar binding poses in the enzyme's binding tunnel. The presence of Mg^{2+} ions stabilizes the substrates inside the active site of the enzyme, supporting the proposed involvement of Mg^{2+} ions.

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The Open-Source Quantum Chemistry Software SERENITY as a Development Platform

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Time-dependent density-functional theory (TDDFT) has been around for almost four decades and has been successfully applied to a wide range of organic and inorganic molecules [1]. Its scope is essentially limited to single excitations [2] and problems regarding e.g. charge-transfer excitations are well known [3]. Still, it can provide a moderately good description of excited states at a relatively low cost in comparison with less favorably scaling correlated wavefunction methods. Analytic TDDFT gradients allow the analysis of excited potential energy surfaces and have been used for studying rather complex phenomena, e.g. in the context of mixed quantum-classical nonadiabatic dynamics [4].

Also the subsystem formulation of TDDFT is known for almost two decades now [5, 6], building upon the corresponding ground-state embedding. It improves the computational scaling in comparison to a supersystem approach and additionally provides insights into the contributions of fragments and their interactions to physical observables. Analytical subsystem-TDDFT gradients have been published in 2016, albeit only in the uncoupled approximation [7]. Furthermore, the corresponding implementation was done in the commercial ADF program. The subsystem quantum chemistry code SERENITY [8, 9] provides an alternative, open-source framework that already features ground-state gradients as well as an implementation of coupled subsystem-TDDFT. It is fully compatible with the usage of projection-based embedding.

This poster showcases our ongoing work regarding both the theoretical formulation as well as the technical realization of subsystem-TDDFT gradients for the coupled formalism and projection-based embedding with the goal of further developing an accessible and general subsystem-TDDFT implementation.

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Accurate Property Data for Small Fluorine-Containing Molecular Systems

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Calculated properties of isolated small molecules, molecular ions and molecular clusters in their electronic ground state, like equilibrium structure (r_e structure) and fundamental frequencies, compare very well with experimental data (for the latter see [1,2] and references therein), if these properties are calculated at sufficiently high level of theory (e. g. with an explicitly correlated coupled-cluster method like CCSD(T)-F12).

Data for selected fluorine-containing systems, both neutral and charged and composed of at most four atoms, will be presented.

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Multi-Reference Configuration Interaction Calculations with Sparrow

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Semiempirical methods provide great computational efficiency, albeit at the cost of accuracy. To account for dynamic correlation effects, extensive (re-)parametrization and other corrections are required. Static correlation effects cannot be adequately modeled in a single-determinant description and require other approaches such as configuration interaction (CI) [1]. Sparrow [2, 3], which is part of the SCINE software stack developed by our group, is a module specializing in semi-empirical electronic structure calculations with semiempirical NDDO and DFTB methods. Recently, we have introduced new features to account for static electron correlation effects and to calculate electronically excited states with NDDO Hamiltonians such as PM3, PM6, OM2, or OM3. In particular, multi-reference CI calculations with spin-symmetry adapted configuration state functions within the graphical unitary group approach (GUGA) have been implemented[4]. We summarize the working principles of GUGA and present how CI calculations can benefit from this approach.

Literature

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Dipole Moment with Pair Coupled Cluster Doubles: Effect of Dynamical Correlation Corrections and Orbital Optimization

