Poster Session 3 (Wednesday, P133–P197)

P133 **Anne-Marie Kelterer** — Graz University of Technology, Austria
Wavelength-Controlled Fragmentation of Mixed-Functionalized Norrish Type-I Acylgermanes

P134 **Pragya Pudasaini** — Humboldt-Universität zu Berlin, Germany
Probing Oxyl Character and Reactivity in a Biomimetic Non-Heme Oxoiron(IV) Complex

P135 **Vania Martins Ramos** — Universidade Federal de São Carlos, Brazil
Systematic Active-Space Construction for the Multiconfigurational Description of a Mn(I) Photosensitizer Candidate

P136 **Sheetal Ranaut** — Indian Institute of Technology Jammu, India
Machine Learning-Guided Molecular Insights into Metal-Catalyzed Asymmetric Reactions: A Case Study with a Pharmaceutically Relevant Version of Suzuki-Miyaura Coupling

P137 **Hamza Rappoun** — Paderborn University, Germany
Spatially Resolved Vibrational Dynamics of Water in Aqueous $Ba(SCN)_2$ Using Machine-Learned Potentials

P138 **Vyshna Ratheesh** — IWR, University of Heidelberg, Germany
Controlling Excited States of Anthracenes through Heteroatom Substitution

P139 **Sreejita Ray** — Freie Universität Berlin, Germany
Combinatorial Structure Search and First-Principles Stability Analysis of Borophene Phases on Ag(111)

P140 **Kassandra Rensinghoff** — Universität Münster, Germany
Vibrational Spectroscopy of Molecules in High Pressure Enviroments with GOSTSHYP

P141 **Charlotte Rickert** — MPI Solid State Research, Germany
The Aperiodic Defect Model: Treating Aperiodic Defects in Fully Periodic Systems with Wavefunction Methods

P142 **Anton Rikus** — University of Münster, Germany
How good are excited-state geometries from subsystem TDDFT?

P143 **Lukas Sebastian Rindt** — Heidelberg University, Germany
Re-purposing Optimization Trajectories: Do Hessians from Quasi-Newton Schemes Yield Reasonable Free Energies?

P144 **Christopher-Matthias Röper** — Universität des Saarlandes, Saarbrücken, Germany
A Perturbative Triples Approach for EOM-CC-(D)EA/(D)IP Treatments of Excited States in Strong Magnetic Fields

P145 **Marco Romanelli** — University of Vienna, Austria
Quantum-classical non-adiabatic dynamics in extended solid-state materials: a SHARC-VASP approach

P146 **Bibek Samal** — University of Regensburg, Germany
Perturbative Spin-Orbit Coupling in CP2K for Molecules, Bulk Materials, and Surfaces

P147 **Joana-Lysiane Schäfer** — Freie Universität Berlin, Germany
Girsanov path reweighting for core set Markov state models

P148 **Timo Scharfe** — University of Augsburg, Germany
FrayedEnds: Basis-Set-Free Quantum Chemistry

P149 **Jonathan Scherlitzki** — Freie Universität Berlin, Germany
A Novel Variational Quantum Trajectory Approach to Nuclear Quantum Dynamics

P150 **Julian Schiefer-Strauß** — University of Innsbruck, Austria
Calculation of Energy Potential Surfaces and Absorption Spectra of Rubidium-Noble Gas Mixtures

P151 **Thomas Schnappinger** — Stockholm University, Stockholm, Sweden
The Cavity-Born-Oppenheimer Framework: Electronic Reshaping and Multireference Effects under Vibrational Strong Coupling

P152 **Friederike Schneider** — Heidelberg University, Germany
Can Triple Excitations Restore Spin Symmetry of Excited States within the ADC Framework?

P153 **Leopold Seidler** — University of Bonn, Germany
Periodic g-xTB — Approaching DFT Accuracy for Periodic Systems at Semiempirical Cost

P154 **Faezeh Shabani** — TU Chemnitz, Germany
From Single α-Helices to Helical Bundles: Electronic Properties and Stability

P155 **Akhilesh Sharma** — Indian Institute of Technology Roorkee, India
Conversion of Light Alkanes into Value–Added Products Over Boron–Based Catalysts

P156 **Omid Shayestehpour** — Paderborn University, Germany
Prokyon – An Open-Source Library for On-the-Fly Machine Learning of Interatomic Potentials

P157 **Kristoffer Simula** — Max Planck Institute for Solid State Research, Germany
Transcorrelation in Solid-State Matter

P158 **Ramandeep Singh** — University of Münster, Germany
Pressure induced luminescence shift in coordination compounds

P159 **Natalia Skałecka** — University of Warsaw, Poland
Constructing systematically convergent Gaussian basis sets for solids

P160 **Stepan Sklenak** — J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic
DFT investigation of the effects of hydration on the reactivity of the low-valency distant binuclear vanadium species balanced in zeolites

P161 **Nathalie Smith** — University of Hamburg, Germany
Neural Network Potentials of 2D Nanoconfined Water: Efficient Training Set Construction and Calculation of Dielectric Properties

P162 **Richard Springborn** — Ruhr-Universität Bochum, Germany
Enhancing the Transferability of Machine Learning Potentials by Training on Atomic Properties

P163 **Ilija Srpak** — Max Planck Institute for Solid State Research, Stuttgart, Germany
A new Molecular Dynamics approach for treating spin-phonon effects in solids

P164 **Luca Steiner** — Freie Universität Berlin, Germany
Fluorine-Specific π-Stacking Accelerates Ring-Opening Copolymerisation

P165 **Tom Erik Steinkopf** — Martin-Luther-Universität Halle-Wittenberg, Germany
Configurational Entropy of Mixing as a Spatially Resolved, Time-Dependent Observable

P166 **Michael Stier** — University of Stuttgart, Germany
Reliable Redox-Potential Simulations of Proteins

P167 **Jesús Lucia Tamudo** — University of Vienna, Austria
Breaking Harmonics Walls: The Anharmonic Vibronic Coupling Approach in Trajectory Surface Hopping Simulations

P168 **Balaram Thakur** — Technische Universität Dresden, Helmholtz-Zentrum Dresden-Rossendorf, Germany
Coordination Corrected Enthalpies for the Thermodynamics of Ionic Materials

P169 **Franz Thiemann** — Leipzig University, Germany
Interactions in N-Heterocyclic Carbene Monolayers on Cu(111) and Au(111) from Periodic Energy Decomposition Analysis and NOCV

P170 **Vishwas Tiwari** — University of Paderborn, Germany
Atomistic Insights into Si(100) Surface Passivation by Water: ReaxFF Molecular Dynamics and Fine-Tuned Machine Learning Interatomic Potential Simulations.

P171 **Johannes Tölle** — University of Hamburg, Germany
Benchmarking Tensor Hypercontraction Techniques for Molecular Systems

P172 **Kai Töpfer** — Freie Universität Berlin, Germany
Machine-Learning Supported Reaction Mechanism Exploration of cis-trans Isomerisation in Retinal

P173 **Aleksandar Trajkovski** — University of Bonn, Germany
Implementations of Molecular Integral-Equation Solvation Models: From 6D-MOZ to RISM-SCF

P174 **Thuy Truong** — University of Augsburg, Germany
Excited-State Pair Natural Orbitals for Shallow System-Adapted Quantum Circuits

P175 **Iordanis Tsakontsis** — Bielefeld University, Germany
Accurate treatment of hyperfine coupling in the diabatic potential model of HI

P176 **Ritaj Tyagi** — University of Regensburg, Germany
Accelerating Large-Scale GW Calculations using Real-Space Resolution of Identity

P177 **Anna Ulrich** — Heidelberg University, Germany
Molecular switches and machines

P178 **Anna Luisa Upterworth** — Martin Luther University Halle-Wittenberg, Germany
Philicity at Play: Entropy, Enthalpy and Miscibility in Alkane–Perfluoroalkane Mixtures

P179 **Natália Lussari Vrech** — Universität Bremen, Germany
Low-Spin Co(III) Stability in Cobalamin Derivatives Under Hydrostatic Pressure: A Computational Investigation

P180 **Henry Wang** — Ruhr-Universität Bochum, Germany
Simulations of Tricalcium Silicate-Water Interfaces using High-Dimensional Neural Network Potentials

P181 **Nils Wegerich** — University of Frankfurt, Germany
Quantum Chemical Study of the Reactivity of a Platinum(II)nitrene with 1,4-Benzoquinone

P182 **Anna Marleen Weidlich** — Heidelberg University, Germany
Absorption spectra of N-heteroacenes

P183 **Jonas Weinhold** — Karlsruhe Institute of Technology, Germany
Spin-State Switching in Trinuclear Exchange-Coupled Systems

P184 **Jonas Weiser** — University of Augsburg, Germany
Extending an Automated Ensemble-Averaged Kinetics Framework for Reverse Intersystem Crossing in Flexible TADF Emitters

P185 **Rahel Weiß** — University of Bremen, Germany
Interactive JEDI Strain Analysis as a Pre-Screening Tool for Mechanophore Design

P186 **Christian Wiebeler** — University of Augsburg, Germany
Molecular Dynamics and Computational Spectroscopy for Systems in Soft Condensed Phase

P187 **Tillmann Lukas Wigger** — Heinrich Heine University Düsseldorf, Germany
Automated Reaction detection with different Bond Order Schemes

P188 **Severin Wittek** — Humboldt University of Berlin, Germany
Improving the scaling of AC0 with laplace-THC

P189 **Lukas Wittmann** — University of Bonn, Germany
A Minimally Empirical and Self-Consistent Implicit Solvation Model for Robust Quantum Chemistry in Solution

P190 **Konstantinos Zois** — University of Vienna, Austria
Simulating a bimetallic rotaxane with classical molecular dynamics

P191 **Carsten Zülch** — Philipps-Universität Marburg, Germany
Small molecular ions as probes for variations of fundamental constants

P192 **Hana Zupan** — Freie Universität Berlin, Germany
Grid-Based Description of Molecular Association

P193 **Christopher Zurek** — RWTH Aachen University, Germany
Accelerating Conformer Reranking with Machine Learning Interatomic Potentials

P194 **Tom-Luka Zwarg** — Heinrich-Heine University, Düsseldorf, Germany
Computational discovery of the initial formation processes of the solid-electrolyte interface and the role of novel additives

P195 **Jan Leodolter** — Graz University of Technology, Austria
Automated Assembly and Characterization of Coordination Cages

P196 **Tobias-Erik Monz** — University of Graz, Austria
Thermodynamic Properties of Various Polymorphs of 2-Thiobarbituric Acid via Quasi-Harmonic Calculations

P197 **Oskar Schweighofer** — University of Graz, Austria
Detailed Pathways of Chemical Reactions in Molecular Crystals Using MLFFs

P133

Wavelength-Controlled Fragmentation of Mixed-Functionalized Norrish Type-I Acylgermanes

A. Culum, M. Drusgala, D. Neshchadin, M. Haas, A.-M. Kelterer (TU Graz/AT)

Novel Norrish-type I acylgermane photoinitiators with mixed functionalization were synthesized to control the formation of different radicals via the excitation wavelength generating various polymer microstructures [1]. Two different aryl-carbonyl chromophores were introduced in tetra-substituted acyl germanes to increase solubility and design absorption characteristics in different wavelength ranges.
TD-DFT (CAM-B3LYP/def2-TZVP) analysis assigned complementary UV/Vis bands to the mesitoyl and *para*-alkoxybenzoyl units enabling wavelength-selective excitation. Photo-CIDNP investigated the competition between two alternative α-cleavages of primary Ge/benzoyl radical pairs in the presence of a monomer quencher (butyl acrylate). By shifting the irradiation window, the balance between mesitoyl- and *para*-alkoxybenzoyl-derived radicals can be systematically tuned, which was confirmed by steady-state LED irradiation NMR experiments.
This effect was investigated in detail by TD-DFT computing the excited state dissociation curves of the different substituents into radicals. Conical intersections and crossings of the excited states before and after the triplet state transition state are responsible for the formation of different radicals depending on the absorbed wavelength. These PEG-acylgermanes combine polar media compatibility with light-tuned radical generation, converting small adjustments in wavelength into mechanistic control during photopolymerization.

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P134

Probing Oxyl Character and Reactivity in a Biomimetic Non-Heme Oxoiron(IV) Complex

P. Pudasaini (Humboldt-Universität zu Berlin/DE), L. W. de Lima (Humboldt-Universität zu Berlin/DE), D. J. Barman (Humboldt-Universität zu Berlin/DE), K. Ray (Humboldt-Universität zu Berlin/DE), M. Roemelt (Humboldt-Universität zu Berlin/DE)

High-valent iron–oxygen species are key intermediates in enzymatic oxidation processes. While commonly described as Fe(IV)=O units, the electronic structure of these species can involve substantial ligand-centered radical character, leading toward an Fe(III)–oxyl description. Distinguishing between these electronic structures is essential for understanding their bonding and reactivity.

Recently, a non-heme oxoiron(IV) complex bearing the TMC-HOR ligand was synthesized as a biomimetic model of human catalase (CAT) and was shown to form 1-syn and 1-anti upon oxidation using different oxidants.[1] The two species exhibit remarkable different reactivity, with 1-syn decomposing upon addition of triethylamine (TEA), while 1-anti remains stable even in the presence of the stronger base triazabicyclodecene (TBD). Furthermore, 1-anti cannot be generated when the precursor is deprotonated prior to oxidation, suggesting an important role of the protonated alcohol functionality and its molecular environment.

