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P67

Nonadiabatic Molecular Dynamics Enables Direct Modeling of Plasmon-Driven Processes at the Single Molecule Level

N. Jahn (University of Potsdam/DE), E. Titov (University of Potsdam/DE)

Research interest in plasmon-driven chemical reactions of functional molecules at nanoscale metals has rapidly increased in recent years in both experimental and theoretical communities. In an ideal scenario, plasmonic catalysis promises selective chemistry under mild reaction conditions ideally involving green light sources with various possible applications in heterogeneous catalysis. However, many of the recently investigated plasmonic systems are highly involved and individual mechanistic steps of the observed chemical transformations are immensely difficult to disentangle experimentally. Moreover, the complexity of the experimentally prepared systems provides a significant challenge for computational modeling, thus impeding joint experimental and theoretical studies targeting reaction mechanisms in plasmon-driven catalysis.
Recently, Wu et al. [1] introduced a numerically efficient theoretical framework to perform nonadiabatic surface hopping dynamics simulations of (relatively) large systems at the semiempirical time-dependent density functional tight-binding level. In principle, the method enables coupled electron-nuclear dynamics simulations of many-electron systems with dense excited-state manifolds, e.g., plasmonic systems, with the capability of directly modeling charge and energy flow at metal–molecule interfaces. In practice, however, the workflow has only been applied to an Au20–CO system [2] thus far, while its applicability to larger functional molecules remains unknown. In our present contribution, we therefore aim to theoretically describe the nonadiabatic dynamics of a covalently linked azobenzene molecule on a tetrahedral Au20 cluster, thereby extending our previous work on azobenzene–gold systems [3]. In accord with recent experimental results [4], we observe that the n$\pi\cdot$ state of AB rapidly decays within a few femtoseconds via coupling to the metal continuum, thus suppressing the AB photoisomerization process. On the other hand, the photoexcited metal primarily relaxes through electron-phonon coupling while retaining its excited-state population. Our findings provide direct atomistic insight into the elementary processes occurring at the AB–gold interface to assist in the future design of functional plasmonic systems.

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P68

Temperature-Dependent Collapse of Surface-Tethered PNIPAM at a Bioactive-Glass-Relevant Silica–Water Interface: A Dissipative Particle Dynamics Study

Azin Mazloom Jalali (Friedrich Schiller University Jena/DE), Delia Brauer (Friedrich Schiller University Jena/DE), Marek Sierka (Friedrich Schiller University Jena/DE)

Thermoresponsive polymer-bioactive-glass (BG) hybrids display temperature-controlled aggregation and ion release, but the conformational response of the grafted polymer layer that underlies this behavior is difficult to resolve experimentally. Here, dissipative particle dynamics (DPD) simulations are used to examine the temperature-dependent conformation of a single poly(N-isopropylacrylamide) (PNIPAM) chain (DP = 100) tethered to an amorphous silica surface, a bioactive-glass-relevant interface, in explicit water. A four-bead coarse-grained model (water, silica, PNIPAM, APTES-derived anchor) with temperature-dependent conservative repulsion parameters represents good-, near-onset-, and poor-solvent states at nominal 278, 298, and 308 K. Radius-of-gyration (Rg) probability distributions and surface-normal monomer concentration profiles quantify chain compactness and polymer-layer thickness; free-chain simulations in bulk water serve as controls that isolate intrinsic solvent-quality effects from surface-tethering effects.

The grafted chain evolves from a broad, multimodal swollen coil at 278 K (most probable Rg 31.0 Å) through a heterogeneous pre-transitional ensemble at 298 K (Rg 25.2 Å) to a sharply localized, surface-proximal globule at 308 K (Rg 10.55 Å). The polymer-rich layer thickness decreases about 4.7-fold (107 to 23 Å) while the local monomer concentration near the surface increases about 4.5-fold. Free-chain controls reach comparable dimensions in the swollen and collapsed limits, but the tethered chain is markedly more compact at 298 K, showing that surface grafting reshapes the intermediate conformational ensemble even though the ultimate collapse is governed by the temperature-dependent polymer-water interaction.

These single-chain results provide a molecularly consistent framework for interpreting the aggregation and enhanced Ca2+ release reported for PNIPAM-grafted bioactive-glass nanoparticles [1]. Partial shell retraction below the macroscopic cloud point can weaken steric stabilization, while the accompanying layer thinning and lateral retraction expose more glass surface to water, rationalizing the counter-intuitive enhancement of ion transport upon heating. The work establishes a single-chain conformational reference linking polymer collapse to colloidal stability and ion-release behavior in responsive organic-inorganic biomaterials, providing the baseline for future multi-chain brush, curved-particle, and ion-transport DPD models.

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Quantum Electrodynamic Corrections in Molecules

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Precise calculations of systems containing heavy elements rely on a relativistic quantum chemical framework, such as the many-body Dirac equation. Beyond Coulombic interactions, there are additional higher-order relativistic corrections from quantum electrodynamics (QED), which improve the results. In this presentation, the leading order QED corrections, precisely the vacuum polarisation (VP) and electron self-energy (SE), are reported for nuclear magnetic resonance (NMR) shielding and nuclear spin-rotation (NSR) tensors of heavy-element containing diatomic molecules. Usually considered in high-precision few-electron atomic calculations, we investigate the scope of QED corrections in many-electron molecules and apply QED effective potentials [1,2] to molecular properties. We compare the QED corrections obtained from atomic-based and molecular-based frameworks [3,4], and identify the main origin of the different contributions. We constrast four-component and two-component approaches and discuss the impact of the QED effects on molecular properties.

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P70

Higher Order Pair Natural Orbital-Based Coupled-Cluster Methods

A. Jiang (University of Georgia)

Local pair natural orbital coupled-cluster methods have seen much success recently, allowing for the application of "chemically accurate" approaches such as CCSD(T) to significantly larger systems. Notably, the DLPNO-CCSD(T) approach of Professor Frank Neese and coworkers has been utilized to run computations on whole proteins such as crambin (636 atoms) and insulin (789 atoms). At the CCSD(T) level of theory, local approximations have errors which are controllable to within 0.25 kcal/mol through tight parameters. Inspired by the work of Neese et al., we developed analogous models for higher orders of coupled-cluster theory through full quadruples (DLPNO-CCSDTQ). These methods allow for an accurate estimate of quadruples contributions such as (Q) and Q-(Q) on the order of 0.01 kcal/mol, as well as the T-(T) difference within 0.1 kcal/mol.

P71

Spin-Orbit Induced Dynamics in Atom-Ion Collisions

Tomáš Jíra (University of Chemistry and Technology, Prague), Marcin Buchowiecki (University of Szczecin)

This study investigates spin-orbit-induced excitation and quenching dynamics in nitrogen cation and helium collisions utilizing a two-dimensional non-adiabatic wavepacket approach. Because these specific reaction pathways are governed entirely by a minimal set of spin-orbit couplings, they provide an ideal baseline for examining multi-state scattering phenomena. The dynamic simulations are constructed from ab initio potential energy curves and effective coupling elements, and the resulting cross sections are rigorously benchmarked against time-independent quantum scattering calculations and semi-classical Landau-Zener approximations. Our comparative analysis demonstrates that the wavepacket framework yields excellent agreement with traditional quantum scattering across a broad range of collision energies. It successfully tracks transition probabilities from just above the activation threshold up to significantly higher energy regimes where standard time-independent computational routines often face numerical instability. Ultimately, this wavepacket approach proves to be a robust and mathematically straightforward tool for modeling complex spin-orbit transitions in atom-ion collisions.

P72

Ultrafast Intersystem Crossing and Transient 2c–3e S–S Bond Formation in [(bpy)Pt(SPh)$_2$]

Jannis Leif Johann (University of Vienna, Austria), Jesús Lucia-Tamudo (University of Vienna, Austria), Leticia González (University of Vienna, Austria)

Ultrafast Intersystem Crossing and Transient 2c–3e S–S Bond Formation in [(bpy)Pt(SPh)$_2$] Transition metal complexes exhibit remarkable structural and electronic versatility, providing a rich platform for exploring excited-state processes governed by the interplay of metal- and ligand-centered electronic structure. An intriguing example of this interplay is given in [(bpy)Pt(SAr)$_2$] (SAr = sulfur-substituted aryl) complexes, which show potential to the formation of a transient two-center–three-electron (2c–3e) sulfur–sulfur bond in the lowest triplet excited state. Here we characterize this phenomenon computationally for the complex [(bpy)Pt(SPh)$_2$] using (TD)DFT and non-adiabatic excited-state dynamics. To investigate the ultrafast excited-state relaxation, we employ an anharmonic vibronic coupling (AVC) model, an extension of the linear vibronic coupling (LVC) approach within the SHARC[1] framework, to propagate a large ensemble of excited-state trajectories for one structural configuration of the complex. The resulting dynamics reveal a clear relaxation cascade: rapid internal conversion and intersystem crossing funnel the initially excited population into the lowest-lying triplet state (T1), which becomes the dominantly populated state on a sub-picosecond timescale. A conformer search on the T1 potential-energy surface shows that a subset of the rotamers—those in which the sulfur-centered orbitals on the two thiolate ligands are favorably aligned—undergo a structural contraction that reduces the S–S distance. The corresponding frontier-orbital picture exhibits the bonding characteristics expected for a 2c–3e interaction.[2] Together, these results support a mechanism in which rapid intersystem crossing populates the lowest-lying triplet state, enabling sulfur-centered orbital realignment and transient S–S bond formation.

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P73

Quantum chemical study of possible reaction pathways between IO and CH3OO

M. Kalinicenko (Bielefeld University/DE), W. Eisfeld (Bielefeld University/DE)

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.
Due to the high reactivity of the IO radical, it is involved in many other important reactions. The reaction with peroxy hydrocarbons, especially CH3OO, is of particular interest because of the lack of reliable experimental reaction rates. 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 CH3OO.
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 enthalpies suggest that several other product channels seem thermodynamically possible. It was possible to calculate a minimum energy path of one possible reactions via a stable adduct and only one barrier with a transition state. 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.

P74

ElemCo.jl: A Julia Package for Electron Correlation Methods

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A Julia package ElemCo.jl for electron-correlation methods is presented. 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, Full CI, a selected CI method CIPHI, EOM-CCSD and EOM-DCSD, etc. Furthermore, the package includes, e.g., the two-determinant coupled-cluster and frozen-reference coupled-cluster methods, which can be used to calculate excited states, and tensor-decomposed distinguishable-cluster methods, 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) or read from a file in the FCIDUMP format, including the possibility to read similarity-transformed (transcorrelated) or embedded Hamiltonians.

The package is open-source and available via the Julia package manager or on GitHub at https://github.com/fkfest/ElemCo.jl. Documentation can be found at https://elem.co.il. The inputs can be generated using the jlmol visualizer https://jlmol.com, which is available as a web-application https://app.jlmol.com and a stand-alone application https://github.com/fkfest/jlmol.