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The electric dipole moment and dipole moment surface of a molecule contain crucial information about its electronic structure and spectroscopic properties. Dipole moment, thus, is regularly used as a tool to assess the accuracy and reliability of electronic structure and consequent electron density of a molecule obtained from a quantum chemical method. Pair coupled cluster doubles (pCCD) ansätze has seen considerable success in recent times for a range of different types of chemical species, utilizing its ability to model strongly correlated systems. [1,2] This work focuses on dipole moments computed with pCCD and its linearized coupled cluster (pCCD-LCC) corrections employing the canonical Hartree–Fock and pCCD-optimized (localized) orbital bases. [3] The performance of pCCD-based methods in terms of dipole moments is assessed against experimental and CCSD(T) reference values. Dipole moment surfaces of two typical examples, HF and CO, are also created using these methods to investigate the performance of pCCD and pCCD-LCC beyond the equilibrium regime. Our work indicates the importance of orbital optimization in the pCCD model and exposes the limitations of the linearized couple cluster corrections in predicting dipole moments, specifically for molecules with multiple bonds. The dipole moment surface of the HF molecule obtained with pCCD, on the other hand, is comparable to multireference methods. Additionally, we also calculate dipole moments of some binary complexes (H_2O---R_g, R_g=He, Ne, Ar, Kr) using the pCCD-in-DFT static embedding method. [4] We show that the performance of the embedding approach is comparable to their supramolecular counterparts.

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Density-Based Many-Body Expansion as a Case Study on Interoperability

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While interoperability had long been recognized as a central issue in the field [1], more recent developments have facilitated complex and highly interoperable workflows [2]. Especially quantum-chemical subsystem and embedding methods, which are at the focal point of our scripting framework PyADF [3], stand to benefit from this [2]. The density-based many-body expansion is one such abstract and highly adaptable subsystem and embedding method [4]. With its recent application to CCSD(T) calculations [5], we have demonstrated the method's adaptability and potential. Herein we employed existing and actively supported tools and standards to achieve the necessary workflow. To ensure efficiency and therefore sustainability in the further development of the density-based many-body expansion, existing standards and tools as well as general best practices in software development all need to be kept in mind, which illustrates a challenge that is faced throughout the field.

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Quantum-chemical investigation of ethylene dimerization on Ni^{2+} NU-1000 metal-organic framework

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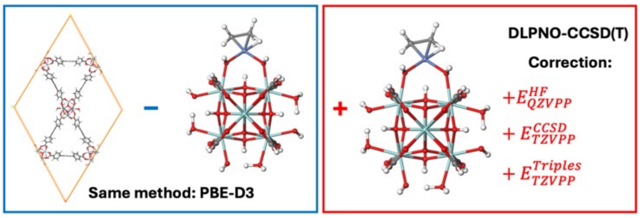
Olefin oligomerization is an important chemical process for converting ethylene to higher C_{12}-C_{18} hydrocarbons. Numerous studies have demonstrated the potential application of metal-organic frameworks (MOFs) containing catalytically active transition metals [1,2]. For example, MOF catalysts with Nickel have shown catalytic activity in ethylene oligomerization with a non-selective mechanism [3]. In most cases, periodic DFT (PBC) in combination with GGA functionals is used to study catalytic reactions in a reasonable timeframe with limited accuracy. However, reaction energies and barriers can be corrected using wave-function based methods on cluster models [4].

Therefore, we performed a systematic benchmark study at different levels of theory based on periodic and cluster models of the catalytic center with Ni^{2+} for the ethylene dimerization process to obtain corrected energy barriers [2]. Results at the DFT level are compared with calculations using CASSCF/NEVPT2 and DLPNO-CCSD(T) to determine accurate energies and barriers for both multi- and single-determinant cases.

This study aims to provide information to build a kinetic model for the full olefin oligomerization mechanism, considering the time and accuracy of the methodological scheme. Ultimately, it will highlight the advantages and disadvantages of using Ni as a catalytic center for olefin oligomerization.

$$E_{corrected} = \left[E_{PBE-D3}^{PBC} - E_{PBE-D3}^{Cluster}\right] + E_{Correction}^{Cluster}$$



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GP3-xTB: A general purpose self-consistent Tight-Binding Quantum Chemical Method