In this study, the electronic structure of these complexes was investigated using density functional theory (DFT) and multireference methods. Particular emphasis was placed on determining whether the experimentally observed 1-anti species is adequately described as an Fe(IV)–oxo complex or exhibits significant Fe(III)–oxyl character. Computational electronic-structure analysis was complemented by calculated M¨ossbauer and resonance Raman parameters to enable comparison with experimental spectroscopic data. Redox and acid–base reactions were additionally investigated to explore the influence of ligand protonation and secondary-sphere interactions.

The combined electronic-structure and spectroscopic analysis reveals a clear distinction between the two isomers. While 1-syn is consistent with an Fe(IV)–oxo description, 1-anti exhibits pronounced Fe(III)–oxyl character, supported by substantial oxygen-centered spin density, Mossbauer isomer shifts, and its characteristic Fe–O vibrational properties. These findings establish 1-anti as a notable example of oxyl character in a biomimetic non-heme iron complex and demonstrate how subtle changes in coordination geometry and ligand environment can substantially alter the electronic structure of high-valent iron–oxygen species.

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P135

Systematic Active-Space Construction for the Multiconfigurational Description of a Mn(I) Photosensitizer Candidate

V. M. Ramos (Universidade Federal de São Carlos/BR), D. Farkhutdinova (University of Vienna/AT), A. P. de Lima Batista (Universidade Federal de São Carlos/BR), and L. González (University of Vienna/AT)

Developing photosensitizers based on earth-abundant first-row transition metals is an attractive strategy for more sustainable and cost-effective light-driven applications.[1] In this context, the Mn(I) complex $[Mn(HMTI)(CN)_2]^-$is investigated as a potential photosensitizer. This system is inspired by its isoelectronic Fe(II) analogue, $[Fe(HMTI)(CN)_2]$, for which a nanosecond metal-to-ligand charge-transfer (MLCT) excited-state lifetime has been reported.[2] Since experimental data are currently unavailable for the study Mn(I) complex, a reliable theoretical description of its excited-state electronic structure is particularly important. The excited-state manifold was first investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.TD-DFT reveals a dense manifold of low-lying singlet, triplet, and quintet states, with several triplet and selected quintet states showing significant spin contamination. This unbalanced description of the low-lying excited states highlights the limitations of a single-reference treatment and demonstrates the need for a multiconfigurational approach. Charge-transfer analysis further indicates that the most intense transition in the visible region has mixed MLCT, ligand-centered (LC), and metal-centered (MC) character, emphasizing the involvement of both metal- and ligand-centered orbitals. To obtain a balanced multiconfigurational description of these states, a sequence of CAS(10,12), CAS(14,14), RAS(14,14), and RAS(18,18) active spaces was investigated by systematically incorporating metal-centered σ and d orbitals together with ligand π and $\pi*$ orbitals. Despite the progressive enlargement of the active space, the low-lying singlet-state pattern remains broadly preserved, with the most intense transition consistently predicted between 1.97 and 2.05 eV. These results identify the orbital components required for the active space and provide a systematic framework for establishing a balanced multiconfigurational description of the low-lying excited states of $[Mn(HMTI)(CN)_2]^-$.

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P136

Machine Learning-Guided Molecular Insights into Metal-Catalyzed Asymmetric Reactions: A Case Study with a Pharmaceutically Relevant Version of Suzuki-Miyaura Coupling

Sheetal Ranaut (Indian Institute of Technology Jammu)

Transition metal-catalyzed asymmetric transformation is a well-known tool for synthesis of a structurally complex molecular motif which can be used in drug discovery. Development of a room-temperature reaction with a high stereo-induction from easily accessible starting materials often requires exhaustive experimentation. The use of data science and statistical modelling dares to circumvent this problem by generating a large number of numerical data for reaction discovery in a time-bound fashion. However, it is still a challenge to identify the molecular features from a machine learning-guided study to control the reaction outcomes, as desired. Herein, we present a gradient boosting-guided protocol on a pharmaceutically relevant version of Rh-catalyzed Suzuki-Miyaura coupling reaction between racemic allyl halide substrates, non-racemic bis-phosphine-based biaryl catalysts, and boronic acid coupling partners. The predictive power of our final model is found to be reasonable with an RMSE of 4.28 – 6.51. The bite angle in the metal-catalyst geometry, the size and volume of the chiral pocket inside the bis-phosphine ligand, and molecular fitting of the coupling partner/allyl halide substrate inside the pocket are found to be of utmost importance for controlling the reaction output, i.e., enantiomeric excess. We have discovered a library of 1577 highly asymmetric ($\geq$ 98% ee) coupling reactions that have experimentally untested combinations of substrate, catalyst, coupling partner, time, and temperature. We have further extracted a subset of 191 reactions doable at 25°C without excessive heating. Our machine learning-guided approach assists a synthetic chemist in accessing easily-tunable molecular parameters to control the outcome of an asymmetric transformation, without the need for experimental trial-and-error methods.

P137

Spatially Resolved Vibrational Dynamics of Water in Aqueous $Ba(SCN)_2$ Using Machine-Learned Potentials

H. Rappoun (Paderborn University/DE), H. Elgabarty (Paderborn University/DE), M. Brehm (Paderborn University/DE)

Understanding how ions influence the dynamics of their surrounding water is important for describing solvation and electrolyte behavior at the molecular level. In this work, we study an aqueous $Ba(SCN)_2$ solution using spatially resolved spectroscopic analysis based on first-principles molecular dynamics (FPMD) simulations [1].
A direct first-principles treatment of the system over experimentally relevant timescales is computationally demanding. We therefore developed a workflow to train a set of machine-learned interatomic potentials (MLIPs) on reference structures, energies, forces, and maximally localized Wannier centers (MLWCs) obtained from short FPMD simulations. The energy and force labels are used to train a MACE [2] MLIP, which is then employed to generate a longer molecular-dynamics trajectory of the electrolyte. Separately, a machine-learning model based on the SCFNN framework [3] is trained on the MLWC positions obtained from the FPMD simulations and used to predict the Wannier centers of water molecules along the MACE trajectory.
We apply time- and space-resolved correlation analysis of the molecular dipoles to obtain radially resolved infrared absorption spectra of water molecules. In addition, radially resolved vibrational correlations are calculated from the atomic velocities. These complementary analyses allow us to characterize correlated and anticorrelated water motions as functions of both frequency and intermolecular distance.
Our results show clear differences between water molecules in the vicinity of Ba^{+2}, those near SCN^-, and those located farther from the ions. Even at a concentration of approximately 0.5 M, the ions noticeably influence the collective vibrational dynamics of the surrounding water and the hydrogen-bond network. Overall, the combination of FPMD and machine-learning models provides an efficient approach for extending first-principles-quality spectroscopic analysis to longer simulation times and for investigating ion-specific effects in aqueous electrolytes.

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P138

Controlling Excited States of Anthracenes through Heteroatom Substitution

V. Ratheesh (University of Heidelberg/DE), A.M. Weidlich (University of Heidelberg/DE), A. Dreuw (University of Heidelberg/DE)

Introducing heteroatoms into acenes is a powerful route to controlling their spectral properties, but a predictive picture that holds between chemically distinct heteroacene families has been hard to pin down. In this work, we apply the algebraic diagrammatic construction (ADC) scheme for the polarization propagator to a diverse set of aza-, phospha-, and halogen-substituted anthracenes, examining how both the nature and the ring position of a substituent govern the two lowest $\pi\pi^*$ states, $^1\mathrm{L}_s$ ($^1\mathrm{L}_b$) and $^1\mathrm{B}_b$. By tracing the diagonal elements of the ADC matrix down the perturbative hierarchy ADC(2) $\rightarrow$ ADC(1) $\rightarrow$ ADC(0), we isolate the physical origin of the intensity redistribution between these states. The orbital-energy gap between the participating particle–hole configurations emerges as the dominant factor controlling their mixing and, in turn, the oscillator strength. Substitution at the apical sites enlarges this gap and yields bright α-bands, while substitution at lateral sites keeps the configuration mixing balanced and transitions weak. Along the halogen series, keeping positions fixed, increasing electronegativity progressively intensifies the $^1\mathrm{L}_s$ band. Together these results provide a unified, physically transparent framework for rationally tuning excited-state brightness in substituted acenes.

P139

Combinatorial Structure Search and First-Principles Stability Analysis of Borophene Phases on Ag(111)

A. Sreejita Ray (Freie Universität Berlin/DE), B. Peer Julius Geister (Freie Universität Berlin/DE), C. Beate Paulus (Freie Universität Berlin/DE)

Borophene, the two-dimensional allotrope of boron, shows an inherent structural polymorphism governed by the density and arrangement of hexagonal holes within its pristine triangular lattice. The substrate-dependent nature of this polymorphism under experimental conditions, observed on Ag(111)1,2, Ir(111)3, Au(111)4, Al(111)5, and Cu(111)6 motivates a systematic theoretical investigation of the thermodynamically accessible phase space. We introduce a combinatorial structure-search algorithm that performs substrate-constrained commensurate cell matching followed by hexagonal hole pattern enumeration and graph-based connectivity filtering and subsequent multi-registry stacking, without prior assumption of phase identity. All screened candidate structures are then relaxed using spin-polarised density functional theory at the PBE+D3(BJ) level of theory. Within a thermodynamic stability window of 0.2 eV above the ground-state $\beta 12$ phase, corresponding to experimental synthesis temperatures up to 800 K, the algorithm predicts several novel borophene polymorphs on Ag(111) besides the known experimental phases. A systematic energetic decomposition and Pearson correlation analysis highlight the role of intrinsic boron–boron bonding governing phase stability. Simulated constant-current STM fingerprinting further identifies three distinct morphological classes, each with characteristic bias-dependent properties. The methodology is broadly applicable to other combinations of two-dimensional materials on substrates where polymorphism is determined by vacancy patterning.

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P140

Vibrational Spectroscopy of Molecules in High Pressure Enviroments with GOSTSHYP

K. Rensinghoff (Universität Münster), A. Pausch (Universität Münster)

Vibrational spectroscopy in high pressure environments provides a sensitive probe of pressure-induced changes in molecular structure and bonding. Experimental advances employing the diamond anvil cell have made infrared and Raman spectroscopy under pressures of several Gigapascals increasingly accessible. Computational methods that can efficiently predict vibrational properties of molecules under such conditions are therefore highly desirable. The Gaussians On Surface Tesserae Simulate HYdrostatic Pressure (GOSTSHYP) model describes hydrostatic pressure by means of repulsive Gaussian potentials distributed over the surface of a molecular cavity, thereby providing an efficient molecular approach to quantum chemistry for high pressure environments. Recent applications have demonstrated its potential for vibrational spectroscopy, including the calculation of pressure-dependent Raman spectra of zwitterionic glycine in good agreement with experiment. However, vibrational frequency calculations with GOSTSHYP have so far relied on numerical second derivatives of the energy, which become computationally demanding even for moderately sized systems. The benefits of analytical second derivatives for high-pressure vibrational calculations have previously been demonstrated for the related X-HCFF approach. Here, we present the derivation, implementation, and application of an analytical nuclear Hessian for the GOSTSHYP model. Starting from the GOSTSHYP energy and its analytical gradient, we derive all Hessian contributions, including derivatives of the molecular cavity, the surface Gaussian potentials, and the corresponding three-center integrals. The resulting expressions have been implemented into the TURBOMOLE program suite and validated against numerical derivatives. First applications demonstrate the use of analytical GOSTSHYP Hessians for the efficient calculation of pressure-dependent harmonic vibrational frequencies and infrared spectra. This development enables routine vibrational analyses of molecular systems under hydrostatic pressure and substantially extends the spectroscopic capabilities of GOSTSHYP.

P141

The Aperiodic Defect Model: Treating Aperiodic Defects in Fully Periodic Systems with Wavefunction Methods

C. Rickert (MPI Solid State Research/DE, Humboldt University/DE), D. Kats (MPI Solid State Research/DE), D. Usvyat (Humboldt University/DE)

Defects are aperiodic perturbations in otherwise periodic systems, yet their electronic structure is almost exclusively treated using periodically repeated supercells. This introduces artificial defect-defect interactions, and, for charged defects, the need for compensating background charges, resulting in slow convergence toward the thermodynamic limit. At the same time, the large supercells required by conventional approaches severely limit the applicability of systematically improvable wavefunction methods.
In this contribution, I will present the Aperiodic Defect Model (ADM) [1], a quantum embedding framework that resolves this conceptual inconsistency by embedding a single defect into the mean field of the pristine periodic system. This eliminates spurious periodicity without sacrificing the rigorous description of the crystalline environment and seamlessly incorporates the local electronic structure of the defect into the extended host. The resulting molecular-like Hamiltonian provides direct access to the powerful toolbox of molecular quantum chemistry, including coupled cluster, multireference, and excited-state approaches, whose application to periodic systems can be very difficult if feasible at all. Altogether, the ADM establishes a general framework for quantitative studies of defects and other localized phenomena in complex periodic materials.
The capabilities of ADM will be demonstrated for a negatively charged monovacancy in phosphorene [2], a demanding benchmark involving structural reconstruction, charge localization, and long-range polarization.