P75

Probing Isotope Effects on Metal–H_2 Chemical Bonding in Cu-, Zn-, and Bimetallic Cu/Zn-HKUST-1 Metal–Organic Frameworks

A. Siyara Kehelwalathenne (University of Leipzig), B. Ralf Tonner-Zech (University of Leipzig)

Metal–organic frameworks (MOFs) are promising materials for hydrogen storage and isotope separation due to their tunable pore structures and strong adsorption sites at open metal centers (OMCs). Chemical affinity quantum sieving (CAQS) enables isotope selectivity through differences in the zero-point vibrational energies and adsorption enthalpies of hydrogen isotopologues.[1,2]
Among MOFs, Cu-based HKUST-1 is a well-studied material for hydrogen isotope separation. Zn substitution is particularly interesting because it has been reported to increase hydrogen isotope selectivity in other MOFs.[3] However, although Zn substitution can strengthen hydrogen adsorption, it can also decrease the pore size. Therefore, mixed Cu/Zn HKUST-1 systems are investigated to explore the effects of partial Zn substitution. Despite extensive studies, how Zn substitution changes the chemical bonding at the OMC remains insufficiently understood.[4]
In this work, DFT calculations at the B3LYP-D4/def2-TZVPP level were applied to investigate the influence of the OMC on $H_2/D_2/T_2$ adsorption. Substitution of Cu by Zn increases H_2 adsorption strength but also induces structural changes and distorts the framework symmetry. When only one Cu atom is substituted by Zn, H_2 adsorbs more strongly at the Zn site than at the Cu site. H_2 adsorption was further studied by progressively increasing the number of adsorbed H_2 molecules up to five. Anharmonic zero-point vibrational energy corrections were calculated using VPT2.
To capture geometric isotope effects upon H_2 adsorption, NEO-DFT (Nuclear–Electronic Orbital DFT) geometry optimizations were performed.[5] Smaller paddle-wheel fragments were used to overcome convergence limitations for the larger systems. Finally, energy decomposition analysis was done to investigate changes in metal–H_2 bonding upon Zn substitution. The interaction is dominated by σ-donation from H_2 to the OMC together with π back-donation. Comparing the individual bonding-energy components will clarify how Zn substitution modifies the metal–H_2 interaction and contributes to changes in hydrogen adsorption and isotope effects.

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P76

Investigation of HCl-H2O electrolyte using AIMD simulations

Jamoliddin Khanifaev (University of Bonn, Germany), Barbara Kirchner (University of Bonn, Germany)

Renewable and eco-friendly energy storage systems are the key elements to address the current global challenges such as the reduction of fossil fuels and climate change. Improving the efficiency of the electrochemical batteries and capacitors is the most promising solution in that direction. To realize this goal in practice, novel electrode materials and electrolytes need to be developed. To achieve the optimal performance of the current and novel electrochemical systems the fundamental mechanistic understanding of the processes takin place within the bulk of electrolytes and at the electrode-electrolyte interfaces has to be gained. Electrochemical processes in liquid electrolytes and at the interfaces exhibit complex nature due to the interplay between various physico-chemical effects such as electrostatic interactions, quantum effects, thermodynamics and hydrodynamic motion. Such effects operate on different length and time scales thus, to tackle this problem, an effective combination of various computational and analytical methods has to be developed. In this work a prototypical HCl-H2O liquid electrolyte is investigated using ab initio molecular dynamics simulation using Quickstep module of CP2K software.[1] HCl concentration range between 0.44 molal and 3.21 molal is considered. Radial distribution functions and coordination numbers of various species within the electrolytes are investigated in detail. It is shown that O-O RDF and coordination number vary with concentration whereas for other species the respective properties are less sensitive to concentration. A particular emphasis of this study is made on HCl dissociation reaction dynamics and energetics. Temporal evolution of proton movement in form of Grotthuss diffusion is monitored and relevant cations, i.e, Eigen and Zundel are investigated. For all concentrations HCl and surrounding 4 H2O molecules are isolated at the instant of HCl dissociation. Identifed clusters are used as input for quantum chemical density functional theory calculation including Cosmo correction, as implemented in Turbomole 7.9 program [2], to estimate energetics of the reactions.

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P77

Analytical gradients and non-adiabatic couplings within the algebraic diagrammatic construction scheme

Mira Kim (Heinrich Heine University Düsseldorf/DE), Dirk Rehn (Ruprecht-Karls University of Heidelberg/DE), Andreas Dreuw (Ruprecht-Karls University of Heidelberg/DE), Shirin Faraji (Heinrich Heine University Düsseldorf/DE)

Accurate description of excited states is crucial for understanding a wide variety of photochemical and photophysical processes. Because these processes involve complex electronic transitions, reliable methods for modeling excited-state properties are essential. The algebraic diagrammatic construction (ADC) family of methods provides a powerful and efficient framework for calculating such properties, offering a good balance between accuracy and computational cost. In this work, we extend ADC methods by implementing analytical energy gradients within the Q-Chem electronic structure package [1]. This extension enables the exploration of excited-state potential energy surfaces (PES), geometry optimizations, and the characterization of minimum-energy crossing points (MECPs). Furthermore, we implement non-adiabatic couplings (NACs) for ADC(2), ADC(2)-x, and ADC(3) using the summed-state approach [2,3]. The performance and applicability of the implementations are demonstrated on selected molecular test systems.

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Emergence in Computational High-Pressure Chemistry: Equations of State of Molecular Clusters

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As a first approximation, many properties of compounds can be understood by considering the smallest possible model system; in the case of certain molecular properties, a single molecule is sufficient. For example, many simulated vibrational modes agree well with experimental spectra using this single-molecule approximation. However, this approach is limited to properties that are mostly governed by intramolecular effects [1,2]. Intermolecular effects like hydrogen bonds or packing effects cannot be captured by single-molecule approaches. In particular, packing effects are important in the context of high-pressure chemistry, as molecules move closer together with increasing pressure. Cluster approaches are one way to include intermolecular effects, but the question remains what cluster size and structure are needed to reproduce experimental data.
In this work, we present an automatic workflow for generating molecular clusters and compressing them in a dynamic, computationally inexpensive approach, linked with the Conformer Rotamer Ensemble Sampling Tool (CREST) [3] using the eXtended Hydrostatic Compression Force Field (X-HCFF) [4]. We show that for simple compounds like hydrogen, methane, and ethane, the resulting equations of state (V/V_0 curves) are in quantitative agreement with experimental data when large clusters of over 100 molecules are used. As the pressure-dependent molecular volumes converge with increasing cluster size, they can be considered emergent properties. This work paves the way for analyzing other pressure-dependent properties, or more complex compounds, using molecular clusters.

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Chemical Reaction Machine Learning: Data-Centric Shortcuts for Reaction Energetics and Transition State Geometries

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State-of-the-art quantum chemical methods for reaction property prediction require proficient users and are too expensive for everyday use in synthetic laboratories. Yet, the toolkit has expanded tremendously during the past decades: Advances in thermochemistry, conformer sampling, and algorithms designed to locate critical points on the potential energy surface (PES) have enabled skilled computational chemists to calculate almost any desired property of almost any given reaction. However, their computational cost prevents routine application in laboratories around the world. Machine learning (ML) offers a paradigm shift, delivering comparable predictions within seconds, yet chemical reaction ML remains unfamiliar to many theoretical chemists, often conflated with machine-learned interatomic potentials (MLIPs) or molecular structure-to-property prediction, which are inherently different in many regards. This talk will introduce direct chemical reaction ML: models that predict e.g., reaction energetics and transition state geometries starting with as little as connectivity information only, similar to how experimental colleagues envision their molecules. Unlike MLIPs, which approximate the PES, chemical reaction ML learns patterns across the chemical transformations themselves, mimicking chemical intuition and enabling rapid screening of synthetic pathways and mechanistic hypotheses. The data used to train such models is also very different from other ML applications in chemistry, has to be high in quality, both regarding the level of theory and the methodology to obtain the required properties. Currently, this data is the rate-limiting step in the field. As for undergraduate students laying the foundation for their chemical intuition, the reactions visited during learning are highly important. Selecting the most informative training data is a non-trivial task, requiring not only chemical domain knowledge but also insights from mathematics, data science, and machine learning: curriculum learning, active learning, and uncertainty quantification. Dataset generation is costly but built on state-of-the-art quantum chemical software and advances. Close collaborations between disciplines — theoreticians and experimentalists, method developers and data curators — are crucial to move chemistry forward. The talk will display ongoing work as well as results and conclusions from generative and predictive frameworks already developed (ChemTorch, GoFlow, ChiFlow).

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Photophysical Properties of a MR-TADF Emitter in Complex Environments

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Thermally activated delayed fluorescence (TADF) emitters are crucial for highly efficient organic light-emitting diodes OLEDs, because they boost light emission by converting triplet excitons into fluorescent singlet excitons without relying on heavy metals. The efficiency of TADF emitters is largely determined by the energy gap between singlet (S1) and triplet (T1) states, as well as key factors like oscillator strength and spin-orbit coupling.[1] Furthermore, the accurate treatment of the chemical surrounding is essential to predict their photophysical behavior in optoelectronic applications. In this study, we employ a hybrid computational approach[2] combining quantum mechanics/molecular mechanics (QM/MM) with density functional theory (DFT), time-dependent (TDDFT), and multireference configuration interaction (DFT/MRCI[3]) to investigate the excited-state behavior of a well-known TADF emitter (DiKTA[4]) in various solvents (acetonitrile, cyclohexane, water), MOF-5 and polymethylmethacrylate (PMMA) as polymer matrix. To account for environmental effects on molecular geometries, we perform QM/MM optimizations using DFT and TDDFT to obtain realistic excited-state conformations.[2] The photophysical properties are subsequently calculated with DFT/MRCI to accurately compute the electronic excitation energies.[3] By applying this method to different environments, we quantify the impact of polarity and rigidity on the above mentioned key TADF parameters. This computational framework can assist in tailoring TADF emitters for specific applications, guiding experimental efforts in material selection for organic light-emitting diodes OLEDs and other optoelectronic devices. Our findings highlight the necessity of incorporating environmental effects in theoretical models to achieve accurate predictions of photophysical behavior in real-world applications.

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Computational investigation on red-light driven molecular motors enabled by triplet-triplet annihilation upconversion

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Light-driven molecular rotary motors convert photon energy into controlled directional motion and offer opportunities in areas ranging from photopharmacology and optogenetics to photoresponsive materials. However, many molecular motors require ultraviolet or high-energy visible light for direct excitation, limiting their application in biological and other light-sensitive environments. Shifting motor operation toward longer wavelengths is therefore an important challenge. Here, we investigate triplet–triplet annihilation photon upconversion (TTA-UC) as an indirect excitation strategy for driving a second-generation Feringa-type molecular rotary motor with lower-energy light. In TTA-UC, two low-energy photons are harvested through a sensitizer–annihilator system and converted into a higher-energy singlet excitation that can subsequently be transferred to the molecular motor. Particular attention is given to organic radical sensitizers with doublet character as alternatives to conventional metal-based photosensitizers. Using quantum-chemical calculations, we evaluated the excited-state energetics and energy-transfer requirements of sensitizer–annihilator–motor combinations involving the radical sensitizers TTM–TPA and BNS and the annihilators perylene and rubrene. The poster presents the energy-transfer pathway from low-energy excitation to molecular rotation, compares the investigated sensitizer–annihilator combinations, and highlights the key energetic design criteria emerging from the calculations. These results provide a basis for the rational design of molecular rotary motors that can be indirectly activated using lower-energy visible light.

P82

Internal conversions with non-adiabatic instanton theory

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Radiationless decay competes with light emission across many applied fields, such as organic electronics and photovoltaics. Whenever an excited molecule returns to its ground state, internal conversion drains population that would otherwise be emitted as light. Controlling this loss channel is central to organic light-emitting diodes and light-harvesting materials, while the same process underlies the photostability of UV-absorbing molecules. I will approach such internal conversions through nonadiabatic instanton theory, which locates an optimal, local tunneling path between a reactant and a product potential energy surface (PES). This instanton is a stationary-action path – minimal with respect to the hopping point between the surfaces and a saddle point with respect to the imaginary time of the transition. Beyond a substantial reduction in computational cost, it grants a classical-mechanical interpretation of the dynamics and, with it, insight into the reaction mechanism. Locating this path is intricate even in simple systems, and especially so in the deep inverted regime or when the two surfaces do not intersect at all; these regimes are governed by so-called branch-point instantons. These have so far been treated rigorously only for harmonic oscillators; since real systems are rarely purely harmonic, I extend the analytical treatment to Morse oscillators by means of a semiclassical Morse propagator. Internal conversion (S1 -> S0) in naphthalene is a prime example of such an anharmonicity-dominated reaction. As the parent of the acene family on which many photoactive materials are built, and a prototypical aromatic for radiationless transitions, it is a natural model system; moreover, its S1 -> S0 conversion can be modeled by two Morse oscillators, so that the essential physics beyond the harmonic picture already emerges from a one-dimensional treatment along the reaction coordinate.