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We present our third-generation extended tight-binding (xTB) model named GP3-xTB. It aims at general-purpose (GP) applicability in chemistry going beyond the special-purpose parametrization for geometries, frequencies, and non-covalent interactions (GFN) of previous xTB-versions [1,2]. The centerpiece of the new method is the adaptive minimal valence basis set q-vSZP [3], which allows for a different radial expansion of basis functions on symmetry-distinct atoms in a molecule. Together with its deep contraction and special optimization on molecular DFT calculations, it substantially improves on previously employed minimal basis sets. Beyond improvements to the basis set, the GP3-xTB Hamiltonian is augmented by three main features: (i) approximate non-local Fock exchange to emulate the behavior of range-separated hybrid DFT, (ii) atomic correction potentials (ACP [4]) to introduce anisotropy into the minimal basis, and (iii) a complete range-dependent expansion of the electrostatic interactions up to third-order to improve the description of charged species. Preliminary results indicate that GP3-xTB approaches DFT accuracy more closely and for a wider range of chemical properties such as barrier heights, ionization potentials, or thermochemistry, than previous semi-empirical methods at only slightly increased computational cost.

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Automatic equation generation with Wick's theorem for single reference coupled cluster theories

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The calculation of electron correlation is of fundamental importance in chemistry. The ab-initio methods i.e. all the post-Hartree-Fock (post-HF) theories are of particular importance to chemists as these can be systematically improved. Second quantisation was introduced to simplify the rigorous algebra involved in the derivation of post-HF methods. Along with the extended run-time for these more rigorous (also more accurate!) theories, the equation generation part becomes quite cumbersome and time-consuming. Wick’s theorem [1] is an elegant and powerful tool for equation generation in second quantisation methods which can simplify the complex operator algebra for the post-HF theories. For the Muti-reference theories, Mukherjee and Kutzelnigg [2], [3] proposed a generalised Wick’s theorem (GWT) which works for the multi-reference (MR) framework. We have developed a Wick’s theorem based automatic equation generation engine as part of the ORCA 6.0 AUTOCI toolchain which works for both the UHF and RHF single reference cases. For RHF, coupled cluster theories upto doubles amplitudes and for UHF, coupled cluster theories upto triples amplitudes (including CCSDT) have been implemented as prototype theories. We plan to implement higher order coupled cluster theories and MR theories (MR-EOM, MR-DSRG etc) in the near future, where commutator algebra is useless and Wick’s theorem is the best tool towards achieving those goals.

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Proton Coupled Electron Transfer in Biomimetic Peptides

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Proton-coupled electron transfer (PCET) plays an important role in several biological processes involving the oxidation and reduction of aromatic residues such as tyrosine and tryptophan. Insight into the environment that influences the mechanism of the PCET and the study of the structure and function of the tyrosyl radical and the adjacent residues are important to understand the enzymatic reactions. Since experimental and computational studies of complex protein systems in which PCET plays an important role, such as photosystem II (PSII) and ribonucleic reductase (RNR), are costly, time-consuming and difficult to manage, the PCET as a phenomenon and its underlying features have often been investigated in biomimetic peptides and proteins instead. [1]

Theoretical studies appear instrumental for a deeper understanding of the reaction mechanism, and the use of multiscale simulations is crucial: Molecular mechanics force-field methods correctly capture the protein environment that influences the molecules involved in the transfer mechanism. Meanwhile, quantum chemistry accurately describes the particle transfers, providing a comprehensive picture of these complex reactions.

The free energy surface of the reaction was obtained by tracking two collective variables along the simulation: 1) the proton transfer as the difference of the distance between the donor and acceptor atoms to the transferred proton and 2) the electron transfer as the difference of the Mulliken charges of the residues involved in the PCET. Well-tempered metadynamics simulations were performed with biasing potentials applied to the proton transfer reaction coordinate.

It turns out that an increased solvent exposure affects the PCET mechanism in two types of biomimetic peptides, and the protein environment alters the free energy landscape and modulates the transfer barrier height. For the PSII-inspired β-hairpin peptides [2], the mechanism of the PCET reaction varies when it occurs between a tyrosyl radical and either a histidine, tryptophan or tyrosine residue. It was also found that the relative orientation of the participating amino-acid residues strongly influences the electron transfer. In addition, an α-helical radical maquette [3] was studied, and the transfer mechanism and barrier height of the transfer reaction were altered by the protein and water environment.

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