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P142

How good are excited-state geometries from subsystem TDDFT?

Anton Rikus (University of Münster), Johannes Neugebauer (University of Münster)

Subsystem time-dependent density-functional theory in the uncoupled approximation (uncoupled frozen-density embedding, FDEu) lowers the cost of excited-state calculations on a chromophore in an explicit environment and resolves the response into fragment contributions. Analytical gradients for FDEu have been available since 2016 and are implemented both in Serenity and in Koala (using the TDA), but the quality of the excited-state geometries they produce has not been assessed systematically. This poster reports such a benchmark.

For a set of chromophore–solvent clusters we optimize both the ground state and the lowest excited state at three levels of treatment: the isolated chromophore, the FDEu-embedded chromophore, and the full supersystem, which serves as the reference (TDA/PBE0/def2-TZVP, revAPBE non-additive kinetic and PBE non-additive exchange–correlation functionals). Every minimum is confirmed by frequency analysis.

FDEu reproduces supersystem vertical absorption energies closely (mean error +5 meV, MAE 23 meV), but the agreement deteriorates markedly at the emissive minimum (+48 meV, MAE 52 meV), with a systematic overestimation. To separate the two sources of this error, the emission error is telescoped through vertical single points in which each method is evaluated at the other's geometry. The two possible decompositions agree to better than 10 meV, so the split is well defined: an electronic contribution of +34 meV (MAE 35 meV) and a smaller, sign-indefinite geometric contribution of +14 meV (MAE 32 meV). The latter carries no definite sign because the optimizer minimizes the total excited-state energy rather than the excitation energy itself.

The outliers are as informative as the averages. Charge-transfer states and S1/S0 seam crossings have to be excluded, since the FDEu chromophore spectrum contains no inter-subsystem excitations and TDDFT cannot describe the near-degeneracy with its own reference. In one cluster the two methods converge to different intermolecular arrangements, hydrogen-bonded versus π-stacked, precisely because the supersystem stabilizes the stacked form through charge-transfer admixture that FDEu structurally cannot represent. Finally, control optimizations started from the supersystem geometry show that excited-state minima are more sensitive to the starting structure than ground-state ones, which sets a practical floor on the accuracy any such benchmark can claim.

P143

Re-purposing Optimization Trajectories: Do Hessians from Quasi-Newton Schemes Yield Reasonable Free Energies?

L. S. Rindt (Heidelberg University), P. Pracht (Heidelberg University)

Second derivatives of the potential energy with respect to nuclear coordinates, known as the nuclear Hessian, are essential for the calculation of molecular vibrational frequencies, thermodynamic properties, and for numerical geometry optimization procedures[1]. However, their computation is often prohibitively expensive, even at DFT level, for moderately sized organic and drug-like molecules. In this work, we explore whether the quasi-Newton framework can be leveraged to reconstruct approximate Hessians from gradients accumulated along the optimization trajectory, requiring only an initial guess Hessian.
Standard single-secant update schemes rarely improve absolute free energies over the pure guess Hessian on a selected dataset calculated with the semiempirical GFNn-xTB methods[2]. Nevertheless, certain variants outperform the guess Hessian for relative free energies on S30L, demonstrating that quasi-Newton update schemes can yield meaningful curvature improvements. We find that single-secant methods are fundamentally limited by their reliance on only the most recent secant condition, causing previously accumulated curvature information to be overwritten.
Multi-secant methods can alleviate this loss, but tend to struggle with redundancy inherent to optimization trajectories. To address these challenges, we propose a rigorous secant selection alongside a novel update scheme that restricts the Hessian corrections to the subspace in which the guess Hessian violates the secant conditions.

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P144

A Perturbative Triples Approach for EOM-CC-(D)EA/(D)IP Treatments of Excited States in Strong Magnetic Fields

C.-M. Röper (Saarland University/DE), M. Bonsignore(University of Pisa/IT), M.-P. Kitsaras(Université de Toulouse/FR), S. Stopkowicz-Franzbach(Saarland University/DE, University of Oslo/NO)

Magnetic White Dwarfs (WDs) provide atmospheric environments where the magnetic field strength can reach magnitudes around 200kT. Electronic structures of atoms and molecules in such environments can differ greatly from the weaker/field-free cases. Spectra from stellar objects enable studying of their atmospheric composition and provide glimpses into the behaviour of species in these environments. Theoretical calculations are needed for their assignment due to experimentally inaccessible conditions.[1] Methods such as finite-field(ff) coupled-cluster(CC) as well as equation-of-motion-CC(EOM-CC) theory[2-4] provide excitation energies and transition probabilities of appropriate quality. For predictions capable of comparison and assignment of observable spectra, triple excitations must be considered. Due to compounding factors leading to varying electronic characters, consistent targeting of states despite different magnetic field strengths and orientations is vital. We exploit the flexibility offered by different EOM-CC variants to target these states consistently. The suite of EOM-CC variants implemented as ff-methods is extended via the DEA/DIP approaches that add/remove two electrons to/from their CC reference states.This gives access to specific multiconfigurational states not attainable via existing EOM-CC variants. The implementation of one-electron transition properties like the transition dipole moments for analysis of available spectra are presented as well. The work of Matthews and Stanton[6] is extended to enable perturbative triples approaches for DEA and DIP, completing approximations at this level of theory for the suite of ff-EOM-CC variants available. This presentation discusses the results of an investigation on several absorption lines of the C+ cation, the presence of which has been hypothesised on WD-J2023, previously established as a hot DQ type(carbon-rich atmosphere) and estimated to exhibit temperatures >25.000 K. We combine different EOM-techniques to probe transitions between excited states, to capture the prominent multiconfigurational character of the target C+-states. DIP, which describes C2 in field-free studies well, is applied to C2 in a magnetic field to probe low-lying transitions.

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P145

Quantum-classical non-adiabatic dynamics in extended solid-state materials: a SHARC-VASP approach

M. Romanelli (University of Vienna/AT), M. Sahre (University of Vienna/AT), G. Kresse , S. Mai (University of Vienna/AT) , L. González (University of Vienna/AT)

Non-adiabatic dynamics in materials encompasses a broad range of phenomena, from charge-carrier transfer and recombination to light-induced structural and electronic changes. Accurately modeling these processes is challenging even for isolated molecules, and becomes more arduous in extended periodic systems. For molecules, Tully's surface hopping [1] is one of the simplest yet successful quantum-classical methods used to model excited-state dynamics. However, its application to extended periodic materials remains far less explored, mainly due to the intrinsic difficulty and high computational cost of accurately describing excited states in solids. For this reason, most state-of-the-art applications still rely on coarse approximations [2,3], such as a simple Kohn–Sham orbital picture to represent the material's excitations and the neglect of the electron-nuclear back-reaction, i.e., the effect of electronic excitation on nuclear dynamics.

By leveraging some of these concepts, we recently developed a new SHARC-VASP [4] interface that extends SHARC [5]—originally designed for molecular systems—to solid-state materials. We investigate the excited-state non-radiative relaxation of bulk silicon using different initial-condition sampling schemes based on either ground-state ab initio MD or Wigner quantum sampling, and discuss the resulting differences. We further explore machine-learning potentials trained on ab initio MD data to accelerate both MD and quantum sampling. Finally, we present an outlook on improving the current excited-state description by incorporating our recently developed restricted open-shell Kohn–Sham scheme in VASP [6], enabling a more accurate and efficient treatment of excited states in solids.

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P146

Perturbative Spin-Orbit Coupling in CP2K for Molecules, Bulk Materials, and Surfaces

A. Bibek Samal (University of Regensburg, Germany), B. Jan wilhelm (University of Regensburg, Germany)

Spin-orbit coupling (SOC) lifts electronic-state degeneracies, modifies ionization energies and band gaps, and gives rise to topological surface states. For large and structurally complex systems containing heavy elements, efficient formulations of SOC are needed. Here, we present a perturbative SOC implementation in CP2K[1] based on relativistic Hartwigsen-Goedecker-Hutter pseudopotentials.[2] The SOC matrix elements are evaluated analytically in a Gaussian atomic-orbital basis, and their sparsity enables linear-scaling construction with the number of atoms. We benchmark the method for the SOC81 molecular dataset[3] and for 88 crystals comprising alkali halides, elemental solids, and compound semiconductors.[4] For the molecules, the SOC-corrected highest occupied molecular-orbital energies agree with all-electron PBE reference values within 42 meV. For the crystals, spin-orbit splittings obtained with the TZV2P-MOLOPT basis agree with all-electron SOC reference calculations with mean absolute deviations below 20 meV. For a Bi2Te3 slab, the method also reproduces the SOC-induced topological Dirac surface state, with bands near the Dirac cone agreeing within 20 meV with plane-wave calculations.[5] These results establish the perturbative HGH-SOC implementation in CP2K as an accurate and computationally efficient approach for molecular, bulk, and surface electronic-structure calculations, with a formulation well suited to large atomistic models.

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P147

Girsanov path reweighting for core set Markov state models

Joana-Lysiane Schäfer (Freie Universität Berlin/DE), Bettina G. Keller (Freie Universität Berlin/DE)

Girsanov path reweighting enables the recovery of unbiased dynamics from path generated under a modified potential energy function. The method is based on reweighting biased path ensemble averages by introducing the relative path probability of observing a path at the target potential compared to the biased potential. A fundamental limitation of Girsanov reweighting arises from the divergence of path probabilities between the two systems with increasing path length. This necessitates the use of kinetic models with high time resolution, such as core set Markov state models, to accurately evaluate reweighted dynamics. In this work, we present a reweighted estimator for core set Markov state models. The approach is implemented within the Deeptime package and validated on both a low-dimensional test system and a molecular system.

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P148

FrayedEnds: Basis-Set-Free Quantum Chemistry

F. Langkabel (Algorithmiq Ltd/FI), T. Scharfe (University of Augsburg, Germany), H.S.T. Truong (University of Augsburg, Germany), J.S. Kottmann (University of Augsburg, Germany)

Basis-set-free quantum chemistry represents the spatial part of the orbital basis without relying on predefined sets of basis functions. The most promi- nent choice, Alpert multiwavelets, formally spans an L^2 basis that is individu- ally truncated for each orbital. The key advantage of such a representation lies in its conceptual simplicity combined with guaranteed numerical precision: the user can essentially ignore the details of the underlying basis. In practice, however, this flexibility has long come at a cost: existing methods required time-consuming re-implementation in first-quantized form, and correlated methods in particular remained computationally expensive. The latter limita- tion was addressed by the direct determination of optimal pair-natural orbitals [1], which delivered a computationally affordable correlated method directly at the basis-set limit. Building on this, [2] decoupled the determination of the orbital basis from the many-body treatment, allowing general, off-the-shelf many-body methods to be used on a compact set of optimal orbitals. Finally, [3] formulated a self-consistent scheme in which the orbital basis and the many-body state are improved cyclically, refining one against the other. This essentially realizes a CASSCF approach with a given number of active orbitals obtained through a different algorithm in a formally complete L^2 basis. Within this fully variational scheme, nuclear and alchemical gradients can be computed directly using the Hellmann-Feynman theorem. By using a basis- set-free approach we open the possibility of defining a fully-differentiable quantum chemistry framework. The formalism can be used for both ground and excited states and shows promise for usage in tandem with quantum computing methods [4], where optimal active spaces are crucial to increasing accuracy while keeping the number of required qubits low.

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P149

A Novel Variational Quantum Trajectory Approach to Nuclear Quantum Dynamics

J. Scherlitzki (Freie Universität Berlin/DE), J. C. Tremblay (CNRS-Université de Lorraine/FR), B. Paulus (Freie Universität Berlin/DE)

Trajectory-based approaches to molecular Quantum Dynamics have been revisited several times throughout the past decades due to their potential to overcome the curse of dimensionality and allow on-the-fly potential energy surface exploration. They have, however, remained less successful than widely used methods such as Multiconfigurational Time-Dependent Hartree (MCTDH) as consequence of numerical challenges or methodological deficiencies. In this work, we investigate the behaviour of a novel factorisation ansatz for the wavefunction that combines time-dependent Gaussian functions with variational expansion coefficients. We derive working equations to solve the time-dependent Schrödinger equation, and propose a dynamical gauge that accounts for the redundancy of the chosen ansatz with respect to the temporal degree of freedom. Taking advantage of the appealing properties of Gaussians, analytical expressions are obtained for all matrices required for the new propagation scheme. Furthermore, we present a proof-of-concept implementation of the method in Python, which explores its numerical efficiency and stability. The new approach is tested on various one-dimensional models, and ideas for the extension to multidimensional dynamics are presented.

P150

Calculation of Energy Potential Surfaces and Absorption Spectra of Rubidium-Noble Gas Mixtures

A. Julian Schiefer-Strauß (University of Innsbruck), B. Michael Hütter (University of Innsbruck), C. Milan Ončák (University of Innsbruck)

Nuclear spin states of noble gas atoms, due to their protection from decoherence via a closed shell, were identified as suitable components for quantum technologies. This protection however begs the question how one can manipulate these nuclei states reliably. One suitable solution are optically controlled interactions via spin exchange collisions with alkali atoms.