P83

The ultranonlocal LAK meta-GGA: An efficient density functional for molecules, materials, and interfaces

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Over the past decade, meta-GGAs have significantly advanced the accuracy–efficiency trade-off in density functional theory, approaching hybrid-functional accuracy while retaining nearly GGA computational efficiency. Meta-GGAs like B97M-V and SCAN provide accurate descriptions of a wide range of energy-related properties. The recently developed Lebeda–Aschebrock–Kümmel (LAK) meta-GGA [1,2] additionally captures the ultranonlocality of the derivative discontinuity to achieve accurate band gaps for the right reason [3].

In our contribution, we briefly explain the non-empirical design strategy of the LAK meta-GGA and highlight its performance for molecular systems [2], covering thermochemistry, kinetics, and non-covalent interactions, and for extended materials, including band gaps [1] and defect formation energies [4].

The combination of high accuracy for both molecules and materials makes LAK particularly promising for a unified description of complex surface and interface problems. Indeed, on a recently established benchmark database for adsorption energies covering layered, porous, ionic, and metallic surfaces, LAK achieves near-chemical accuracy and provides consistent performance across the considered surface classes [5]. Remarkably, LAK achieves the best overall performance among all tested dispersion-corrected GGAs, meta-GGAs, and hybrid functionals, even without adding a dispersion correction. This is because LAK incorporates near-equilibrium dispersion interactions directly into the exchange-correlation functional by design [2].

Finally, we discuss remaining challenges and future directions in meta-GGA development, with particular emphasis on the description of spin-polarized systems and magnetic materials [6].

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P84

Light-induced electron dynamics in open-shell systems via the restricted open-shell method

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The description of correlated, ultrafast electron dynamics in polyatomic many-electron molecules is generally a challenging task - and even more so for open-shell systems. The time-dependent configuration interaction (TDCI) method has been shown to correctly describe the light-induced excitation processes on the natural time scale of the electrons. By employing spin orbitals constructed from molecular orbitals, monitoring the electronic wavepacket evolution in the TDCI framework becomes possible, and the Jellyfish software package provides specialised time-dependent tools to analyse the light-driven dynamics. [1, 2] Investigating the dynamics of an open-shell molecule is a greater challenge, as it requires the construction of the spin-adapted wavefunction to avoid spin contamination and guarantee a physically solid foundation. In this poster, we present and discuss the light-driven electron dynamics simulation in open-shell molecules using a restricted open-shell approach.

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P85

Freezing the Unfreezable: para-Hydrogen Microsolvation Tunes CH5+ Fluxionality

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Understanding how molecular solvation shapes structure and dynamics at the quantum level is a central goal of modern Solvation Science. Protonated methane (CH5+), a highly fluxional molecule known for its large-amplitude motion (LAM) presents a uniquely sensitive system for exploring the effects of microsolvation in para-hydrogen clusters (pH2)n at low temperatures (15 K). We investigate CH5+-(pH2)n using ring polymer molecular dynamics (RPMD) simulations based on highly accurate high-dimensional neural network potentials. These RPMD simulations serve as basis for our IR spectra computation using a neural network dipole moment surface. All networks are parametrized using CCSD(T) theory. We find that microsolvation significantly modulates the LAM of CH5+ as a function of pH2 cluster size n, and for small clusters transiently freezes the CH5+ molecule. This dynamical change leaves clear spectroscopic fingerprints: The emergence of a partial scrambling band and systematic mode shifts connected to the structural differences between frozen and fully flexible CH5+. As larger cluster sizes provide a broader interaction site with pH2, we observe the reentrance of full scrambling of CH5+. Together, the simulation and spectral results are in excellent internal agreement and provide a coherent picture of how para-hydrogen controls the fluxionality of CH5+ at 15 K.

P86

Simulating mechanochemical disassembly pathways of PdnL2n supramolecular architectures

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Mechanochemical activation provides a powerful route to trigger the disassembly of supramolecular PdnL2n architectures, yet the underlying bond rupture and fragmentation pathways remain difficult to resolve at the atomistic level. Here, we apply ramped steered molecular dynamics to probe force-induced Pd-N bond rupture in a Pd2L4 cage and a giant Pd12L24 nanosphere, complementing experimental ultrasound-induced disassembly studies of these systems.[1] Because of the size of these solvated assemblies, conventional ab initio dynamics are impractical for this problem. Therefore, the machine-learned interatomic potential (MLIP) Universal Model for Atoms S (UMA-S)[2] was fine-tuned for Pd-N bond dissociation in coordination chemistry using a dataset of over 1.6 million structural configurations spanning six different relevant molecular motifs. Fine-tuning was necessary to correct structural artifacts as the pre-trained model produced unphysical, asymmetric distortions upon geometry optimization, whereas the fine-tuned potential enables stable, reactive simulations of solvated supramolecular assemblies beyond the reach of conventional quantum chemical approaches. The simulations of Pd2L4 reveal that the onset of cage disassembly is strongly influenced by how force is transmitted through the ligands. Pulling two adjacent ligands apart, referred to as cis pulling, promotes Pd-N bond rupture more efficiently than trans pulling, where force is applied to two opposite ligands. Across all pulling scenarios, ligand dissociation is observed, leaving behind Pd-coordinated fragments whose composition depends on the pulling geometry. In the Pd12L24 nanosphere, multipoint pulling reveals a stepwise disassembly mechanism in which successive Pd-N bond rupture events progressively fragment the nanosphere into smaller Pd-coordinated species and free ligand. These results demonstrate how fine-tuned MLIPs can extend computational mechanochemistry from small mechanophores to large, reactive supramolecular coordination assemblies, opening a route to molecular-level mechanistic insights in systems previously beyond computational reach.

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P87

First-Principle Investigations on BN-Modulated Graphene Nanoribbons

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Using spin-polarized PBE first-principles calculations, we investigate saturated and unsaturated BN-modulated zigzag graphene nanoribbons[1, 2]. Structural relaxation reveals that the changes in the local geometry leads to electron density redistribution, modifying the magnetic behavior of the nanoribbons. The localized spin-polarized edge-states of the pristine zigzag nanoribbon are preserved in BN-modulated systems. However, in the BN modulated systems, the geometrical asymmetry leads to unequal contributions on the edges, giving rise to a net magnetic moment in system. This can be further tuned based on the BN content, resulting in a tunable net magnetic moment perpendicular to the ribbon. Bader charge analysis is employed to examine the charge distribution and its correlation with the magnetic response. In addition, the electronic structure shows a spin-dependent band-gap variation upon BN modulation, indicating a strong dependence of the electronic properties on the edge chemistry. These trends are also relevant to 2D BN/graphene lateral heterostructures, where interface engineering may provide another route to control edge-state magnetism[3]. Overall, these preliminary results suggest that BN modulation is an effective strategy for tuning the magnetic and electronic properties of graphene nanoribbons.

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Mixed Metal Oxides in the Gas Phase: The Study of the FeAlO3+ and Al2O3+ Clusters

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Elucidating the atomistic structure of active sites in heterogeneous catalysis remains a fundamental challenge, due to their intrinsic complexity and dynamic nature under operating conditions. The study of those systems involves techniques such as matrix isolation and gas-phase clusters, which enable detailed structural and electronic characterisation at the molecular level. In the realm of gas-phase clusters experiments, the investigation of mixed metal oxide catalysts uses action spectroscopy approaches, where mass-selected ions (emulating the catalyst's active site) are characterised by techniques such as infrared photodissociation spectroscopy (IRPD) and X-ray absorption spectroscopy (XAS) [1]. Aluminium oxide (alumina) is a prototypical oxide material widely employed in heterogeneous catalysis, both as an active phase and as a support, due to its chemical and physical properties. The incorporation of transition metals into the alumina framework has emerged as an effective strategy to tailor catalytic performance, for instance, in isobutane synthesis [2]. In this regard, the study of the active site of iron-doped alumina is pivotal to understanding its catalytic activity. Herein, FeAlO3+ and Al2O3+ clusters were investigated as model systems for iron-doped alumina active sites by combining IRPD and XAS with electronic structure calculations. Structural assignment is achieved through comparison of experimental spectra with simulated harmonic infrared. The results indicate that the measured cluster adopts a "key-like" structural motif. Further insight into the electronic structure is obtained from X-ray absorption spectroscopy at both the oxygen K-edge and iron L-edge. The combined analysis reveals that FeAlO3+ is best described as an oxyl species with a general quintet spin state, in which the iron centre is in the +3 oxidation state. These findings afford a detailed atomistic picture of a prototypical iron-doped alumina motif, highlighting the power of combining action spectroscopy with simulations to resolve structure–property relationships in complex oxide systems. This work provides fundamental insights into the nature of the active sites in mixed metal oxides and establishes a framework for the rational design of improved catalytic materials.

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P89

CO Reactivity on Pristine and Co- and Cu-Substituted NiF2(F2) (001) Surface Models: A First-Principles Study

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Electrochemical fluorination on a nickel anode in anhydrous hydrogen fluoride (Simons process) is an important industrial route towards fluorinated compounds. Despite its widespread application, its mechanism is not well understood. It is believed to involve higher-valent nickel fluorides formed in situ under electrochemical conditions. The existence of higher-valent nickel centres on the anode was confirmed recently. [1] To study the reactivity of higher-valent nickel surfaces, we constructed a twice-oxidised NiF2(F2) (001) surface model. This surface model contains both a higher-valent nickel centre and a surface [F2]- unit, which is readily available as a fluorine source. Previously, we have investigated the reactivity of methane [2], ethene [3] and carbon monoxide [4] on this surface. In the case of CO, we have also considered explicit co-adsorption of up to two HF molecules. Within this model we were able to reproduce most of the experimentally observed products. As nickel is the only metal experimentally known to facilitate Simons-type fluorination, a computational comparison with other related transition metals may provide further insights into the underlying mechanism. Here, we present the results of the CO adsorption study on the pristine surface. Furthermore, we extend it with models in which either a surface or subsurface nickel atom is substituted by cobalt or copper. The interaction of CO with these modified surfaces is then investigated and compared with that on the pristine NiF2(F2) surface.

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P90

Excitonic effects in layered Poly(heptazine imide) from many-body perturbation theory

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Poly(heptazine imide) (PHI) has emerged as a promising, metal-free photocatalyst and charge storage material in solar batteries, owing to its suitable band gap and favorable band edge positions.[1][2] Despite such broad application potential, a comprehensive understanding of its photo-response, especially excitonic effects and their dependence on spatial confinement and interlayer couplings remains elusive. Herein, we employ many-body perturbation theory, i.e., simulations on the GW/BSE level, to account for self-energy corrections and electron-hole interactions, both neglected in single-particle approaches such as TDDFT. We investigate the quasiparticle band structure and excitonic effects in various PHI models, including monolayer, bilayer, and bulk structures with different stacking configurations. The simulations reveal localized, Frenkel-type excitons with high binding energies that are modulated by the structural dimensionality and the degree of interlayer stacking. Specifically, the eclipsed AA-stacking configuration exhibits a larger interlayer distance and a reduced quasiparticle band gap. Such configurations exhibit dark bound excitons that are long-lived, due to the out-of-plane band dispersion and concomitant forbidden optical selection rules, compared to their bright excitonic counterparts. We hypothesize that the existence of dark bound excitons is instrumental to charge accumulation and delayed photocatalysis observed in PHI materials. Conversely, the staggered AB-stacking configuration with reduced interlayer distance and broken structural symmetry gives rise to bright bound excitons together with an increased quasiparticle band gap. Our findings provide insights into the optoelectronic properties of layered PHI materials and demonstrate the possibility of property engineering via controlled stacking configurations. The results offer guidance for the rational design of PHI-based functional devices.