The presented work investigates the potential energy curves and absorption spectra of the rubidium-noble-gas exciplexes RbNe, RbAr, RbKr and RbXe. The interaction was calculated using ab initio electronic-structure calculations, mainly Multi-Reference Configuration Interaction (MRCI) along with Spin-Orbit-Coupling calculations as well as hyperfine-splitting evaluations with DIRAC. The results were used to find possible quasi-bound states between the two atoms as well as their excitation energies. In the asymptote, energies show low deviation to the corresponding experimental values.

The ground- and excited-state energies in addition to the corresponding dipole moments were subsequently used to reconstruct the absorption spectra of such metallic vapor-noble gas mixtures. In order to obtain realistic results, the interatomic distances were weighted by an already known and widely used probability distribution, where the Boltzmann-factor is expanded by the area enclosing one of the atoms. This weighing is essential, since the energies of the exciplex depend strongly on the distance between the interacting atoms, which in general leads to a line-broadening.

Special attention was paid to the visibility of the so-called red- and blue-Satellites, i.e., sidebands which occur on the energetically low and high side of the principal absorption lines. Their appearance is related to extrema in the excitation energy curves and can therefore be used to gain further insight in the underlying exciplex interaction. The achieved results agree with available experimental data and provide further insight into the binding behaviour and spectroscopic properties of rubidium-noble-gas complexes.

P151

The Cavity-Born-Oppenheimer Framework: Electronic Reshaping and Multireference Effects under Vibrational Strong Coupling

T. Schnappinger (Stockholm University, Stockholm/SE)

When molecules are placed in a non-classical photonic environment, such as an optical or nanoplasmonic cavity, strong light-matter coupling can form hybrid states called polaritons. Recent experiments have shown that, in the vibrational strong coupling (VSC) regime, when quantized cavity modes couple to molecular vibrational degrees of freedom, the resulting hybrid states can alter chemical and physical properties. The Cavity-Born-Oppenheimer (CBO) framework is a robust and extensible quantum chemistry approach that accurately captures these complex interactions [1,2]. In this contribution, I will provide a general introduction to the CBO framework and its recent methodological extensions, which are designed to capture VSC phenomena. Specifically, I will discuss the development of the CBO Configuration Interaction (CBO-CI) method, which provides a rigorous, ab initio foundation for describing ground and excited states under strong coupling. Since the cavity frequency in VSC is much lower than electronic transitions, the cavity does not hybridize electronic states into polaritons. Instead, the cavity vacuum induces a static, amplified reshaping of the electronic structure. This acts as a vacuum-field Stark-like effect, shifting dipoles and lifting degeneracies without electronic resonance. Furthermore, I will discuss the collective nature of VSC in molecular ensembles. We will explore the multireference character of these systems by analyzing Self-Consistent Field (SCF) stability within the CBO-Hartree-Fock (CBO-HF) approach. Under strong-coupling conditions, cavity-mediated interactions can induce critical SCF instabilities, resulting in cavity-induced, broken-symmetry CBO-HF solutions. These results emphasize the importance of multireference techniques for accurately characterizing the ground-state electronic structure, collective dynamics, and potential modifications to molecular property landscapes under VSC. To facilitate these investigations, all of the discussed methods have been implemented in the Psi4-CBO program package. Built upon the foundational architecture of the Psi4 quantum chemistry software and developed in Python, Psi4-CBO offers a comprehensive and accessible toolkit for understanding polaritonic chemistry and the nuanced molecular changes induced by quantum light.

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P152

Can Triple Excitations Restore Spin Symmetry of Excited States within the ADC Framework?

F. Schneider (Heidelberg University/DE), J. Leitner (Heidelberg University/DE), A. L. Dempwolff (Heidelberg University/DE), A. Dreuw (Heidelberg University/DE)

Algebraic diagrammatic construction (ADC) methods are accurate and systematically improvable quantum chemical methods for the description of excited states, built upon Møller–Plesset perturbation theory. The recently introduced fourth-order scheme, ADC(4), achieves a mean absolute error (MAE) of only 0.09 eV for singly excited states of closed-shell molecules, a substantial improvement over the MAEs of ADC(2) and ADC(3) of 0.20 eV and 0.23 eV, respectively.[1] Its performance for open-shell systems, however, has not been explored yet. Spin contamination (SC) remains a key challenge in open-shell calculations and a central criterion for assessing the accuracy of single-reference methods. Lower-order ADC methods are susceptible to SC,[2] and while higher-order correlation effects (triple and quadruple excitations) are known to reduce SC of excited states in coupled-cluster theory,[2] this aspect has not been studied in the context of ADC.
Here, we present the first implementation of the consistent second-order $\langle S^2 \rangle$ evaluation for ADC(4) and investigate whether spin symmetry can be restored through the inclusion of triple excitations. We find that SC is reduced systematically for unrestricted Hartree–Fock reference states: the MAE of $\langle S^2 \rangle$ decreases from 0.0126 au at the ADC(2) level to 0.0076 au at the ADC(4) level for first-order properties, and from 0.0078 au to only 0.0017 au for second-order properties, respectively. This shows that ADC methods have the potential to systematically remove SC.

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P153

Periodic g-xTB — Approaching DFT Accuracy for Periodic Systems at Semiempirical Cost

L. M. Seidler (University of Bonn), T. Kühne (Center for Advanced Systems Understanding/DE), T. Froitzheim (University of Bonn), T. Bredow (University of Bonn), A. Hansen (University of Bonn), S. Grimme (University of Bonn)

It is well known that certain condensed systems and properties benefit greatly from the inclusion of non-local exchange. Examples include the description of electron-phonon couplings, polaron formation, and charge localization in general—phenomena central to the study of energy materials and heterogeneous catalysis. However, periodic non-local exchange interactions require dense k-point meshes and regularization techniques to reach convergence to the periodic limit. Due to the often prohibitive computational demand of non-local exchange, large-scale studies must frequently rely on lower-level semi-local density functionals such as PBE or r^{2}SCAN, or on machine-learning interatomic potentials trained on their data.

Here, we present the extension of the g-xTB method [1] to periodic systems both via a γ-point periodic algorithm implemented in the open-source `tblite` library, and a complete k-point periodic algorithm via an interface to CP2K. g-xTB improves upon the established GFNn-xTB family of semiempirical methods through several key advances, including a charge-adaptive minimal basis approaching double-ζ quality, the new and improved D5 dispersion correction, and a complete tight-binding expansion up to fourth order for a more accurate description of charged systems. However, the most important improvement is the inclusion of approximate non-local exchange in a range-separated fashion, imitating its reference method ωB97M-V/def2-TZVPPD. Consequently, g-xTB exhibits characteristic features of RSH functionals, including large frontier-orbital gaps, accurate reaction barrier heights, and balanced thermochemistry. Overall, it reaches DFT-level accuracy for molecular systems, as demonstrated by a WTMAD-2 of 7.6 kcal mol^{-1} on the GMTKN55 benchmark suite.

Preliminary results of the periodic implementation show improvements over GFN2-xTB, e.g., in X23b lattice energies (MAE 2.05 kcal/mol) and relative DMC-ICE13 polymorph energies (MAE 0.23 kcal/mol), cutting errors at least in half compared to GFN2-xTB. Overall, our periodic implementation demonstrates that g-xTB transfers well to extended systems, preserving the favorable properties of its RSH reference method. At the same time, the new terms introduce only a limited computational overhead, retaining comparable efficiency to other semiempirical methods. Periodic g-xTB therefore provides a fast and accurate approach to modeling extended systems beyond the semi-local approximation.

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P154

From Single α-Helices to Helical Bundles: Electronic Properties and Stability

A. Faezeh Shabani (TU Chemnitz/DE), B. Paul Kluge (Leipzig University/DE), C. Georg Kuenze (Leipzig University/DE), D. Florian Guenther (São Paulo State University/BR), D. Sibylle Gemming (TU Chemnitz/DE)

α-Helices and their higher-order assemblies are fundamental structural motifs in biology and promising building blocks for bioelectronic devices. Their intrinsic polarity and chirality make them particularly interesting for understanding charge transport and chiral-induced spin selectivity (CISS), yet the relationship between molecular sequence, helix length, and higher-order organization remains incompletely understood. In this work, we use density-functional tight-binding (DFTB+) calculations to investigate peptide systems across two structural levels, from individual α-helices to helical bundles. For single helices, we examine polyalanine and sequence-modified peptide models to investigate how helix length and side-chain chemistry influence their electronic structure. We find systematic changes in molecular orbital energies with increasing helix length, consistent with the additive macrodipole arising from the aligned peptide-bond dipoles and terminal groups. Analysis of the electronic structure further reveals how side chains and termini influence the spatial distribution of electronic states, providing insight into possible charge-transport pathways along the helix. These results demonstrate how molecular design can be used to tune the electronic properties of peptide-based molecular wires. We then extend this molecular picture to helical bundles, in which multiple α-helices assemble into supercoiled, chiral architectures. Using DFTB+, we investigate the energetic factors governing different bundling motifs and assess the contribution of dispersion interactions and solvation to their stability. This provides a connection between the intrinsic properties of individual helices and the structural organization of their higher-order assemblies. By combining electronic-structure analysis of individual helices with energetic and structural analysis of helical bundles, this work establishes a multiscale framework for understanding how molecular polarity, chirality, and intermolecular interactions shape peptide architectures. The results provide design principles for peptide-based electronic and chiral materials, with potential implications for bioelectronics, electronic hyperpolarization, and CISS.

P155

Conversion of Light Alkanes into Value–Added Products Over Boron–Based Catalysts

Akhilesh Sharma, Puneet Gupta (Indian Institute of Technology Roorkee, India)

The oxidative dehydrogenation (ODH) of light alkanes over metal–free boron–based catalysts has recently emerged as a promising strategy for the selective production of value–added chemicals. Among these catalysts, boron oxide (B_2O_3) [1] and borocarbonitride nanotubes (BCNNTs) [3] have attracted considerable attention for their remarkable catalytic performance. In 2023 [2], *ab initio* molecular dynamics (AIMD) simulations identified catalytically active structural motifs in molten B_2O_3 at 850 K. However, the catalytic roles of these active sites in the activation of methane and propane, as well as the mechanistic pathways governing product selectivity, remain poorly understood. In this work, we employ a combination of *ab initio* CASSCF/NEVPT2 and DFT calculations to investigate the reaction mechanisms of methane [4] and propane [5] over the liquid B_2O_3 active sites in the presence of singlet ($^1O_2$) and triplet ($^3O_2$) oxygen.
Our calculations reveal that B–B motifs are the most catalytically active sites, enabling efficient methane conversion into formaldehyde (HCHO) and propane into propylene and ethylene. In contrast, cyclic B–O–B motifs exhibit substantially higher activation barriers, indicating significantly lower catalytic activity. Orbital analyses further demonstrate distinct activation mechanisms: oxygen lone–pair donation governs reactivity at B–O–B motifs, whereas σ(B–B) bond donation drives bond activation at B–B sites. In addition, mechanistic investigations of methanol oxidation over BCNNTs provide detailed insights into the formation pathways of HCHO and the undesired over–oxidation product CO_2. These findings provide fundamental mechanistic insights for the rational design of efficient catalysts for selective light–alkane oxidation.

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P156

Prokyon – An Open-Source Library for On-the-Fly Machine Learning of Interatomic Potentials

O. Shayestehpour (Paderborn University/DE), H. Elgabarty (Paderborn University/DE), R. Schade (Paderborn University/DE), M. Brehm (Paderborn University/DE)

Machine-learned interatomic potentials (MLIPs) have emerged as a transformative tool in computational chemistry, offering a bridge between the high accuracy of ab initio electronic structure methods and the efficiency of classical force fields. By learning the potential energy surface (PES) from quantum mechanical (commonly DFT) reference data, these models enable the simulation of complex systems at time and length scales previously deemed inaccessible.

A significant challenge remains in the reliability of state-of-the-art models when they encounter under-represented regions of chemical and configurational space in their reference data. Static ML models often struggle with extrapolation; when a simulation explores configurations far from the training set, the model may produce unphysical results without warning.

We present Prokyon, an open-source library to provide on-the-fly machine learning to existing electronic structure packages. Prokyon mitigates the risks of extrapolation by implementing active learning workflows based on Bayesian uncertainty quantification (UQ). The library monitors the model's predictive variance in real-time. Whenever the model's uncertainty exceeds a specified confidence threshold, the library triggers an automatic fallback to the underlying electronic structure method. This new data point is then used to refine the model on-the-fly, ensuring that the simulation remains physically grounded even in novel regions of the PES.

Our initial implementation targets CP2K as a primary host package, chosen for its high efficiency in generating reference data. Prokyon is designed for broad interoperability, with future integrations planned for other major codes including ORCA, CPMD, and Quantum Espresso. By providing a standardized interface for adaptive, Bayesian-guided learning, Prokyon aims to make robust, high-fidelity ML-based atomistic simulations more accessible to the broader computational chemistry community.