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P91

Investigation of H3O+-nHe geometries and He-migration

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The H3O+-nHe cluster is chosen as a benchmark-system to investigate molecular systems in superfluid environments. Interesting questions include, e.g., the onset of rotational decoupling with increasing number n of He-atoms. As a first step towards quantum dynamic calculations for the H3O+-nHe clusters, the potential energy surfaces are analyzed. H3O+-nHe clusters ranging from three to thirteen helium atoms are investigated. Specifically, geometries of potential minima, transition state geometries for He-migration and dissociation energies are examined and characterized. The onset of new solvation shells with increasing number of He-atoms are studied. The minimum geometry of the H3O+-4 He cluster turns out to be of special interest, differing from the geometry obtained by imaginary-time pathintegral calculations.(by Schran et al.) In this context, the influence and importance of zero point energies of the minimum geometries is discussed. Future steps might include, e.g., quantum dynamics calculations studying He-migration, vibrational predissociation and rotational decoupling using methods like MCTDH.

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Development and combination of novel basis set convergence accelerators for CCSD(T) and demonstrations on large molecular complexes

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While the local natural orbital (LNO) method of our group [1] enables relatively routine access to CCSD(T) for systems with hundreds of atoms, approaching their complete basis set (CBS) limit still remains highly challenging. Namely, large atomic orbital (AO) basis sets often augmented with diffuse functions are needed, leading to higher cost.
To accelerate the convergence to the CBS limit, we introduce and combine here three efficient tools developed recently in our MRCC program suite. The present authors introduced a novel, general Floating Orbital Grid (FOG) approach that automatically generates a non-atom-centered basis (with center position, exponents, etc.) between or around interacting monomers. The advancement over the common single midbond functions is that FOG is applicable irrespectively of the size, shape, and number of the interacting units.
Then, we combine the FOG method with complementary basis set convergence accelerators, namely an LNO-accelerated density-based basis set correction (DBBSC) [3]; and a highly accurate explicitly correlated CCSD(F12*)(T+) approach [4]. Benchmarks on medium-sized complexes demonstrate that the FOG method added to X-ζ AO bases by itself performs as well as augmented X-ζ or $(X+1)$-ζ interaction energies. Remarkably, combining FOG with DBBSC or F12 methods using double-ζ basis delivers the accuracy of conventional quadruple-ζ quality energies (MAE $\sim$ 0.4 kcal/mol) at a cost significantly lower than triple-ζ. This outstanding performance extends to complexes of real-life drug molecules with full-sized protein binding pockets (300+ atoms), supramolecular binding, and catalyst–substrate interactions, where LNO-CCSD(T)/double-ζ + FOG + DBBSC computations reproduce CBS references within 0.5 kcal/mol.
Together, these advances systematically accelerate the AO basis set convergence to the CBS limit of CCSD(T) or even LNO-CCSDT(Q) [5]. This enables high-throughput computation of CCSD(T)-level benchmark results to assist the development and assessment of lower-cost (DFT, SQE, ML) models [6].

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Effects of Mechanical Strain and Local Curvature on Hydrogen Isotope Selectivity in Graphene Membranes

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Atomically thin graphene is a promising platform for hydrogen isotope separation due to its impermeability to most atoms and selective proton permeation [1]. The experimental work of the Lozada-Hidalgo group demonstrated that mechanically exfoliated monolayers of graphene can effectively separate hydrogen ion isotopes, achieving a separation factor (H+/D+) of 10 at room temperature [2]. Under environmental conditions, graphene membranes are not perfectly flat [3]. Thermal fluctuations and hydration forces induce intrinsic in-plane and out-of-plane corrugations. Experimental studies have shown that high-proton-conductivity regions are observed near ripples, wrinkles, and strained regions, indicating that local lattice deformation is a key factor in hydrogen isotope transfer [4]. In this work, we investigate how controlled biaxial tensile strain (1–5%) and local curvature influence isotope selectivity (H+, D+, T+) in graphene membranes. Moderate tensile strain increases interatomic spacing and reduces the activation barrier for proton transfer, while local curvature modulates the barrier according to its out-of-plane deformation. The results provide insight into how biaxial strain and ripples can modulate proton conductivity and isotope separation performance in graphene membranes.

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P94

Deriving and Benchmarking Triplet–Triplet Exciton Couplings for Density Functional Tight-Binding

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Triplet–triplet exciton interactions are central to multi-exciton processes in organic semiconductors, yet their quantitative description remains challenging for large molecular systems. In this work, we focus on establishing and validating a density functional tight-binding (DFTB)-based framework for computing triplet–triplet exciton couplings. First, we benchmark DFTB triplet excitation energies and relevant electronic properties against higher-level electronic-structure methods for representative organic semiconductor molecules and dimers. This provides a systematic assessment of the accuracy and transferability of the underlying DFTB parametrization for triplet states. On this basis, we derive a working expression for the effective triplet–triplet coupling that separates Coulomb and exchange-like contributions, formulated in terms of DFTB quantities such as transition densities or state-specific density matrices. The resulting scheme is designed to be computationally efficient while retaining a clear physical interpretation of the individual coupling components. These benchmarking and derivation steps lay the groundwork for future applications of DFTB to multi-exciton phenomena in extended organic semiconductor systems, such as triplet–triplet annihilation and singlet fission.

P95

QM/MM investigation of structure and reactivity of PSTK dependent on the protonation state of the Thiaminediphosphate cofactor

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Thiamine diphosphate (ThDP), the active functional form of vitamin B1, is a common cofactor for a multitude of enzymatic systems. This ThDP cofactor is known to exhibit uncharacteristically low pKa values at key sites.[1] The low pKa values have been attributed to the protonation of the cofactor and nearby residues[1] both of which are central to the catalysis as well as regulation.[2] We are, therefore, investigating the ThDP cofactor using QM and combined QM/MM methods. Of interest is the behavior of both the isolated ThDP molecule as well as the assembly of the cofactor in the pocket of its host protein. Due to the dimeric structure of the protein, cooperativity between active sites needs to be taken into account in the investigation of the catalytic action.[1] Conformational analysis and the corresponding energies, pKa values, the electric fields acting upon the cofactor as well as the hydrophobicity of the surrounding cavity will be used in combination to provide quantitative insights into the forces acting on the cofactor and the protein environment. Our findings will shed light on the functionality of the protein and open avenues for biomimetic molecular design and catalysis.

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P96

Accelerating plane wave Hartree-Fock and hybrid functional calculations

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Hartree-Fock and hybrid functional calculations with plane wave basis sets are often demanding to converge. Despite their popularity in modern computational solid-state physics, corresponding convergence acceleration schemes still lag behind their counterparts in DFT calculations as well as Hartree-Fock calculations performed with localized basis sets. This work aims at enabling the well-established commutator direct inversion in the iterative subspace acceleration scheme, CDIIS in short, for plane wave calculations with an acceptable overhead per iteration. It builds on previous work that introduced the projected CDIIS method and presented results for large systems (hundreds of electrons). Our results show that this approach is also applicable to smaller systems (less than a hundred electrons) efficiently and therefore is a promising candidate for general use in Hartree-Fock and hybrid functional calculations. Results were produced with the Vienna ab Initio Simulation package (VASP) and the density-functional toolkit (DFTK), proving applicability across different code bases.

P97

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

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Machine learning potentials have become essential tools in chemistry and materials science, providing accurate and efficient representations of high-dimensional potential energy surfaces for atomistic simulations. Among these, high-dimensional neural network potentials (HDNNPs) offer an approach for modeling complex molecular systems. In this work, we compare two generations of HDNNPs, namely 2G-HDNNPs and 4G-HDNNPs, in their ability to describe organic molecules in aqueous solution. 2G-HDNNPs are highly effective for systems in which the atomic properties are dominated by local chemical environments. By relying on descriptors such as atom-centered symmetry functions (ACSFs) constructed from the neighborhood of each atom within a finite cutoff radius, they accurately capture short-range bonding and local interactions. However, this locality also represents their main limitation: interactions from atoms beyond the cutoff, such as non-local charge transfer, cannot be described explicitly. To overcome this limitation, 4G-HDNNPs incorporate a physically motivated treatment of non-local charge transfer through charges obtained from a global charge equilibration (QEq) scheme that respond to structural changes throughout the entire system. As a result, they can capture non-local charge-transfer effects and long-range electrostatic interactions, making them particularly well suited for systems in which the electronic structure depends on distant atomic environments. In this work, we demonstrate and compare the performance of both approaches for organic molecules solvated in water, demonstrating the advantages of 4G-HDNNPs for systems with non-local charge-transfer effects.

P98

Assessing the frozen natural virtual orbitals and frozen core approximations for fully self-consistent GW

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The GW approximation of many-body perturbation theory has historically been performed in an approximate one-shot perturbative fashion known as G_0W_0. However, some recent methodological advances now allow to systematically perform "exact" GW calculations, *i.e.*, fully self-consistent GW, for realistic systems. While this latter has the same formal scaling as G_0W_0, the self-consistency inevitably introduces a prefactor proportional to the number of iterations. In this work, we investigate two approximations that reduce the computational cost of each single iteration and therefore of the overall self-consistency procedure. These two approximations are defined by discarding some set of orbitals, namely core and high-lying (natural) virtual, in the computation of the dynamic GW self-energy. The errors, as well as the computational benefits, introduced by these two approximations are systematically assessed for molecules first - on a set of 34 small molecules as well as 24 medium-sized organic acceptors - and then for solids where some simple semi-conductors and insulators are considered.

P99

Electronic states of diarylethene switch-gold nanocluster hybrids

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Diarylethenes (DAEs) are promising photochromic molecules because of their thermal stability, reversible switching, and high fatigue resistance under repeated light irradiation[1]. Coupling DAEs with gold nanoclusters may further enhance their optoelectronic performance due to the tunable plasmonic properties and signal-enhancement capability of gold nanostructures[2]. In this work, we investigate how interaction with Au10, Au19, and Au20 clusters modifies the electronic and optical properties of open- and closed-form (stiff) DAE switches[3]. Ground-state properties are studied using density functional theory (DFT) at the B3LYP+D3(BJ) and ωB97X-D levels of theory. Excited-state properties are calculated using linear response time-dependent DFT (TD-DFT) with the same functionals. The excited states are further analyzed using the Fraction of Transition Density Matrix (FTDM) analysis[4], which distinguishes local (molecular or gold) excitations from charge-transfer contributions. The calculated UV-Vis spectra show clear spectral changes upon DAE adsorption on gold clusters, indicating that metal-molecule interactions significantly affect the electronic and optical properties. These results provide insight into the design of gold-DAE hybrid systems for nanoscale optoelectronic and sensing applications.