P157

Transcorrelation in Solid-State Matter

K.Simula (Max Planck Institute for Solid State Research), M. di Mauro (Max Planck Institute for Solid State Research), T. Jian (Max Planck Institute for Solid State Research), N. Bogdanov (Max Planck Institute for Solid State Research), A. Alavi (Max Planck Institute for Solid State Research)

Accurate ab initio electronic structure theory for solids remains a long-standing challenge: the most reliable correlated methods of quantum chemistry are limited by bottlenecks in system size, correlation treatment, and basis-set requirements. Pushing these methods toward larger, more strongly correlated systems while reaching the complete-basis-set limit at tractable cost is among the central challenges in the field today.
Transcorrelation (TC) is an explicitly correlated framework that addresses these problems. The second-quantized Hamiltonian is similarity-transformed with respect to a Jastrow factor — a real-space correlator borrowed from variational Monte Carlo that imposes the electron-electron cusp — folding correlation into an effective Hamiltonian with modified two- and three-body interactions. Since this transformation preserves the total energy while lowering the reference energy, less correlation remains to be recovered from virtual-space excitations. This compactification makes lower-level methods more accurate, while the explicit real-space cusp greatly accelerates basis-set convergence. A recently developed pseudopotential framework further accelerates the TC methods, particularly for large systems with heavy atoms [1-2].
Together, these features tackle all three bottlenecks for solid-state simulations: triple-zeta basis sets already suffice for convergence in bulk silicon; CCSD(T) reaches quantitative accuracy for point defects; and long-range Jastrow factors with TC embedding shrink the orbital space required to capture correlation.
In this talk I will present the current state of TC theory in solids, covering both method and applications: the periodic TC formalism and pseudopotentials in TC, followed by basis-set and method convergence in bulk silicon, recent formation energies of silicon self-interstitial defects [3], and magnetic interactions in cuprate and nickelate superconductors.

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P158

Pressure induced luminescence shift in coordination compounds

A. Ramandeep Singh (University of Münster/DE), B. Mohammadreza Rahmani (University of Münster/DE), C. Nikos L. Doltsinis (University of Münster/DE)

The phoshorescence of square-planar Pt (II) complexes is known to red-shift upon aggregation [1,2]. This effect can be exploited to control the emission wavelength of Pt (II) complexes by external pressure [3]. In this work, we investigate the pressure-dependent phosphorescence of a new square-planar Pt (II) complex both in solution and in MOFs by a combination of periodic DFT, QM/MM and classical molecular dynamics.
The monomeric Pt(II) complex shows a large red shift of 0.27 eV, when subjected to hydrostatic pressures ranging from 100 kbar to 170 kbar using DCM as solvent. The reason being shortening of Pt-ligand bonds with increasing pressure and interaction of monomeric Pt(II) complex with the solvent. The Pt(II) complex also shows a red shift of 0.7 eV, when embedded inside the ZIF-8 MOF upon isotropic compression from 0 bar to 50 kbar, again due to shortening of Pt-ligand bonds with increasing pressure and the electronic interaction of monomeric Pt(II) complex with the MOF.
The properties observed during these simulations make Pt (II) complexes promising candidates for pressure sensing and other stimuli-responsive photonic applications.

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P159

Constructing systematically convergent Gaussian basis sets for solids

N. Skałecka (University of Warsaw/PL), D. Zgid (University of Warsaw/PL)

In Gaussian basis-set calculations for solids, the increasing condition number of the overlap matrix can lead to severe numerical difficulties and, in some cases, prevent calculations for heavier elements. This issue is particularly challenging for correlated relativistic calculations of solids using Gaussian orbitals.
In our approach, we systematically optimize atomic basis sets using even-tempered basis functions while introducing an additional penalty for excessive interatomic overlap. This strategy has the potential to provide a systematically improvable basis-set construction with a variable number of basis functions, enabling controlled convergence toward the basis-set limit and, potentially, basis-set extrapolation.
We will investigate this construction for both molecular and solid-state systems and assess its convergence, numerical stability, and transferability across different physical systems.

P160

DFT investigation of the effects of hydration on the reactivity of the low-valency distant binuclear vanadium species balanced in zeolites

A. Stepan Sklenak (Heyrovsky Institute/CZ)

The distant binuclear cationic sites were firstly identified using theoretical modeling in the context of the study of the N2O decomposition over the Fe(II) cation exchanged zeolites: ferrierite, the beta zeolite, and ZSM–5 [1]. We devised that the presence of the active sites formed by the distant binuclear Fe(II) centers explained the exceptional activity of Fe–ferrierite in comparison with the Fe–beta and Fe–ZSM–5 catalysts [1]. The first chemical step of the N2O decomposition is the formation of the Alpha–oxygen species [1-2] [i.e., (Fe(IV)=O)2+] which exhibits unique oxidation properties reflected in an outstanding activity in the oxidation of methane to methanol at room temperature [2]. Furthermore, we firstly predicted using the power of periodic DFT calculations that these distant binuclear cationic sites were able to split dioxygen to yield pairs of the distant Alpha–oxygen species. Subsequently, experiments were performed at room temperature and the theoretical prediction of a cleavage of dioxygen to give a pair of the temperature and the theoretical prediction of a cleavage of dioxygen to give a pair of the distant Alpha–oxygen atoms was confirmed experimentally and thus splitting dioxygen was discovered [3]. The effects of various transition metals [4] and zeolite topologies were investigated [5] employing periodic DFT were studied. In this contribution, we report on our periodic DFT investigation regarding the effects of hydration on the reactivity of low-valency early transition metal cations, namely vanadium.

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P161

Neural Network Potentials of 2D Nanoconfined Water: Efficient Training Set Construction and Calculation of Dielectric Properties

N. Smith (University of Hamburg/DE), C. Herrmann (University of Hamburg/DE)

The structure and dynamics of water's hydrogen bonding network are still not fully understood, which is why water is the focus of many theoretical studies utilizing Molecular Dynamics (MD) simulations to investigate its properties. One way to compute the energies and forces to propagate the simulated trajectories is the usage of Neural Network Potentials (NNPs) which enable the representation of the potential energy surface with ab initio accuracy at a fraction of the computational cost. In nanoconfinement, a lot of properties of water change, e.g. dielectric properties. [1] Theoretical evaluations of water's dielectric properties often involve MD simulations in the pico- to nanosecond range – time scales which NNPs make feasible. Numerous approaches to train NNPs of nanoconfined water can be found in the literature;[2-5] however, they do not include a systematic evaluation of which confined structures need to be included in the training set to generate a NNP with the ability to extrapolate to arbitrary degrees of confinement. In this work, committee NNPs in combination with an Active Learning (AL) procedure are used to determine which water film thicknesses in 2D nanoconfinement and which water densities included in the dataset dominate the NNP performance and accuracy. Furthermore, an outlook on the usage of the constructed datasets to train multi-valued machine-learned dipolar models [6] is given which makes the calculation of static dielectric properties of both bulk and nanoconfined water possible: The multi-valued dipolar models enable MD simulations at fixed values of the dielectric displacement, reducing the simulation times needed in order for the dielectric properties to converge.

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P162

Enhancing the Transferability of Machine Learning Potentials by Training on Atomic Properties

R. Springborn (Ruhr-University Bochum/DE), G. Schmitz (Ruhr-University Bochum/DE), J. Behler (Ruhr-University Bochum/DE)

Machine Learning Potentials (MLPs) have become an established tool for describing potential energy surfaces of complex systems, since they combine ab initio accuracy with reduced and linear-scaling computational costs. In most MLPs, linear scaling is achieved by leveraging the nearsightedness of electronic matter. Instead of directly predicting the total energy, these models yield atomic contributions that sum up to the total energy [1]. In practice, trained MLPs may exploit this freedom for error compensation. Using High-dimensional neural network potentials (HDNNPs) as an example, we show that the atomic energies predicted by these models are mathematically not unique, since the training process can introduce systematic offsets between different local structural motifs, which cancel out to yield the correct total energy. This compensation mechanism is robust as long as the relative abundance of different motifs in the application set closely matches that of the training set.

However, because the systematic offsets of the model depend on the statistical distribution of motifs encountered during training, systematic deviations—such as variations in overall composition or shifting structural characteristics—can prevent the cancellation of these offsets. This breakdown in error compensation can lead to shifts in the total energy, independent of the potential's intrinsic accuracy.

To remedy these uncertainties, we analyze the mechanisms of error compensation and propagation in detail, demonstrating results on various systems. We show that utilizing physically motivated atomic energy partitioning schemes during the training process can effectively mitigate these artificial errors and enhance the transferability and reliability of the resulting models.

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P163

A new Molecular Dynamics approach for treating spin-phonon effects in solids

I. Srpak (Max Planck Institute for Solid State Research, Stuttgart, Germany), M.J.Willatt (Max Planck Institute for Solid State Research, Stuttgart, Germany), S. Althorpe (University of Cambridge, United Kingdom), A. Alavi (Max Planck Institute for Solid State Research, Stuttgart, Germany)

The most common working assumption in quantum chemistry is that the system being studied is stationary, which may not always be true. While for most systems, motion can just be a frustrating smear around the average behaviour, there are systems where dynamical nature and electronic structure are invariably entangled. One class of such problems is the spin-phonon systems where the spin-spin interactions modify the potential energy surface and the motion of atoms affects the spin-spin interactions. In particular we are studying spin-Peierls distortions in the antiferromagnetic isotropic Heisenberg model on one- and two-dimensional lattices where the coupling constants are position dependent. For a long time people have approached this problem with various Monte Carlo schemes, which required numerous assumptions and approximations. These approximations would severely limit the applicability of the method and quality of the resulting description. We present an alternative approach rooted in Molecular Dynamics. By expanding and combining Stochastic Series Expansion method to discrete imaginary time path integral formalism, we can use path integral molecular dynamics to calculate the statistical observables of these systems accounting for the nuclear quantum effects faster and while retaining the quality of the description. By understanding the decorrelation effect that the spin-phonon coupling has on the spin-spin interactions, we can use machine-learned forces trained on Monte Carlo data to break the curse of the exponential scaling and study the phase diagrams and different solid phases arising from the spin-phonon interactions. We showcase the method capturing the thermal and quantum effects on one dimensional lattices and the rich phase behaviour of two dimensional systems, with a particular focus on the honeycomb lattice.

P164

Fluorine-Specific π-Stacking Accelerates Ring-Opening Copolymerisation

L. Steiner (Freie Universität Berlin), C. Fornacon-Wood (Universität Bayreuth), A. Plajer (Universität Bayreuth), B. Paulus (Freie Universität Berlin)

The copolymerisation reaction of fluorinated and non-fluorinated styrene oxide with phthalic anhydride yields degradable polymers with high molecular weights and recoverable fluorine. These polymers represent an important step towards a closed fluorine economy. [1-3] To understand the effect of fluorine substituents on reaction kinetics, we calculated Gibbs free energies of intermediates and transition states using a carefully evaluated computational prototol: Initial conformer sampling with the CREST/CENSO approach, PBEh-3c optimised geometric structures, single-point energies at the ωB97M-V/def2-TZVPPD level, and the COSMO-RS model (BP/TZVPD) to quantify the effect of solvation. The conformer sampling revealed π-stacking interactions, with the catalyst, additional monomers and the polymer chain. [1,2] Our results indicate that fluorine-specific π-stacking stabilises key intermediates and provides a molecular explanation for the experimentally observed rate acceleration, which occurs exclusively for heterofluorinated monomer combinations. Additionally we studied the degradation of these polymers as they allow to fully recover fluorine by methanolysis. [3] Fluorinated phthalic acid becomes defluorinated by methanolate, attacking as nucleophiles in an aromatic substitution reaction. Furthermore, methanolate attacks the backbone of the copolymer. Both corresponds to a very fast reaction, according to the surprisingly low barrier of 31.7 kJ/mol.

P165

Configurational Entropy of Mixing as a Spatially Resolved, Time-Dependent Observable

Tom Erik Steinkopf (Martin-Luther-Universität Halle-Wittenberg), Daniel Sebastiani (Martin-Luther-Universität Halle-Wittenberg)

Mixing and demixing govern the efficiency of many processes in chemistry, process engineering and materials science, yet their thermodynamic description rests predominantly on averaged models that capture local heterogeneity and non-equilibrium contributions only indirectly. This work determines the configurational entropy of mixing explicitly and with spatial resolution from molecular dynamics trajectories. Locally smoothed particle densities yield local mole fractions and hence an entropy density $s_{mix}(r)$, whose volume integral $\Delta S_{mix}(t)$ is a genuine time-dependent observable rather than an equilibrium average. Fitting a saturation model separates two physically distinct quantities for every component combination and temperature: the equilibrium plateau as the thermodynamic target, and a relaxation time characterising interdiffusion. Alkane/perfluoroalkane mixtures serve as the reference system, since their pronounced non-ideality exposes the deviation of the entropy of mixing while keeping enthalpic and entropic contributions separable.

Work to date has converted a functioning pipeline into a defined measurement protocol: separately equilibrated pure slabs docked into a cubic box with a sharp interface, a consistent equation of state throughout, and a production length that follows the mixing kinetics. These changes make the fitted parameters interpretable as converged physical quantities.

The continuing work targets the method itself and how molecular properties shape its output: the response to the smearing width σ and broadening kernel, toward a transferable calibration; the implicit role of molecular size and molar volume; the disproportionate weight of terminal ($CH_3 \rightarrow CF_3$) over interior ($CH_2 \rightarrow CF_2$) substitution; and the effect of fluorination architecture on non-ideality — validated against independent entropy routes.