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P100

How to model Spin-Crossover cages in solution

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Spin-crossover (SCO) systems are transition-metal, often Fe(II), complexes capable of switching between low-spin (LS) and high-spin (HS) configurations, in response to external stimuli, such as temperature. This phenomenon is governed by a balance between enthalpic and entropic contributions. [1] Spin-crossover cages, consisting of multiple Fe(II) centers, are of particular interest because they can serve as molecular sensors in solvent environments. Yet their rational design remains largely empirical, underscoring the need for a computational workflow capable of guiding experimental efforts. The aim of this project is to develop a computational methodology with predictive power. Starting from a series of mononuclear Fe(II) complexes in various solvents, for which experimental data for the SCO temperature T1/2 are available, we showcase the challenges and limitations of current computational methodologies. As a first step, a DFT screening of different functionals and dispersion correction schemes was performed to obtain HS and LS energies, while adding thermal and entropic corrections with the standard rigid-rotor-harmonic oscillator model (RRHO).[2] The switching temperatures T1/2 show an extreme dependence on the chosen density functional, which could be attributed to a lack of accurate ΔEHS-LS prediction due to the single reference character. Comparison with experimental data revealed, however, that the local hybrid functional LH20t yielded very good results. To obtain benchmark reference data, CASSCF/NEVPT2 calculations were performed but the multireference treatment over-stabilizes the HS configuration, which is not sufficiently corrected by NEVPT2, leading to a qualitatively incorrect negative ΔEHS-LS. Strategies to improve the description of dynamic correlation are currently underway. In addition, the RRHO model was not able to correctly capture T1/2 modulations arising from different solvents. These initial results show the shortcoming of currently available methods and the need for more realistic chemical models accounting for explicit environments.[3]

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P101

Static DFT Is Enough for Reactive Chemistry, Not for Dispersion: MACE Potentials for Methanol on Si(001)

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Reactive machine-learned interatomic potentials (MLIPs) are currently filling the cost-accuracy gap between DFT and force fields for dynamic modeling of chemical reactions. MLIP training based on fine-tuning of foundational models is currently the most data-efficient way of obtaining performance and transferrable models. MLIPs trained on AIMD frames and active learning approaches are most commonly used. In this project, we aim at probing the lower bound of required ab-initio data for MLIP training by fine-tuning MACE based foundational models on static DFT data. We therefore use available DFT geometry optimizations, NEB calculations and optimized transition state structures from our previously investigated reaction network of methanol on Si(001), previously investigated by Göbel et al. [1] We compare the fine-tuning of MACE-MP0 with its multiheaded successor MACE-MH1. By splitting of the train/test set and exclusion of a full reaction path from the train and testset, we investigate accuracy and transferability of the obtained ML models. We find that the static-only dataset is enough to enable chemically sensible reactive MD simulations of methanol adsorption on Si(001) at 500 K that recover the reaction network from the dynamics, particularly when using multihead models. Furthermore, we find that training with and without D3 dispersion corrections yields energetically indistinguishable models for the tested configurations. We trace this back to a gap in the sampled configuration space of the training set: reaction-path frames never populate the longer-range structures representing the molecule approaching the surface, so the label choice is inert regardless of whether dispersion is included in the DFT reference. More generally, this identifies the sampled configuration space, rather than the choice of reference labels, as the binding constraint when MLIPs are trained from reaction-network data.

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P102

Fragment Molecular Orbital Methods for Excited States and Nonadiabatic Dynamics in Large Molecular Assemblies

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We present a fragment molecular orbital (FMO)-based electronic structure method for simulating optical properties and nonadiabatic excited-state dynamics in large molecular assemblies containing hundreds of electronically coupled molecules.
In our approach, the excited states are represented in a quasi-diabatic basis of local-excitation and charge-transfer configurations. Matrix elements of the full electronic Hamiltonian are obtained from embedded monomer and dimer calculations. For computational efficiency, we employ a tight-binding approximation, yielding FMO-LC-TDDFTB, although the formulation can be combined with higher-level electronic-structure methods as well. Analytical energy gradients enable nonadiabatic dynamics using Ehrenfest propagation and its collapse-to-a-block decoherence correction.
To demonstrate the accuracy, efficiency and scope of the method, we studied a range of organic materials. Relative to unfragmented LC-TDDFTB, fragmentation introduces only small deviations in excited-state energies while greatly reducing computational cost. The ground-state self-consistent calculation scales nearly linearly, whereas the effective scaling of the excited-state calculations is approximately quadratic to cubic, depending on fragment size [1]. We simulated exciton transport in an aggregate of 30 anthracene molecules comprising 720 atoms, following the migration and delocalisation of an initially localised excitation over picosecond time scales [2]. We further investigated the bacterial light-harvesting complex LH2, treating all 27 bacteriochlorophyll chromophores within a unified fragment-based framework. This enables on-the-fly nonadiabatic dynamics of the complete pigment aggregate beyond a conventional Frenkel-exciton description and resolves energy flow between the B800 and B850 pigment rings.
The method has also been combined with a generalised Tavis–Cummings Hamiltonian to describe strong light–matter coupling between large molecular aggregates and quantised photon modes [3]. Adding photonic states to the quasi-diabatic basis yields a polaritonic Hamiltonian that enables the calculation of polarisation-dependent spectra and dispersions in aggregates containing hundreds of molecules. All methods are implemented in the open-source DIALECT software package [4, 5].

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P103

Diffusion Mechanisms of Oxygen in $CaMnO_3$ Perovskites and Related $CaMnO_{2.5}$ Ordered Oxygen Vacancy Structures

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Perovskite oxides with the ABO_3 composition are promising redox materials for various applications of two-step thermochemical cycles, such as thermochemical energy storage (TCS) and splitting of H_2O or CO_2. Their tunable composition and defect chemistry allow them to be tailored to various applications. Under reducing conditions, these materials undergo significant non-stoichiometric reduction ($ABO_{3-\delta}$, $0 < \delta < 0.5$), leading to the formation of oxygen vacancies (V_O) and a subsequent topotactic phase transition: The initial perovskite structure with disordered V_O at a low reduction extent ($\delta \approx 0$) transforms into ordered oxygen vacancy (OOV) phases at a high reduction extent ($\delta \approx 0.5$). These two limiting cases provide the background for this study: The perovskite $CaMnO_{3-\delta}$, being a promising candidate for TCS, and its corresponding maximally reduced OOV structure $CaMnO_{2.5+\delta}$ are investigated for their redox thermodynamics and oxygen diffusion kinetics using first-principles density functional theory (DFT). At low reduction ($\delta \approx 0$), the formation energy of isolated V_O is calculated as 1.94 eV, with (nearly) isotropic diffusion barriers of 0.7 eV in all crystallographic directions. At $\delta = 0.5$, two energetically favorable OOV structures are identified for $CaMnO_{2.5}$: First, the experimentally observed structure with all Mn atoms showing a pyramidal 5-coordination, and the V_O being aligned in lines parallel to the crystallographic *c*-direction. Second, a Brownmillerite-type phase with alternating layers of octahedral and tetrahedral Mn atoms and the V_O being aligned in lines parallel to the *a*-direction. Both OOV structures have a formation energy of 1.80 eV per V_O; however, they reveal significant differences in diffusion pathways and activation energies compared to the disordered perovskite phase. The results demonstrate that both the V_O formation energy and the oxygen mobility are strongly dependent on vacancy ordering, with implications for the rational design of perovskites with tailored thermodynamics and redox kinetics. This work provides fundamental insights into how the defect structure changes with reduction and governs oxygen diffusion kinetics, which is key knowledge for optimizing perovskites in energy applications.

P104

Impact of higher-order terms on parity-violating rotational transitions in chiral molecules

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The potential energy surface of a molecule is invariant under inversion of the nuclear coordinates when assuming only electromagnetic interactions, leading to a parity-conserving nuclear-motion Hamiltonian. Consequently, the eigenfunctions describing nuclei moving in such a potential can be chosen to have a well-defined parity [1,2]. However, within the framework of electroweak quantum chemistry, parity is violated. The presence of the weak interaction, mediated by the Z^0 boson, transforms the potential energy surface into a parity-nonconserving one for systems containing more than three atoms [3]. Within this study, perturbation theory is applied for predicting parity-nonconserving energy contributions to rotational transitions within a vibrational state. Predictions are accomplished for the prototypical chiral molecule CHAtFI, for which large parity-violating effects have been found in previous studies [4]. In zeroth-order, the rovibrational wavefunction is a pure product of rigid rotor and harmonic oscillator wavefunctions, whereas refined models construct it from rotational-vibrational perturbation theory [5]. This approach incorporates the coupling between rotations and vibrations, comprising Coriolis forces, centrifugal distortion and changes in molecular shape during vibration. The purpose of this work is to compare the results obtained with and without including third-order derivatives of the parity-nonconserving part of the Born-Oppenheimer hypersurface. Implications for previous estimates of parity-violating contributions based solely on the gradient, which is analytically available in our group [6], are discussed.

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P105

Unraveling GaPt with Machine-Learned Force Fields: Intermetallic Compounds and Oxide Interaction

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Heterogeneous catalysis constitutes a vivid research area; a recently developed new concept is the usage of supported catalytically active liquid metal solutions (SCALMS). SCALMS are based on a matrix metal with a low melting point like gallium, containing catalytically active elements like platinum dissolved in it at low concentrations. The dynamic nature of the liquid metal alloy allows for the formation of isolated catalytic sites, with the gaseous reactants being unable to enter the matrix metal. This enables for the combination of advantages of heterogeneous and homogeneous catalysis, like easy product separation and defined properties of isolated reaction sites.
The dynamic nature of this systems, without stable individual bonds between the atoms, makes the simulation of SCALMS a difficult task. The need for sufficiently large simulation cells and simulation times makes machine-learned force fields (ML-FFs) the method of choice for molecular dynamics (MD) simulations. Since they do not rely on any preselected geometries or bonding situations, they enable the description of highly dynamical SCALMS. Their linear scaling with system size further enables the simulation of large time and length scales.
This poster presents how ML-FF simulations can be used to study the real-time formation of different intermetallic phases in liquid GaPt SCALMS model systems, and the resulting structures are compared to literature and experiments. Furthermore, a brief insight into the interaction of liquid GaPt alloys with oxide layers is given.

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P106

Modelling the quantum dynamics of protonated methane as a benchmark for fluxional molecules

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Protonated methane, CH5+, is the prototypical example of a fluxonial molecular system and its infrared spectroscopy is considered "one of the holy grails of rotational-vibrational spectroscopy". The ro-vibrational states of CH5+ display a unique level scheme, which results from a complex entanglement of rotational and tunneling motions. In this work a new model for the quantum dynamics of CH5+ based on the work of Wodraszka and Manthe is presented. The model uses the symmetry of the multi-well system for the representation of the vibrational wavefunctions as well as the rotational wavefunctions, leading to a minimal model. This minimal model agrees closely with numerically exact calculations, while the new rotational functions lead to a symmetry-compliant representation of the wave function and provide an alternative picture of the entanglement of internal motion and rotation.

P107

Orbital-Resolved Graph Neural Networks for Interpretable Prediction of K-edge XAS in Transition Metal Complexes

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The structural and electronic diversity of transition metal complexes (TMCs) poses a persistent challenge for accurate spectral prediction. To address this, a dataset of transition metal complexes is presented, providing high-quality pre-edge X-ray absorption spectra for a broad range of nickel complexes drawn from the tmQM dataset [1]. For each complex, the Ni K-edge pre-edge features were computed, providing detailed information about 1s to 3d transitions, oscillator strengths, and their sensitivity to the local coordination environment (geometry and ligand identity) and oxidation state. To enable Explainable AI (XAI), the dataset is further enriched with orbital-resolved features, including molecular orbital compositions, atomic contributions to transitions, and decomposed oscillator strengths. These features go beyond spectral prediction; they allow machine learning models to reveal which orbitals, atoms, and structural motifs govern pre-edge signatures, transforming black-box predictions into chemically interpretable insights. By bridging the gap between small-molecule datasets such as QM9 [2] and the chemically rich transition-metal space, this work aims to accelerate the interpretation of XAS spectra.

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P108

Mechanistic Insights in Natural and Modified Hammerhead Ribozyme from MD-QM/MM simulations

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Hammerhead ribozymes are catalytically active RNA motifs that have been studied extensively, both experimentally and computationally. However, the molecular mechanism of RNA self cleavage and the role of ions remain debated. Although Mg2+ ions were identified in X-Ray structures, the role of cations in the nucleophile activation and product stabilization are still an open question.[1] Moreover, recent experimental results show that epigenetic modifications on key bases may affect and even increase the catalytic activity of the Hammerhead ribozyme. Molecular Dynamics (MD) simulations are a powerful tool to investigate active site dynamics and obtain mechanistic insights into the altered reactivity induced by sequence modifications.

We devised a computational MD-QM/MM workflow to study the molecular mechanism of RNA self-cleavage in natural Hammerhead ribozyme. MD trajectories are simulated with the standard 12-6-4 Lennard-Jones-type non-bonded parameters for Mg2+by Li and Merz [2] and with the improved nucleic acid-ion force field developed in our group.[3] Additionally, we parametrized the proposed modified nucleobases following the modXNA approach and RESP scheme and incorporated the pseudo-nucleobases into the Hammerhead motif with good structural stability.

The MD simulations verify the positions of two magnesium cations within the active site of the Hammerhead ribozyme. While the simulation with 12-6-4 Lennard-Jones model shows advantages in capturing the positions of magnesium cations in the active region, the new force field demonstrates a better description of the inline-alignment of the nucleophilic attack. MD simulations with the deprotonated general base show the reorientation of the proton of 2'-OH, which supports the predicted nucleophile activation mechanism by the proton abstraction via general base catalysis. These results are foundational for the understanding of ribozyme activity and provides fundamental knowledge into the enhanced activity of modified RNA sequences.

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P109

Using Constrained DFT for modelling excited states in periodic systems

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Constrained Density Functional Theory (CDFT) offers a set of tools that, when carefully used, can access the low-lying energy states that cannot be achieved using conventional DFT [1]. In its broader definition it encompasses not only constrains on electron density, but also on spin, which allows for modelling of excited states. This study uses such spin constrain, complemented by the creative usage of Hubbard potential, in solid state plane-wave theory calculations to break the symmetry of a supramolecular unit cell and allow for localization of both electron and electron hole on singular molecules in selected excited states. Combined with GGA functionals and ΔSCF approach it gives a cheap method of describing a change in phosphorescence spectrum due to platinum complex's interaction with its molecular environment. After an initial success in modelling a supramolecular crystal with a flat platinum (II) complex, where a similar crystal had an added hydrogen bond to the platinum atom shifting the phosphorescence spectrum by 13 nm [2], two more systems were selected to be studied. Set of similar crystals sharing a platinum complex, but different in their chemical environment were found in literature with differing spectra [3], and the same approach was used to try and recreate the experimentally measured differences in phosphorescence. Additionally, a pair of crystals where our earlier attempts failed to show a difference in absorbance spectra in higher-level solid state calculations were also studied [4]. CDFT offered not only computationally efficient but also quantitatively correct results. Studies of all mentioned systems allowed for refining the method as well as finding its limitations and strengths.

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P110

Non-van der Waals Heterostructures from an Integrated Computational Approach

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Heterostructure interfaces formed by stacking two-dimensional (2D) materials provide a promising route toward achieving advanced electronic and magnetic functionalities at the nanoscale. The automated construction and computational investigation of these systems rely on precise lattice matching between the constituent 2D materials. The resulting supercells can contain hundreds or even thousands of atoms, considering that the individual 2D layers are often subjected to structural strain. In addition, the relative rotational alignment (twist angle) between layers introduces an extra degree of freedom, generating moiré patterns that can be exploited to tailor and enhance interfacial electronic and magnetic properties.

In this work, we perform a high-throughput screening of non-van der Waals (non-vdW) 2D heterostructures. Non-vdW 2D materials originate from non-layered bulk crystals [1] and can be synthesized through both top-down exfoliation techniques and bottom-up growth methods. Our methodology utilizes AFLOW-Hetbuilder, a recently developed computational tool based on the coincidence lattice algorithm for constructing stacked 2D material systems [2–5]. We investigate interfacial binding phenomena across a broad range of heterobilayers, focusing on their structural, electronic, and magnetic properties [6].

The formation of strong covalent and ionic interactions at the interfaces results in the development of hybrid interface bands and pronounced magnetic coupling effects. Additionally, we compare the binding energetics of non-vdW heterostructures with those of conventional van der Waals (vdW) heterostructures. The unique interfacial characteristics of non-vdW 2D heterostructures establish them as promising candidates for advanced technologies, with potential applications in electronics, spintronics, and energy-storage devices [6].

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P111

Modelling the Collective Dynamics of Photoinduced Dimerization in a Metal–Organic Framework

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Photoinduced dynamics and reactivity are well understood at the single-molecule level. How these dynamics unfold collectively among many molecules embedded in a periodic matrix, and how they translate into a macroscopic response, remains largely unexplored. One reaction suited to explore this is the [2+2] photodimerization, which we study within a metal–organic framework (MOF) whose stilbene-derived linkers serve as the reacting units, organised by the periodic matrix [1]. We develop a program that automates construction of the periodic framework model from its linker and metal node and sets up the resulting structure for molecular dynamics simulations. The workflow can be generalised for investigations of molecular frameworks with variable network topologies. The molecular environment and framework dynamics of the MOF are described by our previously developed force field MOF-FF [2], which permits molecular dynamics at length and time scales beyond the reach of electronic-structure methods. The force-field description is validated against DFT calculations and the experimentally observed macroscopic structural response. To achieve an efficient and reliable description of the light-induced dynamics, we mimic the excited-state dynamics of the organic linkers by switching the interatomic potential from reactant to product bonding. Combined with the atomistic representation of the molecular matrix, this approach captures the collective dynamics and follows how the photodimerization of individual and multiple centres impacts the periodic structure. Since the photoinduced reaction is assumed not to proceed to completion throughout the crystal under experimental conditions, the spatial pattern of dimerized linkers matters. Our approach therefore enables us to systematically correlate different patterns of reacted linkers with the resulting macroscopic response of the crystal. We present an automated workflow, its validation, and the resulting macroscopic response, and outline how this approach can be extended to other frameworks to elucidate how the reaction cascades into macroscopic effects.

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P112

A benchmark study of density functional approximations for predicting the electrical properties of transition metal oxides

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The choice of pseudopotentials (PPs) and density functional approximations (DFAs) is critical for developing a reliable computational cookbook for predicting electrical properties using first-principles methods. In our recent work, we showed that the choice of PPs has only a negligible influence on calculated electrical properties of several transition metal oxides (TMOs). However, experimentally determined atomic structures provide better agreement with experimental electrical conductivity than computationally relaxed structures [1].
In this work, we benchmark a broad range of DFAs, including LDA [2], GGA [3], meta-GGA [4], hybrid functionals [5], and Hubbard corrections [6] with tabulated values from AFLOW [7] and with self-consistently calculated values across a wide range of materials, covering metallic systems to insulators, and including magnetic cases. We compute band gap and intrinsic electrical conductivity using Wannier functions as implemented in the BoltzWann code [8]. We use an automated workflow manager, AiiDA [9], to calculate our benchmarking results.
We report the preliminary benchmarking results by direct comparison with experimental data. We identify strengths and limitations of each functional class and provide a cookbook for best practice DFAs for specific material sets. The take-home message of our work is that improving the band gap prediction does not necessarily improve the prediction of the activation energy of electrical conductivity.

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P113

Hydrogen Bond Strength and vSFG spectroscopy of the Water-air Interface

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In present work, we use the strength of hydrogen bonds (HBs) as calculated from energy decomposition analysis based on absolutely localized molecular orbitals (EDA ALMO) for the water molecules on the water-air interface to decipher the vSFG spectra. The contributions of hydrogen bonded water molecules to the different frequency range is examined as a function of HB strength, inter-molecular charge and intra-molecular asymmetry. Similarly, we also establish a linear relationship between the HB strength/charge transfer and instantaneous vibrational frequency of the OH modes of water molecules.

P114

Capturing emergent behaviour in complex reaction networks through quantum chemistry-based kinetic modelling

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Understanding the behaviour of complex chemical systems requires going beyond the description of individual elementary reactions and establishing how microscopic reaction mechanisms give rise to experimentally observable outcomes. However, constructing predictive kinetic models for such systems remains challenging due to the presence of multiple competing pathways, coupled equilibria and reaction steps governed by different kinetic regimes.

We present a quantum chemistry-informed kinetic modelling approach applied to a complex reaction network inspired by the prebiotic nucleotide activation chemistry reported by Liu et al. [1], in which methyl isonitrile serves as a chemical activating agent. By combining quantum chemical calculations of reaction energetics with mechanistic kinetic modelling, we construct a reaction network describing the formation of activated nucleotide species under different reaction conditions.

The developed model incorporates approximately 30 elementary processes, including barrier-mediated transformations, protonation equilibria, conformational interconversion and diffusion-controlled steps. By translating molecular-level reaction energetics into time-dependent concentration profiles, the approach enables direct prediction of product yields and comparison with experimental observations.

Despite the complexity of the reaction network and the inherent uncertainty associated with quantum chemical energy estimates, the model reproduces key experimental trends, including the relative efficiency of different activation conditions and the effects of pH and reagent concentrations on product formation. These results demonstrate how quantum chemistry-informed kinetic modelling can provide mechanistic insight into complex reaction networks and establish a connection between molecular-scale energetics and emergent chemical behaviour.

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P115

Resonance Raman Spectroscopy of a BODIPY Derivative: Computational Insights from Monomer to Dimer

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BODIPY dyes are an important class of chromophores with strong absorption, high photostability, and tunable electronic properties, making them attractive for applications in molecular photonics, bioimaging, sensing, and light-harvesting systems. Understanding how intermolecular interactions and aggregation influence their excited-state properties and vibrational signatures is therefore of considerable interest. Resonance Raman spectroscopy is particularly well suited to this purpose, as it selectively probes vibrational modes coupled to electronic excitations and provides direct insight into vibronic interactions.

Here, we investigate one-photon absorption and resonance Raman spectra of a BODIPY derivative in its monomeric and dimeric forms using a time-dependent formalism. In this approach, the relevant polarizability tensor elements are expressed in terms of Fourier transforms of time-dependent correlation functions involving nuclear wavepackets propagated on excited-state potential energy surfaces. This formulation describes the spectroscopic response through nuclear wavepacket dynamics, thereby avoiding the explicit sum over intermediate vibronic states required in the corresponding time-independent formulation.

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) are used to systematically characterize the electronic structure and construct model potential energy surfaces. Vertical-gradient, adiabatic-shift, and adiabatic-Hessian approximations are assessed, together with the influence of exchange-correlation functional, basis set, molecular conformation, and explicit and implicit solvation. The monomer serves as a reference system for establishing and validating the computational workflow through comparison with experiment. Among the harmonic models considered, the vertical-gradient model provides a favorable balance between computational cost and agreement with experimental spectra.

For the dimer, the treatment is extended beyond the Born–Oppenheimer approximation by constructing a vibronic-coupling Hamiltonian that explicitly accounts for the coupling between electronic and nuclear degrees of freedom. The resulting quantum dynamics are treated using the multiconfiguration time-dependent Hartree (MCTDH) method, enabling the interplay between vibronic coupling, exciton dynamics, and the resulting spectroscopic signatures to be investigated.

Overall, the developed framework combines systematic electronic-structure calculations and time-dependent resonance Raman simulations with a beyond-Born–Oppenheimer treatment of the dimer, providing a route to investigate the role of vibronic coupling and exciton dynamics in BODIPY aggregates.

P116

Electron attachment as a route to exotic reactivity: the case of sulfur heterocycles

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Electron attachment can open the way to unusual reactivity, including the opening of the aromatic ring of benzene. [1] Here, we explore whether ring opening induced by low-energy electrons also occurs in a series of sulfur heterocycles: thiophene, benzothiophene, and dibenzothiophene. We combine negative-ion mass spectrometry with electronic-structure calculations to investigate electron attachment, fragmentation, and possible ring-opening reactions in these molecules. We observe that parent anion clusters dominate the negative-ion mass spectra, while the minimum cluster size required for detectable attachment decreases with increasing molecular size. This is consistent with the negative electron affinities of the isolated molecules. Clustering lowers the vertical attachment energy and provides a way to dissipate the excess energy of the incoming electron, allowing the initially formed anion to survive long enough for detection. The decreasing HOMO–LUMO gaps and vertical attachment energies across the series support this picture. Electron attachment also produces strikingly different fragmentation patterns in the isolated molecules. In thiophene, the parent anion dominates over the anion formed by hydrogen loss; in benzothiophene, the two channels have comparable intensities, while in dibenzothiophene the parent anion is no longer detected. Fragmentation into smaller ions is also increasingly suppressed with molecular size. To understand these differences, we identify energetically accessible anionic structures that can be reached through bond cleavage and hydrogen migration. In contrast to the cyclic precursors, these structures are thermodynamically favorable for electron stabilization: the corresponding anionic geometries lie below their neutral counterparts. We also determine threshold energies for hydrogen loss, which produces closed-shell cyclic anions. The similar energetics of these competing processes do not, however, explain their markedly different experimental efficiencies. This points to an important role of reaction dynamics, which we plan to investigate in future work. Overall, the results show how increasing molecular complexity can strongly affect electron-driven reactivity in sulfur heterocycles.