P166

Reliable Redox-Potential Simulations of Proteins

M. Stier (University of Stuttgart/DE), J. Kästner (University of Stuttgart/DE)

The simulation of protein redox potentials is crucial for understanding various biological processes. However, such simulations remain challenging due to the complexity of these systems, arising from the electronic structure of the redox center and the dynamics of the surrounding protein and solvent environment. Moreover, the large system sizes preclude a full quantum mechanical (QM) treatment.
Commonly applied hybrid quantum mechanical/molecular mechanics (QM/MM) methods are often unsuitable due to nonpolarizable force fields, making pure QM calculations on cluster models a more reliable choice. However, truncating a solvated protein with several thousand atoms to a small cluster model introduces errors. Therefore, we recently proposed and tested a methodology for the simulation of redox potentials in proteins, as outlined below [1].
First, redox properties were computed using density functional theory (DFT) for a diverse set of ten proteins with cluster models of varying sizes, ranging from 200 to 1500 atoms, including full protein calculations. Our results show that cluster models containing approximately 500 atoms are sufficient, as truncation errors become smaller than the typical DFT errors beyond that size.
Second, the standard redox potentials of ten proteins were computed using the 500-atom cluster models within a snapshot-based approach grounded in Marcus theory. In our approach, QM/MM geometry optimizations were performed on snapshots from a classical molecular dynamics trajectory. The resulting QM/MM geometries were truncated to 500-atom cluster models, and redox potentials were computed from vertical reduction energies using DFT.
Comparison with experimental redox potentials revealed a mean absolute error (MAE) of 0.12 V, achieved without any reference calculations, which is only slightly larger than the previously estimated intrinsic DFT error. These findings are not only significant for improving redox potential predictions but are also broadly relevant for electronic structure calculations in complex systems involving charge changes, such as protonation/deprotonation, electron transfer, and electrocatalysis.

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P167

Breaking Harmonics Walls: The Anharmonic Vibronic Coupling Approach in Trajectory Surface Hopping Simulations

A. Jesús Lucia-Tamudo (University of Vienna), B. Leticia González (University of Vienna)

In this contribution, we present anharmonic vibronic coupling (AVC) Hamiltonians in combination with trajectory surface hopping (TSH) dynamics, providing a more flexible description of potential energy surfaces (PESs) than standard linear vibronic coupling (LVC) models. Furthermore, the reparametrization procedure has been automated, considerably reducing the manual effort traditionally associated with the reconstruction and fitting of multiple vibrational modes. LVC models constitute a widely employed framework for nonadiabatic quantum dynamics simulations due to their efficient parametrization of the PESs involved in excited-state relaxation processes. However, standard LVC models rely on the harmonic approximation and on a local expansion around a reference geometry, limiting their applicability in systems displaying large-amplitude motions, conformational flexibility, or strongly anharmonic vibrational modes governing the nonadiabatic dynamics. To overcome these limitations, some quantum dynamics studies have previously explored reparametrized vibronic Hamiltonians capable of reconstructing problematic regions of the PES beyond the harmonic approximation [1]. TSH provides a computationally cheaper alternative to fully quantum dynamical propagation. Nevertheless, standard on-the-fly TSH simulations remain computationally demanding due to the need to evaluate electronic energies, gradients, and couplings at every time step of the dynamics. For this reason, previous studies introduced the combination of standard LVC Hamiltonians with TSH dynamics as an efficient alternative to computationally demanding on-the-fly simulations [2–5]. However, these approaches still relied on the harmonic LVC approximation, thus inheriting the same limitations associated with anharmonic and flexible systems. Combining AVC Hamiltonians with TSH therefore preserves the computational efficiency characteristic of the standard LVC/TSH framework while considerably extending its applicability. Our results show that the proposed methodology is capable of reproducing the main features of photoinduced relaxation dynamics, including intersystem crossing, in systems where the standard LVC approach fails, while maintaining a very low computational cost.

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P168

Coordination Corrected Enthalpies for the Thermodynamics of Ionic Materials

A. Balaram Thakur (Technische Universität Dresden, Helmholtz-Zentrum Dresden-Rossendorf), B. Rico Friedrich (Technische Universität Dresden, Helmholtz-Zentrum Dresden-Rossendorf)

Thermodynamic stability parameters, such as the formation enthalpy and energy above the convex hull, are fundamental descriptors for the discovery and design of new materials. Density Functional Theory (DFT) generally provides reliable thermodynamic predictions for systems in which compounds and their elemental reference phases have a similar chemical bonding nature, e.g., in metallic alloys. However, DFT accuracy worsens for chemically dissimilar systems such as ionic compounds. In these cases, the calculated formation enthalpies can deviate significantly from experiment, with mean absolute errors (MAE) of at least 100 meV/atom, leading to unreliable stability predictions. While advanced methods, such as hybrid functionals, may improve the accuracy, they are computationally expensive and still do not generally reach experimental accuracy. To overcome these limitations, empirical correction schemes such as the Fitted Elemental-phase Reference Energies (FERE) [1] and the Coordination-Corrected Enthalpy (CCE) [2,3] methods have been developed. FERE shifts the elemental reference energies but does not generally achieve experimental accuracy. In contrast, the CCE approach explicitly accounts for the local bonding environment through oxidation-state- and coordination-dependent corrections. Such an approach substantially improves the accuracy of formation enthalpies while maintaining the computational efficiency of standard DFT. In this work, we extend the CCE methodology within the AFLOW [4] framework to halides, chalcogenides, and pnictides, intending to significantly broaden the applicability of CCE beyond oxides. These classes of compounds cover a wide range of technologically relevant materials for energy storage, electronics, catalysis, and optoelectronics, and also exhibit diverse bonding environments. By deriving systematic bond-based correction parameters for these anion chemistries, we achieve more accurate formation enthalpies and more reliable predictions of thermodynamic stability. This extension enhances the robustness of high-throughput computational materials screening and provides a more general framework for accelerated materials discovery across chemically diverse inorganic compounds.

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P169

Interactions in N-Heterocyclic Carbene Monolayers on Cu(111) and Au(111) from Periodic Energy Decomposition Analysis and NOCV

F. Thiemann (Leipzig University/DE), P. Melix (Leipzig University/DE), R. Tonner-Zech (Leipzig University/DE)

Understanding why an adsorbate binds where it does, and how tightly a self–assembled monolayer can pack, requires more than adsorption energies. Energy decomposition analysis for extended systems (pEDA) [1] combined with natural orbitals for chemical valence (NOCV) quantifies the driving forces of molecule–surface bonding under periodic boundary conditions. We apply it to *N*–heterocyclic carbenes (NHCs) on Cu(111), relevant to area–selective atomic layer deposition [2], using PBE–D4, periodic pEDA/NOCV in AMS–BAND, and scanning tunneling microscopy (STM).

I_{iPr}^{NHC}, the isopropyl–substituted carbene, chemisorbs by extracting a Cu terrace atom and binding to the resulting adatom ($\Delta E_{bond} = -289$ kJ/mol). Unusually for an adsorption, the bond is electronic rather than dispersive (dispersion 24%), with electrostatics contributing 72% of the attractive terms, while diffusion barriers of 3.6–4.7 kJ/mol leave the surface complex highly mobile. NOCV resolves σ–donation (65% of ΔE_{orb}) and π–backdonation into the NHC π^* (16%), consistent with a charge transfer of 0.25 e. Comparison with Au(111) shows identical bonding character but larger NOCV channels (σ–donation -256 on Au versus -176 on Cu, π–backdonation -56 versus -44 kJ/mol), following from the carbene–metal distance relative to the bulk nearest–neighbor spacing rather than its absolute value.

Periodic fragmentation models separate adsorbate–surface from lateral interactions. Lateral interactions are attractive ($\Delta E_{int} = -63$ kJ/mol) and 87% dispersion–driven, with only a small electronic contribution (-9 kJ/mol). The periodic analysis uncovers a cooperative, non–additive effect inaccessible to single–molecule models: direct Pauli repulsion between neighbors is small (29 kJ/mol), yet their presence raises the adsorbate–surface Pauli repulsion from 778 to 871 kJ/mol, setting the packing limit. Simulated STM images reproduce the experimental pattern and identify the wingtip rotamer. Resolving bonding channels and lateral interactions in one periodic framework thus provides a quantitative basis for tailoring carbene monolayers on coinage–metal surfaces.

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P170

Atomistic Insights into Si(100) Surface Passivation by Water: ReaxFF Molecular Dynamics and Fine-Tuned Machine Learning Interatomic Potential Simulations.

V. Tiwari (University of Paderborn/DE), C. Gu (University of Paderborn/DE), H. Elgabarty (University of Paderborn/DE), M. Brehm (University of Paderborn/DE)

The passivation of silicon surfaces is important in several industrial settings, such as for semiconductor device fabrication and photovoltaic applications. In this study, we use ReaxFF reactive molecular dynamics simulations combined with fine-tuned Machine Learning Interatomic Potential (MLIP) to extend our understanding of mechanism of Si(100) surface passivation in presence of water at various temperatures (300K,350K,383K). Simulation results indicate that the surface termination occurs predominantly through dissociative adsorption leading to the formation of silanol-terminated silica networks on the surface. At higher temperatures the atoms possess sufficient kinetic energy to reorganize into thermodynamically more stable structures as compared to room temperature where the hydroxylation is more disordered. The fine-tuned MLIP model confirms the key structural features obtained from ReaxFF, validating the latter as an approach for capturing essential passivation behavior. These findings provide atomistic insights into water-driven silicon passivation and may guide room-temperature passivation strategies. Our strategy also highlights a computationally efficient approach to the passivation of reactive surfaces, as a preliminary and necessary step in numerous theoretical studies. This protocol can be also utilized for wider varieties of solid electrolyte interphase system, to prepare a realistic, passivated surfaces for advance theoretical studies.

P171

Benchmarking Tensor Hypercontraction Techniques for Molecular Systems

Niklas Paulicks (University of Hamburg), Johannes Tölle (University of Hamburg)

Exploiting sparsity in the two-electron integral (ERI) tensor is a crucial step toward reducing the computational cost of many-body electronic structure methods. In recent years, a range of tensor factorization techniques, such as the tensor hypercontraction (THC) approach [1], have been developed to achieve this goal. In particular, linear optimization techniques based on least-squares (LS) fitting are of special interest because of their algorithmic simplicity, which may enable their application to large-scale systems.
Unfortunately, the landscape of these THC techniques remains highly fragmented, and many closely related methods have been developed independently in the literature, including LS-THC [1], interpolative separable density fitting (ISDF) [2], and RI-RS [3]. In this talk, I will present a unifying perspective on these approaches, which has enabled their efficient implementation in a newly developed library, pyTHC [4].
This new library enables, for the first time, a systematic comparison of the various linear THC techniques on an equal footing. To this end, I will present an in-depth assessment of these methods for the GMTKN55 benchmark database [5].

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P172

Machine-Learning Supported Reaction Mechanism Exploration of cis-trans Isomerisation in Retinal

Kai Töpfer (Freie Universität Berlin), Bettina G. Keller (Freie Universität Berlin)

Rare events such as chemical reaction are transitions across an energy barrier. To rationalize the mechanism of such rare events and calculating their reaction rates, the search for an optimal reaction coordinates has long been very active field of research.[1] Using the minimum energy path (MEP) as reaction coordinate simply neglects entropic contributions and dynamic effects. Alternatively, the committor function offers a complementary perspective in which the transition state is defined as an isocommittor surface at which trajectories reach the reactant or product with equal probability. I will present our findings on the reaction mechanism of the cis-trans isomerization of retinal in gas phase and various solvation environments.[2] We apply the recently developed AIMMD algorithm,[3] where the committor of isomerization reaction is learned by a Neural Network (NN) function from short, dynamically unbiased trajectories that form a transition path ensemble (TPE) and are generated by two-way shooting molecular dynamics (MD) simulations. MD simulations are performed using self-developed machine-learned interaction potentials (MLIPs) and adaptively trained universal MLIPs to provide ab initio accuracy for comparatively low computational costs.[4] The low-dimensional approximation of committor function is obtained through symbolic regression, which yields a human-interpretable reaction mechanism in terms of a small set of internal degrees of freedom.
We observe a significant deviation of the TPE from underdamped Langevin dynamics with time scales in the range of hundreds of femtoseconds compared to the MEP obtained from overdamped simulations in the nanoseconds regime. Overdamped simulations do not show the asymmetric distribution of kinetic energy along different internal coordinates at various stages of the isomerization reaction, as seen in the TPE. Such differences must be taken into account when calculating accurate reaction rates with respect to experimental results, e.g., transition state theory.[5]

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P173

Implementations of Molecular Integral-Equation Solvation Models: From 6D-MOZ to RISM-SCF

L. Wittmann (University of Bonn/DE), A. Trajkovski (University of Bonn/DE), S. Grimme (University of Bonn/DE)

Solution-phase property computations need to balance physical rigor with computational efficiency. On one hand, explicit-solvent simulations provide a microscopic description of the solvent structure but require extensive sampling of the configurational space. On the other hand, continuum models are very efficient but most often do not describe solvent structure directly. Molecular integral-equation theories based on the Ornstein–Zernike equation [3] and approximate closure relations provide an intermediate approach, yielding equilibrium solvent distributions and thermodynamic quantities without trajectory-based sampling. We present the Modular and Open-source Implicit Solvation Toolbox (MOIST) [1,2], which provides implementations of molecular integral-equation methods including six-dimensional molecular Ornstein–Zernike theory (6D-MOZ) [3], as well as fast and robust implementations of one- and three-dimensional reference interaction site models (1D- and 3D-RISM) [4,5]. 6D-MOZ retains the relative translational and orientational dependence of molecular correlations and is systematically improvable through the intermolecular interaction potential and orientational resolution, but at substantial computational cost. For less computationally demanding applications, 1D-RISM provides bulk site–site solvent correlations, while 3D-RISM resolves solvent-site distributions around a solute [4,5]. MOIST also supports self-consistent coupling of RISM to electronic-structure methods, providing a molecularly resolved extension of continuum reaction-field models in which equilibrium solvent-site distributions generate a reaction-field contribution to the solute's electronic Hamiltonian. The coupling is available through embedded-cluster RISM-SCF (EC-RISM) [6] and the more efficient constrained-spatial-electron-density formulation, RISM-SCF-cSED [7]. MOIST itself is open-source [1,2] and will be available within the next major releases of ORCA and TURBOMOLE.