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P117

Heteroatom Doping for Enhanced Domain-Based Charge Transfer in Organic Dyes

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This work presents a computational investigation of domain-based charge transfer in π-conjugated organic dyes using localized orbitals of pair-coupled cluster doubles (pCCD). The equation-of-motion pCCD with singles (EOM-pCCD+S) approach enables quantitative and directional analysis of charge-transfer processes among the donor (D), bridge (B), and acceptor (A) domains. A series of 33 carbazole-based prototypical organic dyes was systematically designed by introducing nitrogen (N), oxygen (O), and sulfur (S) heteroatoms at three positions within the π-conjugated bridge, generating mono-, di-, and tri-doped structures. The results reveal that both the type and position of heteroatom doping play a crucial role in controlling the direction and magnitude of charge transfer. For mono-doped dyes, the forward donor-to-bridge-to-acceptor (D $\rightarrow$ B $\rightarrow$ A) charge transfer increases when the heteroatom is shifted toward the acceptor, with nitrogen-doped systems exhibiting the strongest charge-transfer character. In di-doped dyes, enhanced charge transfer is observed when the heteroatoms occupy the terminal bridge positions, particularly when nitrogen is positioned closer to the acceptor. Nitrogen-doped systems consistently exhibit greater forward charge transfer than their oxygen- and sulfur-doped counterparts. Among all investigated systems, the tri-nitrogen-doped dye (NNN) exhibits the highest directional D $\rightarrow$ B $\rightarrow$ A charge transfer of 42.6%, demonstrating the effectiveness of increasing nitrogen content within the π-bridge for promoting charge-transfer efficiency. These findings demonstrate that strategic heteroatom doping provides an effective approach for tuning directional charge-transfer pathways in π-conjugated organic dyes and offers valuable molecular-design principles for developing efficient organic sensitizers for dye-sensitized solar cells (DSSCs).

P118

REMP up your ADC

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The algebraic diagrammatic construction (ADC) family of methods is a robust and widely used approach for computing excited states of molecular systems of realistic size.[1] In particular, its formulation in an intermediate-state representation provides convenient access not only to excitation energies but also to excited-state and transition properties. As a perturbation-theoretical method, ADC fundamentally depends on the choice of the Hamiltonian partitioning. Traditionally, the Møller-Plesset (MP) partitioning has been employed. In this work, we introduce a novel ADC scheme consistent through third order, derived from the hybrid, parametrized REMP partitioning,[2] which was recently proposed and successfully applied to the ground state by R. Fink and coworkers. REMP is obtained by setting the unperturbed Hamiltonian to a mixture of the respective ones of the "Retaining the Excitation degree" (RE)[3] and MP perturbation-theoretical approaches. As such, REMP-ADC enables excited-state calculations to benefit from the same tunable mixing of MP and RE, and effectively bridges the already established standard ADC and RE-ADC methods.[4] REMP-ADC(2) and REMP-ADC(3) were implemented in adcc and benchmarked against high-level theoretical reference data. We find that REMP-ADC(3) provides highly accurate excitation energies, with a mean absolute error of 0.12 eV, improving upon the performance of both standard ADC(3) and RE-ADC(3), while maintaining the formal arithmetic scaling of N^6. Remarkably, this optimal performance is achieved with a 15% MP contribution in the mixing, which is consistent with the recommended mixing ratio for the REMP ground state.

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P119

Optimized grids for the real-space resolution of the identity in low-scaling GW

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The GW approximation is a Green's-function-based method for calculating charged excitations in molecules and materials [1]. Low-scaling formulations using Gaussian basis sets have enabled GW calculations for systems containing thousands of atoms [2]. These formulations employ the resolution of the identity (RI). However, the resulting three-index RI tensors still require substantial memory, and matrix operations involving these tensors remain computationally expensive. The real-space resolution of the identity (RI-RS) represents three-center integrals on a numerical real-space integration mesh [3,4]. In this representation, a three-index tensor is factorized into products of two-index matrices using numerical integration. Tensor operations involving three-index quantities can therefore be replaced by matrix operations involving only two-index quantities, leading to cubic computational scaling with system size for GW calculations with a small computational prefactor [5]. The computational cost and accuracy of RI-RS, however, depend critically on the selection of the real-space grid points for the numerical integration [4,5,6]. Until now, grids have been available primarily for the def2-TZVP basis set [4,5]. Here, we optimize compact atom-centered RI-RS grids for additional Gaussian basis sets, including the MOLOPT basis-set families used in CP2K [7,8]. We benchmark the resulting grids against conventional Coulomb-metric RI and determine the number of real-space points required to converge GW calculations. We further examine their transferability across different molecular environments and the numerical robustness of the grid optimization.

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P120

Simulating Chloroalkane-Methanol Binary Liquid Mixtures and Correlating with Femtosecond Thermal Lens Spectroscopy

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Understanding thermal transport in associated liquid mixtures requires molecular-level insight into the interactions governing energy dissipation1. In this work, molecular dynamics simulations are employed to investigate the thermal transport pathways in MeOH-chloroalkane binary mixtures (Dichloromethane, chloroform, and carbon tetrachloride), with femtosecond thermal lens spectroscopy serving as experimental validation2. Although the chloroalkanes exhibit negligible absorption at the excitation wavelength, their incorporation into methanol produces pronounced composition-dependent changes in the photothermal response. Molecular dynamics simulations performed using GROMACS-2023 reveal that the observed behavior originates from changes in the local liquid structure. Analysis of hydrogen-bond dynamics, O···Cl interactions, and intermolecular organization demonstrates that specific solvent-solvent interactions govern thermal energy transport. In particular, the MeOH-Carbon tetrachloride system exhibits solvophobic clustering arising from polar-nonpolar interactions, leading to distinct thermal transport characteristics compared with the other binary mixtures. Hydrogen-bond lifetime analysis indicates a highly dynamic local environment across all compositions, while structural correlations provide a molecular-level explanation for the experimentally observed photothermal response. The combined simulation and experimental approach establishes a direct relationship between the liquid's microscopic structure and macroscopic thermal transport.

P121

Understanding the Electronic Structure of a Radical-Functionalized Azobenzene MOST Candidate

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Azobenzenes substituted with Gomberg radicals present a challenging computational problem due to their pronounced multireference character and the strong dependence of the electronic structure on the molecular conformation and the choice of initial electronic state. We investigated the electronic and photochemical properties of these molecules to assess their photoswitchability and establish a computational strategy for treating systems beyond the reach of conventional multireference methods. A combination of different DFT-based methods was employed supported by NEVPT2 calculations to characterize the electronic ground state as well as low-lying excited states and explain experimental observations. Our results demonstrate that carefully selected single-reference approaches provide a qualitatively reliable description of complex open-shell systems that are otherwise computationally prohibitive.

P122

Development and benchmarking of vibe-qc, a molecular and periodic electronic-structure code targeting correlated methods for solids

Michael F. Peintinger (Mulliken Center for Theoretical Chemistry)

vibe-qc is a Python/C++17 electronic-structure code for molecules and solids. Its long-term goal is an ab initio Cyclic Cluster Model (AICCM) that brings correlated wavefunction methods to periodic systems. Because the CCM is a real-space Gamma-point method, in which a finite cluster subject to periodic boundary conditions represents the infinite crystal, the molecular method stack is a direct prerequisite: a correlated method available for molecules transfers to the periodic cluster without reformulation in reciprocal space. This contribution reports the current state of the code and benchmark results on molecular and periodic chemical systems. The molecular stack comprises restricted and unrestricted Hartree-Fock and Kohn-Sham DFT with analytic nuclear gradients and the full libxc functional library, Moller-Plesset theory (MP2, RI-MP2, SCS/SOS, and the B2PLYP and DSD-PBEP86 double hybrids), DLPNO-CCSD, CASSCF and internally contracted CASPT2, TDDFT, D3(BJ)/D4 dispersion, effective core potentials, and CPCM solvation. Semi-empirical methods are also implemented. Periodic boundary conditions are currently treated at the Hartree-Fock and Kohn-Sham DFT level through three routes: a BIPOLE/Ewald path with multi-k analytic gradients, GDF, and a GPW route, together with band structures and densities of states. Correctness is established by continuous benchmarking against established quantum-chemical codes. Molecular and periodic total energies are validated against reference implementations across the available methods, covering both self-consistent-field results and density-fitted variants. Representative tests span closed- and open-shell main-group molecules, geometry optimizations and harmonic frequencies, heavy-element complexes via ECPs, and ionic solids. Reproducible reference outputs and automatic per-job citation tracking are part of the standard workflow. The code is developed largely with AI coding assistance, which shortens the path from method specification to a testable implementation and shifts the limiting factor for reliability from implementation effort to verification. We therefore treat systematic benchmarking against reference data as the decisive activity and present the supporting results accordingly.vibe-qc is a Python/C++17 electronic-structure code for molecules and solids. Its long-term goal is an ab initio Cyclic Cluster Model (AICCM) that brings correlated wavefunction methods to periodic systems.

P123

High-Order Response Functions with Duschinsky Coupling and Finite Temperature: Application to Two-Dimensional Resonance Raman Spectroscopy

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Coherent multidimensional spectroscopy offers a wealth of information about ultrafast dynamical processes in molecular systems.[1] In this work, we derive closed-form expressions for multi-time correlation functions underlying higher-order nonlinear spectroscopic response functions within the harmonic approximation.[2] Our method includes displacements, frequency changes, and Duschinsky rotation between the vibrational modes of different electronic states while retaining polynomial scaling with the number of degrees of freedom. Finite temperature is accounted for without summation over vibrational eigenstates. To show the capabilities of our method, we apply it to calculate fifth-order two-dimensional resonance Raman (2DRR) [3,4] spectra of two-mode model systems and naphthalene. Comparison with the displaced harmonic oscillator model shows that Duschinsky rotation modifies the positions and relative intensities of diagonal and cross peaks. Overall, our results demonstrate that 2DRR spectroscopy is particularly sensitive to changes in normal coordinates between electronic states and can provide distinct signatures of Duschinsky coupling in molecular systems.

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P124

Combining DFT, MLP, and Monte-Carlo Approaches to Model Area-Selective Deposition Processes

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Area-selective atomic layer deposition (AS-ALD) has emerged as a key strategy for nanoscale patterning in advanced material design complementing conventional lithography processes. However, achieving high selectivity and process reliability requires precise control of the surface chemistry. Here, computational approaches are used to reveal the fundamental mechanisms governing reactivity and selectivity. These insights enable predictive tuning of inhibitor and precursor chemistry as well as substrate functionalization, guiding the rational design of selective deposition processes.
For inhibitor based AS-ALD several studies investigating the interactions of the inhibitor with the non-growth surface are available. However, comprehensive investigations of interactions between precursor molecules and the blocking layer are still sparsely available as a realistic model for the blocking layer must be derived at first. With the present work we want to highlight the currently available approaches to derive realistic blocking layer models. These approaches span a wide range of size scales and balance accuracy against computational cost. Density functional theory (DFT) is frequently employed to identify the most stable blocking layer configurations with high accuracy. However, its use is typically restricted to a small number of structural variations and relatively small surface cells, which limits direct comparison to experimental coverages and defect structures. Random sequential adsorption (RSA) simulations provide an extremely fast way to generate inhibitor layers models on large surface models containing hundreds to thousands of adsorbates. As RSA simulations naturally sample many distinct packing motifs on extended surfaces, they are often closest to experiment. Still, RSA simulations rely on the quality and physical realism of the initial input parameters. More recently, machine-learning potentials (MLP) have enabled molecular dynamics and metadynamics simulations that are orders of magnitude faster than DFT while approaching DFT accuracy when trained on suitable reference data. These approaches enable us to explore the dynamical evolution and restructuring of blocking layers on large systems and timescales, albeit at higher cost than static RSA simulations. We firmly believe that the interplay of all three methods will enable efficient as well as accurate modelling of interactions between precursors and blocking layers in future investigations.

P125

From Hydrostatic to Anisotropic Compression: The Development of two new Mechanochemical Simulation Methods

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Two new mechanochemical simulation methods that subject molecular systems to anisotropic strain are introduced. The implementations were developed for the Python-based chemical framework PySCF[1,2] for electronic structure simulations. Both methods are based on existing approaches for hydrostatic compression, namely the recently developed eXtended Hydrostatic Compression Force Field[3] (X-HCFF) method and the Gaussians on Surface Tesserae Simulate Hydrostatic Pressure[4–6] (GOSTSHYP) model. Anisotropy in the new approaches is introduced by placing a family of planes of a certain width in or along the van-der-Waals cavity of the system. The width of the family of planes determines the extension of the middle cylindrical part and the two outer half-shells. In the half-shells, the pressure is increased with distance to the origin of the planes' normal vector. This models these high-pressure sites as potential impact zones of a collision as for example in a ball milling setup. Therefore, the pressure is decreasing with distance to the origin of the plane in the middle part. On average, the same effective a priori pressure as in the original X-HCFF and GOSTSHYP approaches is applied, merely the distribution differs. With these new approaches named eXtended Anisotropic Compression Force Field (X-ACFF) and Gaussians On Surface Tesserae Simulate Anisotropic Strain using Half-shells (GOSTSASH), first insights into the underlying mechanisms occurring under anisotropic compression on the molecular level can be gained. Initial results for molecular model systems for both methods of hydrostatic and anisotropic compression are compared and presented.

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P126

SHARC meets Q-CHEM: interface for TDDFT dynamics with non-adiabatic and spin-orbit couplings for arbitrary states

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Recent developments in quantum chemistry have enabled reconstruction of spin-orbit couplings between all multiplet components based only on the information provided by a single individual transition, making evaluation of arbitrary spin–orbit couplings possible with single-reference methods. This approach implemented in Q-Chem is based on applying the Wigner–Eckart theorem for the triplet excitation operators, construction of the reduced excitation matrix elements with spin–orbit integrals, and applying the Wigner–Eckart theorem again to the spin–orbit reduced matrix elements. Single-reference methods have also progressed in treatment of the strong electron correlation. For example, the spin-flip approach implemented within a variety of methods enables an accurate treatment of spin near degeneracy. In this contribution, we interface these approaches to treat excited-state dynamics within the SHARC package. We demonstrate applicability of the approach to the reverse LIESST process of $[Fe(tpy)2]^{2+}$, requiring spin–orbit couplings between quintet and triplet state manifolds, which we treat with spin-flip TDDFT.

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Can a solvated electron reach the reactant?

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Electron-induced chemistry has been extensively explored in gases, solids, and even plasma, whereas corresponding processes in liquids remain comparatively understudied. A major experimental challenge is that electrons emitted from an electron gun can be strongly attenuated by the vapor phase above a liquid surface before reaching the solution. Here, we address this limitation by reducing the vapor-phase thickness using a continuous-flow liquid microjet and investigate whether incident electrons can penetrate the vapor layer and induce chemical reaction in solution. We chose electron-induced nitrate reduction as a model system. The resulting nitrite was detected through a well-established analytical reaction with 2,3-diaminonaphthalene, yielding a fluorescent triazole derivative. However, the experimental fluorescence spectra were crowded and difficult to assign reliably by inspection alone. To identify which molecular species contributed to the observed emission, we conducted excited-state calculations, vibronic effects modelling, excimer modelling, and pKa estimates by means of quantum chemistry. By combining the quantum chemical computations with a cleverly designed experiment, we address the central question: Can an incident electron reach the solvated reactant?

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Tensile Testing on an Atomistic Scale: Gold–Carbene Interfaces under Mechanical Strain

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Self-assembled monolayers (SAMs) of N-heterocyclic carbenes (NHCs) on gold offer superior chemical and thermal stability compared to their thiol-based counterparts, making them attractive for functionalized surfaces exposed to mechanical stress.[1] Despite advances in NHC–functionalized surfaces – both experimentally and theoretically, mechanistic insight into the effects of mechanical strain is still lacking. Here, we present periodic density functional theory (DFT) simulations of the force-induced detachment of two representative NHC classes, an imidazole derivative (IMe(Me) 2) and the stronger Σ donating and π accepting cyclic alkyl amino carbene (CAAC(Me) 2), adsorbed on Au(111).[2,3] By mapping the complete force-extension pathway, we find that both NHCs extract a two- atom gold cluster before an Au–Au bond in the gold lattice ruptures. Counterintuitively, despite CAAC(Me)2 exhibiting a stronger adsorption energy than IMe(Me)2 (by 0.28 eV), its rupture force is significantly lower by a factor of two. The force-extension pathways reveal distinct structural evolution of the carbene–Au interface, accompanied by differences in Au coordination and vertical fragmentation energies during detachment. Bader charge analysis shows the extracted Au–carbene fragment retains a nearly constant charge for IMe(Me)2 over much of the pulling range, whereas CAAC(Me)2 exhibits continuous charge depletion, reflecting distinct charge-transfer pathways at the two interfaces. These results provide the first atomistic insight into the mechano–response of NHC- functionalized gold interfaces and establish a framework for rationally designing more robust carbene-based surface coatings.

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Spin–Orbit Coupling in TDDFT: From the Tamm–Dancoff to the Random Phase Approximation

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Many light-induced molecular processes involve transitions between states of different spin multiplicity, which are formally forbidden in non-relativistic quantum theory. Intersystem crossing, a nonradiative transition between such states, is important in photochemistry and photophysics, with applications spanning molecular photonics, energy conversion, biomedicine, and materials science. Spin–orbit coupling (SOC) provides a key mechanism for facilitating these otherwise spin-forbidden transitions, making the accurate evaluation of SOC matrix elements essential for describing such processes and their associated spectroscopic properties. Several approaches have been developed for the theoretical evaluation of SOC matrix elements. In this work, the Breit–Pauli spin–orbit Hamiltonian is treated within the spin–orbit mean-field (SOMF) approximation. For electronically excited states, time-dependent density functional theory (TDDFT) provides a computationally efficient framework applicable to relatively large molecular systems. SOC matrix elements within TDDFT are often evaluated using the Tamm–Dancoff approximation (TDA), in which only excitation amplitudes are retained. While the TDA simplifies the underlying eigenvalue problem, it neglects the de-excitation contributions included in the random phase approximation (RPA). Here, an existing TDA-based implementation is extended to the RPA formalism by solving the non-Hermitian Casida equation and incorporating both excitation and de-excitation amplitudes (X and Y) into the evaluation of SOC matrix elements. The implementation is validated and benchmarked using a set of 14 molecules. SOC matrix elements obtained with RPA are compared with their TDA counterparts to assess the influence of de-excitation contributions and identify cases in which the two approaches differ significantly. The results quantify the effect of going beyond the TDA and assess the relevance of de-excitation contributions to SOC matrix elements within the TDDFT formalism.

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Electron Dynamics and Spin Selectivity in Chiral Molecules and Interfaces

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Chiral-induced spin selectivity (CISS), i.e., the phenomenon by which electron transport through chiral molecules becomes spin-selective, has been well-observed in experiments [1,2]. However, a quantitative theoretical explanation remains challenging, especially because experimentally measured spin polarizations are orders of magnitude larger than expected from the intrinsic spin-orbit coupling of organic molecules alone [3,4].
In this work, we systematically investigate charge and spin dynamics in several experimental settings using relativistic real-time time-dependent density functional (RT-TDDFT) simulations. We observe chirality-dependent spin dynamics when a chiral molecule adsorbs on a ferromagnetic substrate. This can in turn modify the magnetic state of the ferromagnet, in agreement with CISS adsorption experiments [5]. We further demonstrate that RT-TDDFT yields spin-resolved photoelectron spectroscopy signals up to tens of percent, in unprecedented quantitative agreement with CISS experiments [6]. In addition, real-time pump-probe simulations qualitatively agree with time-resolved photoelectron circular dichroism (TR-PECD) experiments [7] and predict a spin polarization of up to ten percent in prospective spin-resolved TR-PECD experiments.
Overall, this work emphasizes that a dynamical, nonequilibrium description of the molecule-metal interface provides important insight into the interplay between molecular chirality and electron spin.

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Molecular Insights into Alkene Hydrogenation with Manganese(I) NacNac Catalysts

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Manganese(I) complexes have emerged as earth-abundant alternatives to precious-metal catalysts for hydrogenation reactions,[1-2] yet efficient Mn(I) catalysts for alkene hydrogenation remain scarce and are hitherto predominantly based on phosphine, pincer, or N-heterocyclic carbene ligands.[3-5] Here, we investigate a novel Mn(I) NacNac catalyst system for alkene hydrogenation, combining experimental studies with DFT calculations to elucidate its mechanism and underlying reactivity.[6] The mechanism of alkene hydrogenation catalyzed by manganese(I) NacNac complexes was investigated using density functional theory (DFT) in conjunction with experimental mechanistic studies. The calculated catalytic cycle reveals an outer-sphere pathway involving a manganese hydride as the catalytically active species, with hydride transfer to the alkene identified as the rate-determining step. Further analysis provides insights into the intricate role of methanol in the catalytic cycle. Computed activation barriers across a range of substituted styrene substrates reproduce the experimentally observed reactivity trends, with electron-deficient double bonds showing enhanced reactivity. Furthermore, the differing catalytic activities of substituted NacNac manganese complexes can be rationalized based on their electronic and structural properties, providing a molecular-level understanding of catalyst and substrate effects. These results demonstrate the predictive potential of DFT for relating catalyst structure and substrate electronics to catalytic reactivity, providing a computational basis for the rational design and optimization of this promising type of hydrogenation catalysts.

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Deciphering the Solvent Dependence of Hydrogen Generation from Seawater and Silicon Waste

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Hydrogen is a promising sustainable energy carrier and an essential reducing agent in chemical synthesis. This work explores a green, waste-valorizing route for hydrogen generation under mild conditions, developed in cooperation with our experimental collaborators.[1] The process utilizes untreated seawater, strongly basic catalysts (OH^-/$OtBu^-$), and industrial polymethylhydrosiloxane (PMHS) waste. Interestingly, experimental data reveal that dimethyl sulfoxide (DMSO) exerts a unique and massive accelerating effect, vastly outperforming other solvents. To elucidate the underlying reaction mechanism without conformational complexity, density functional theory (DFT) calculations were performed using a simplified $HSiMe_3$ model. The reaction proceeds via the addition of the base (OR^-) to the electrophilic silicon, forming a pentavalent intermediate ($[HSiMe_3(OR)]^-$). This intermediate prefers an axial configuration and subsequently generates H_2 via the formation of a dihydrogen bond ($H^{\delta-} \cdots H^{\delta+}$ interaction). This pathway aligns well with literature reports on related systems.[2] Overall, the computational data predict OH^- to be a significantly more effective catalyst than $OtBu^-$. However, modeling the unique accelerating effect of DMSO proved computationally challenging. As standard continuum models (COSMO, CPCM) and more sophisticated implicit approaches (SMD, DCOSMO-RS) were insufficient to reproduce the observed solvent effects, the methodology was extended to include explicit microsolvation. Preliminary evaluations indicate that neither purely implicit nor these combined implicit/explicit models currently capture the full extent of the observed solvent dynamics, underscoring the severe complexity of the specific solute-solvent interactions. Ultimately, this ongoing investigation aims to comprehensively rationalize the reaction mechanism, providing predictive insights to guide experimental development while serving as a benchmark study to evaluate the performance of various solvation strategies in highly specific environments.

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