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P174

Excited-State Pair Natural Orbitals for Shallow System-Adapted Quantum Circuits

H.S.T. Truong (University of Augsburg, DE), J.S. Kottmann (University of Augsburg, DE)

Pair natural orbitals (PNO) offer an efficient way to represent molecular correlated wave functions. In prior works [1,2] it was shown that pair natural orbitals can be determined directly within a multiresolution analysis (MRA) framework and subsequently be employed for general many-electron methods. In this work, we extend the use of MRA-MP2-PNOs from ground- state calculations to excited states, in particular with respect to the design of shallow system-adapted quantum circuits. However, direct application showed that MRA-MP2-PNOs do not provide sufficient accuracy for excited states unless computational expensive orbital refinement [3,4] is performed in a state-averaged manner. To overcome these limitations, we extend the MP2- PNO basis by including configuration interaction singles (CIS) [5] vectors and the corresponding configuration interaction singles and doubles (CIS(D)) pair natural orbitals (CIS(D)-PNOs). We demonstrate the approach using the separable pair approximation (SPA) [2], which approximates the separable pair wave function as a tensor product of electron-pair functions. Since the SPA ansatz is formulated in terms of electron pairs, single excitations cannot be described directly. To correctly capture the excited states, we introduce suitable orbital rotations to keep the hardcore-bosonic character of the qubit state. The accuracy and performance of this approach are compared to the full configuration interaction (FCI) calculations for different molecules.

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P175

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

I.Tsakontsis (Bielefeld University), N. Weike (Bielefeld University), M. Vossel (Bielefeld University), W. Eisfeld (Bielefeld University)

The accurate treatment of relativistic couplings like spin–orbit (SO) coupling into diabatic potential models is an important but very difficult task. To this end, the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) approach has been developed over the past years [1]. The central idea of ERCAR is the representation of the system's operators in an asymptotic diabatic basis consisting of direct products of atomic and fragment states. This allows to treat relativistic coupling operators like SO coupling analytically within the atomic basis states. This idea is extended to the incorporation of hyperfine coupling into the diabatic potential model.
Hyperfine coupling is due to the magnetic dipole and the contact interaction as well as the electric quadrupole interaction. The corresponding operators can be expressed in the angular moment operators $\hat{I}$ for nuclear spin and $\hat{J}$ for total angular momentum of the atomic fine structure states. The magnetic dipole and contact interactions both are proportional to $\hat{I} \cdot \hat{J}$ while the electric quadrupole operator is more complicated. The diabatic basis of an existing ERCAR model can be complemented by nuclear spinors and the hyperfine coupling operators are easily evaluated in that basis. Diagonalization of the resulting full diabatic ERCAR model yields the hyperfine structure energies and states for any molecular geometry of interest.
The new method is demonstrated using an existing accurate diabatic potential model for hydrogen iodide (HI) [2] to see the effects of hyperfine coupling. As a proof of principle study, the hyperfine coupling effect of the $^2P_{3/2}$ ground state and spin–orbit excited $^2P_{1/2}$ state of Iodine combined with the $^2S_{1/2}$ ground state of hydrogen are added to the ERCAR Hamiltonian and the effect of hyperfine coupling is investigated. Since both atoms have a non-vanishing nuclear spin, the hyperfine coupling needs to be treated in analogy to the multi-atom variant of the ERCAR approach [3].

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P176

Accelerating Large-Scale GW Calculations using Real-Space Resolution of Identity

Ritaj Tyagi, Maximilian Graml, Rémi Pasquier, Jan Wilhelm (Institute of Theoretical Physics and Regensburg Center for Ultrafast Nanoscopy (RUN), University of Regensburg, Regensburg, Germany)

The G_0W_0 approximation provides accurate bandgaps and quasiparticle energies compared to standard density functional methods, but its $O(N^4)$ scaling and huge memory costs severely restrict its applicability. In recent years, various low-scaling formulations have reduced this computational cost to the cubic or even quadratic regime [1–4]. While many of these approaches have extended the accessible system size, they often suffer from large computational prefactors, numerical noise, uncontrolled truncation errors, or are restricted to non-periodic systems. A promising approach is the real-space resolution-of-identity (RI-RS) framework introduced by Duchemin et al. for non-periodic systems [2,3]. Unlike conventional Gaussian-based formulations, RI-RS projects orbital-pair densities onto a real-space grid, thereby eliminating the need for three- and four-center integral tensors while retaining sub-meV accuracy in quasiparticle energies.

Motivated by this, we extended the formalism and developed a massively parallel RI-RS G_0W_0 implementation in CP2K [5] capable of treating systems with more than 10,000 atoms. Built on the distributed block-compressed sparse row-matrix (DBCSR) library [6], this method aggressively exploits the inherent block-sparsity of atomic orbitals, polarizability matrices, and self-energy operators ensuring efficient memory usage and excellent parallel scalability on modern HPC architectures.

We demonstrate this approach on nanoscale non-periodic systems, including nanographene flakes and silicon clusters, reaching sizes previously inaccessible for deterministic G_0W_0. Compared to CP2K's existing low-scaling GW implementation using truncated RI [1], our RI-RS approach achieves speedups of up to 100× while maintaining sub-meV accuracy. Finally, we outline the extension of the RI-RS formalism to fully periodic boundaries for Γ-point calculations in large unit cells. This brings accurate quasiparticle calculations to unprecedented length scales and paves the way for large-scale Bethe–Salpeter equation (BSE) calculations for optical absorption spectra of large, disordered cells and associated excited-state gradients.

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P177

Molecular switches and machines

A. L. Ulrich (Heidelberg University), P. Kantak (Heidelberg University), S. Amirjalayer (Heidelberg University)

Molecular switches and machines underlie many essential biological processes, including muscle contraction and peptide synthesis. Incorporating such motifs into synthetic materials is therefore a promising design strategy for the development of responsive functional materials. Mechanically interlocked molecules (MIMs) in combination with metal–organic frameworks (MOFs) are particularly well suited. The restricted configurational phase space of the MIM confines motion to well-defined pathways, while the MOF offers a tuneable scaffold that arranges the MIMs into a periodic lattice.
Our previous work has shown that neighbouring mechanically bonded rings (MBRs) within these frameworks can move in a coupled, cooperative fashion.(1) However, additional control of the dynamics by external stimuli has so far not been investigated. Here, we focus on deciphering the influence of mechanical compression and decompression of the framework on the coupled dynamics. Such an external stress can arise for example by gas uptake and release, or changes in environmental conditions.
To elucidate how the external mechanical force modulates the potential energy surface and thus influences the molecular-level dynamics, including the translational and rotational pathway, we performed molecular dynamics simulations. The mechano-responsivity of the shuttling and rotational dynamics of individual and coupled MBRs in UWDM-4(2) was studied by employing a machine-learned force field trained specifically for this system based on DFT calculations(3). Moreover, mechano-responsivity was studied at varying temperatures to reveal the coupling of both external stimuli.
The MD simulations demonstrate that slight compression of 1-3% increases the MBR shuttling rate and gives rise to a previously unobserved intermediate state. In this case the MBR resides between its two shuttling stations rather than moving directly between them. Detailed analysis of the trajectories indicates that compression of the framework introduces an altered translational pathway not accessible in the unperturbed framework. These atomistic simulations underscore the potential of mechano-responsivity for externally controlling and tuning the dynamics of molecular machines in functional materials.

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P178

Philicity at Play: Entropy, Enthalpy and Miscibility in Alkane–Perfluoroalkane Mixtures

A. L. Upterworth (Martin Luther University Halle-Wittenberg/DE), D. Sebastiani (Martin Luther University Halle-Wittenberg/DE)

What drives molecular mixing and demixing at the atomic level remains a simple yet unresolved question. In a computational study of the elementary atomic interactions that govern phase behavior, we address this challenge using molecular dynamics simulations. Specifically, we investigate how the miscibility of an alkane–perfluoroalkane mixture responds to changes in the Lennard-Jones interaction potential parameters, that tune their lipophilic and fluorophilic characters. One particular challenge is measuring the instantaneous degree of mixing. We demonstrate that an approach based on a state function for the configurational entropy of mixing enables direct access to the system's state of mixing from the simulation trajectory.[1] Furthermore, we provide an enthalpic explanation of this specific mixing state by decomposing the total energy of mixing into effective interaction strengths.[2] Thereby, we elucidate how the complex interplay of direct and indirect enthalpic effects and entropic contributions induced by changes in the atomic interaction parameters determines the free energy of mixing, leading to either mixing or demixing.

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P179

Low-Spin Co(III) Stability in Cobalamin Derivatives Under Hydrostatic Pressure: A Computational Investigation

N. Lussari (Univesität Bremen/DE), M. Breier (Univesität Bremen/DE), T. Neudecker (Univesität Bremen/DE)

The deep sea represents a challenging environment where life is subjected to hydrostatic pressure reaching up to 0.1 GPa at regular seafloor conditions and over 1.0 GPa near hydrothermal vents. Direct measurements are extremely difficult, so there is a genuine and important gap in our knowledge of how biomolecules behave under these conditions. Cobalamin (Vitamin B12) is a universal cobalt–corrin cofactor, but only a subset of bacteria and archaea can produce it. At ambient pressure, cobalt sits in a low-spin Co(III) d^6 singlet state, and while one crystal structure at 1.0 GPa has been reported, no spin-state study of cobalamin under pressure exists. Besides temperature and light, pressure can induce spin crossover (SCO) in transition metal complexes. Our goal is to detail the pressure response of its metal–ligand coordination sphere (Co–Ligand and Co–Imidazole), which are hypothesized to be the most sensitive to compression, by simulating the behavior of these systems under pressure.

For Co(III) d^6, 3D compression could drive a LS singlet ($t_{2g}^6 e_g^0$) $\rightarrow$ HS triplet or quintet ($t_{2g}^5 e_g^1$ / $t_{2g}^4 e_g^2$) transition, populating antibonding e_g orbitals and expecting longer, weaker metal–ligand bonds. Geometry optimizations and zero-point corrections were obtained at TPSSh(D3BJ)/def2-TZVP using the X-HCFF distortion model in Q-Chem 6.3, simulating pressures from 0.1 to 4.0 GPa, with energy corrections from the PV method. Multireference validation was performed at HCI-CASSCF(14,12)/def2-SVP using the HUMMR program.

The Co(III) low-spin singlet remained the ground state across all ligand variants tested up to 1.0 GPa, with no SCO detected until 4.0 GPa. The z-axis coordination bonds with Co are responsible for the main stress dissipation, while the corrin ring remains rigid. The triplet state is consistently more compressible than the singlet, as population of the antibonding e_g orbital directly weakens axial bonds. CN^- and Me-cobalamins show superior pressure resilience. Multireference calculations revealed that although DFT gives a good energy description, it misassigns spin density in high-spin states. For instance, while DFT delocalizes unpaired density onto the corrin ring at 2.5 GPa, HCI-CASSCF localizes it on cobalt d-orbitals (d_{xy}, d_{xz}, d_{yz}), highlighting the necessity of multireference methods for accurate spin-state descriptions in corrinoids in deep-sea environments.

P180

Simulations of Tricalcium Silicate-Water Interfaces using High-Dimensional Neural Network Potentials

H. Wang (Ruhr-Universität Bochum/DE), J. Behler (Ruhr-Universität Bochum/DE)

Calcium silicates are widely used as binding materials in cementitious systems where the hydration process is essential for developing the desired mechanical properties. Upon contact with water these minerals undergo a complex series of reactions of which the actual mechanisms remain mostly unclear. Insights into the behavior of water at calcium silicate surfaces at an atomistic level are therefore crucial to reach a better understanding of general hydration reactions of this class of materials. Tricalcium silicate is the most prominent species in context of cementitious systems and is characterized by a particularly high reactivity with water. These characteristics make it a good model system and particularly interesting to study. Molecular dynamics (MD) have been a key tool to examine processes along solid-liquid interfaces. However, conventional approaches faced a trade-off between accuracy and simulation length. Force fields struggle with description of the chemical reactions while ab initio methods are restricted to small systems. The advent of machine learning potentials (MLP), which allow to represent the energies and forces of electronic structure calculations at lower cost, offered a solution to these problems. In this study, we use High-Dimensional Neural Network Potentials (HDNNP),[1,2] a computational efficient MLP method, to investigate interfaces of liquid water with tricalcium silicate. We present high-accuracy, large-scale MD simulations of the (001) surface of M1 alite, one of the two major polymorphs, interacting with water at 300 K in nanosecond scale.

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P181

Quantum Chemical Study of the Reactivity of a Platinum(II)nitrene with 1,4-Benzoquinone

N. Wegerich (University of Frankfurt/DE), M. C. Neben (University of Göttingen/DE), K. A. Fiebig (University of Frankfurt/DE), S. Schneider (University of Göttingen/DE), M. C. Holthausen (University of Frankfurt/DE)

Nitrenes (R–N) are subvalent nitrogen compounds, therefore exhibiting remarkably high reactivity toward different substrates. Depending on the electronic environment they can feature a triplet or (multireference) singlet ground state. By substituting the organic rest R with a (heavy) transition metal like Pt, spin–orbit coupling (SOC) effects are introduced, potentially promoting multi–state reactivity [1–3].
We herein report a quantum–chemical mechanistic study of the reaction of a triplet platinum(II) nitrene with 1,4–benzoquinone (BQ) toward an aziridine as well as the rearrangement to an enamine, both of which were observed experimentally. The nitrene was generated *in situ* by photochemical dissociation of an azide precursor in toluene. The reaction with BQ proceeds through an electrophilic attack at one of the C=C double bonds ($\Delta^{\ddagger}G_{195} = 17$ kcal mol^{-1}). Subsequent transition to the singlet surface leads to the barrierless formation of the aziridine. Alternative reaction pathways were ruled out by kinetic arguments.
The subsequent rearrangement to the enamine was observed experimentally over the course of three days in toluene-d_8 at room temperature. Quantum–chemical results rule out a thermal process ($\Delta^{\ddagger}G_{298} = 47$ kcal mol^{-1}). Instead, the reaction occurs in the first excited state [4], in which an electron is excited from the nitrogen π–lone pair into the first π^*–orbital of the BQ scaffold. This enables a low–energy C–N bond dissociation and subsequent $1,2$–H shift ($\Delta^{\ddagger}G_{298} = 18$ kcal mol^{-1}) to the enamine.

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P182

Absorption spectra of N-heteroacenes

A. M. Weidlich (Heidelberg University), A. Dreuw (Heidelberg University)

Acenes are a class of organic molecules that have attracted considerable interest in both experimental and theoretical research due to their unique electronic structure and broad range of applications. Among these, their use as organic materials in electronic devices is particularly promising, where the properties of their low-lying excited states largely determine their suitability for specific applications. Chemical functionalization provides an effective means of tuning these optical properties, with nitrogen substitution representing a widely employed strategy. To systematically investigate the effect of nitrogen substitution on the excited states of N-heteroacenes, absorption spectra are simulated using time-dependent density functional theory (TD-DFT) at the TDA/CAM-B3LYP/6-311G* level of theory. Excitation energies, oscillator strengths and transition densities are computed to establish relationships between the excited states of N-heteroacenes and their unsubstituted acene counterparts, as well as to identify excitations unique to the substituted systems. In addition, the influence of the increasing acene length on the absorption spectra and the emergence of diradical character is examined.

P183

Spin-State Switching in Trinuclear Exchange-Coupled Systems

A. Jonas Weinhold (Karlsruhe Institute of Technology, DE), Z. Karin Fink (Karlsruhe Institute of Technology, DE)

Coordination compounds that exhibit switchable spin states are of great interest due to their potential applications in molecular spintronics. While spin-crossover (SCO) phenomena, which are reversible transitions between low-spin (LS) and high-spin (HS) states, have been extensively studied in mononuclear systems, the cooperative dynamics of these phenomena in polynuclear complexes remain largely unexplored.
This study focuses on trinuclear iron(II) complexes featuring a triangular arrangement of exchange-coupled metal centres with C_3 symmetry.[1] We employ a multi-method computational approach to analyse the electronic structure and spin state characteristics of the complexes. Geometry optimisations and vibrational frequency calculations are performed using density functional theory (DFT)[2]. The electronic structure and spin state behaviour are investigated, including the effects of spin-orbit coupling, using active space self-consistent field (CASSCF) and complete active space spin-orbit configuration interaction (CASOCI)[3] methods. By diamagnetic substitution, spin Hamiltonian parameters can be extracted for zero-field splittings and magnetic exchange couplings.
A Z/E isomerism of an imine bond within the ligand framework introduces structural variability, enabling a comparative analysis of the influence of the structure on the spin-state behaviour. Furthermore, the theoretical analysis suggests that E- and Z-isomers can be distinguished by their characteristic vibrational signatures in IR spectra. This provides a simple experimental method for differentiating between the two isomers. The calculations reveal that the exchange coupling between the iron centres is remarkably weak, whereas spin-orbit coupling is significant and must be explicitly accounted for in computational models.

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P184

Extending an Automated Ensemble-Averaged Kinetics Framework for Reverse Intersystem Crossing in Flexible TADF Emitters

J. Weiser (University of Augsburg/DE), C. Wiebeler (University of Augsburg/DE)

Thermally activated delayed fluorescence (TADF) enables metal-free OLEDs with up to 100% internal quantum efficiency through reverse intersystem crossing (RISC) from dark triplet states to emissive singlet states.[1] In flexible donor-acceptor emitters, RISC rates are especially sensitive to geometry-dependent fluctuations of singlet-triplet gaps and spin-orbit couplings (SOCs). Rate models built on single optimized geometries can substantially misrepresent the kinetics of such flexible emitters by ignoring the conformational ensemble and the involvement of higher-lying triplet states.[2] We have developed an automated quantum-chemical workflow that restores both effects:[3] A conformational search on the triplet surface identifies representative macrostates that are subsequently expanded into Wigner-sampled nuclear ensembles. For each geometry, singlet-triplet gaps and SOC matrix elements are then calculated at the TD-DFT level. The global RISC rate follows from Fermi's golden rule as a Boltzmann-weighted sum over the thermally populated triplet channels. Because the couplings are evaluated between adiabatic states, each channel also implicitly carries second-order spin-vibronic coupling borrowed from the respective higher triplets. This recovers over an order of magnitude of the rate for the flexible emitter 3DPA2FBN while accurately reproducing the rate of the rigid benchmark emitter 4CzIPN. We are currently extending this framework along its two dominant error sources: First, TD-DFT overestimates the singlet-triplet gap in 3DPA2FBN, so we introduce a correction of the ensemble gaps against spin-component-scaled post-HF references through a Δ-machine learning approach that propagates the correlated correction across all sampled geometries at a fraction of the cost. Second, the harmonic Wigner approximation poorly represents the large-amplitude, anharmonic torsional modes that mediate RISC in flexible emitters. We therefore replace it with anharmonic sampling from various molecular dynamics approaches based on semiempirical, ab initio, and machine learning methods, while ensuring the sampled geometries remain compatible with the subsequent excited state calculations.

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P185

Interactive JEDI Strain Analysis as a Pre-Screening Tool for Mechanophore Design

R. Weiß (University of Bremen/DE), A. Plump (University of Bremen/DE, T. Neudecker (University of Bremen/DE)

Predicting which bond in a mechanophore activates under a given pulling geometry is central to their design, and is typically approached by elongating a structure along a chosen coordinate and relaxing at each step until rupture. We present an interactive implementation of the JEDI (Judgement of Energy DIstribution) strain-energy decomposition,[1,2] intended as an inexpensive pre-screening instrument for the design of mechanophores. JEDI partitions the harmonic deformation energy over redundant internal coordinates, giving a per-bond strain measure rendered directly as a color map on the molecular structure while the user deforms it. Porting the analysis to a C++ core exposed to Python, together with targeted optimization of the per-frame path, reduces the cost of a single strain evaluation to well under a millisecond, comfortably within a 60 Hz frame budget. The engine requires only a relaxed reference geometry, its Hessian, and a stream of distorted structures to evaluate against them; it is intended to be attached to any interactive chemistry environment. We demonstrate it within SCINE Heron,[3] using Sparrow as the semiempirical driver and with optional haptic force feedback. Emulating a CoGEF (Constrained Geometries simulate External Force) distortion of trans-1,2-diethylbenzocyclobutene and 1,1-Dichloro-2,3-diethylcyclopropane at the PM6 level, the redistribution of strain can be followed while the structure is manipulated, up to the rupture of the bond reported in published calculations.[4] Strain analysis is no longer the limiting factor; the electronic structure calculations now determine the achievable frame rate. Development is ongoing, with user-defined pulling directions and faster electronic-structure backends as the immediate next steps.

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P186

Molecular Dynamics and Computational Spectroscopy for Systems in Soft Condensed Phase

C. Wiebeler (University of Augsburg/DE)

Molecular dynamics is a wide-spread simulation technique, which (i) we have employed to elucidate photophysical processes based on potentials from electronic structure calculations [1] and (ii) can be used to obtain structural insights into biological macromolecules like proteins and DNA using classical force fields [2, 3]. Complementary to this, computational molecular spectroscopy allows to establish structure-property relationships. For example, our calculations helped to assign chemical shifts and hyperfine couplings to atoms of chromophores [4]. We have also combined both in the framework of quantum mechanics/molecular mechanics (QM/MM) simulations to understand the molecular origin of the difference in optical absorption between the photoproduct (Pg) and dark state (Pr) of the photoreceptor protein Slr1393 [5]. Furthermore, our QM/MM-optimized structures provided further details of structural rearrangements in the binding pocket [6]. Currently, we are working on unraveling the mechanisms leading to thermally activated delayed fluorescence in donor-acceptor cyanoarenes [7] and on the parametrization of metal ions [8], which is a prerequisite for classical MD simulations.

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P187

Automated Reaction detection with different Bond Order Schemes

T.L. Wigger (Heinrich Heine University Düsseldorf/DE), J. Meisner (Heinrich Heine University Düsseldorf/DE)

Automated reaction discovery using ab initio molecular dynamics (AIMD) is a field in computational and theoretical chemistry. It aims to identify various reaction pathways originating from a defined molecular system and to build comprehensive reaction networks. A central and crucial requirement for constructing these networks is the reliable automated reaction detection from resulting trajectories. Conventional distance-based criteria and simple bond order schemes are often insufficient to accurately identify bond breaking and bond forming events, as both neglect the underlying electronic structure. This limitation becomes even more pronounced in transition metal systems, where the complex and flexible nature of metal ligand interactions further challenges such simplified approaches. A more sophisticated description of bonding is therefore essential for reliable reaction discovery. In this study, we present a systematic comparison of various bond order analysis methods to evaluate their performance in automated reaction detection. We investigate Mayer, Wiberg, Mulliken, Fuzzy and Laplacian bond orders, as well as approaches derived from Intrinsic Bond Orbitals (IBOs) and Natural Bond Orbitals (NBOs). The main focus is on evaluating the consistency, sensitivity, and interpretability of each bond order scheme in identifying bond breaking and bond formation events. Special attention is given to challenging systems involving transition metal complexes. The results illuminate the strengths and inherent limitations of the respective approaches, they serve as a well-founded guideline for selecting the optimal bond order scheme for robust, automated reaction discovery workflows in organic and organometallic chemistry.

P188

Improving the scaling of AC0 with laplace-THC

S. Wittek (Humboldt University of Berlin/DE), M. Roemelt (Humboldt University of Berlin/DE)

This work presents an efficient approach to capture dynamic electron correlation for a complete active space self-consistent field (CASSCF) wave function as a reference. The basis for this work is the linearized variant of the adiabatic connection approximation (AC0) [1]. This method only involves the use of one- and two-electron density matrices, resulting in a more favorable scaling with active space size than for example NEVPT2. To enhance the scaling of AC0 with basis set size, the Tensor Hypercontraction (THC) [2] method is used in combination with a Laplace Transform of the energy denominator [3]. Laplace-THC-AC0 is an approach that can efficiently calculate dynamic electron correlation for large systems and big active spaces, making it a promising complement to our recently developed CFG-HCI approach [4].

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P189

A Minimally Empirical and Self-Consistent Implicit Solvation Model for Robust Quantum Chemistry in Solution

L. Wittmann (University of Bonn, Germany), S. Grimme (University of Bonn, Germany)

Implicit solvation models are often the workhorse in computational quantum chemistry, but their reliability can deteriorate for more complex systems [1]. We present GEMS, a fully self-consistent and general implicit solvation model that aims to enable robust quantum-chemical computations in solution and is constructed from physically motivated and interpretable components. The solvent is represented by a simple density model derived from basic quantum-mechanical properties of the solvent [2]. Its overlap with the solute electron density defines the solvent–solute boundary, allowing the cavity to adapt self-consistently to changes in the electronic structure, state, and molecular geometry [3,4]. This density-based boundary is used to evaluate nonlocal electrostatics, continuum-integrated DFT-D5 dispersion, explicit cavitation, and translational/rotational entropy losses upon transfer to solution.

For practical applications, GEMS is fully differentiable [4,5], allowing efficient geometry optimizations and Hessian computations. The model's computational cost is typically less than twice that of the corresponding gas-phase calculation, and extension to new solvents requires only the solvent geometry, mass density, and dielectric permittivity. We evaluate GEMS on a compiled set with more than 12,000 experimental data points, including diverse solvents and properties such as solvation free energies and acid dissociation constants. On these benchmarks, GEMS reaches the accuracy of SMD and COSMO-RS for simpler neutral organic molecules, while showing particularly promising results for more challenging cases such as larger molecules and zwitterions [1].

The model will be available in ORCA and in the new Modular and Open-source Implicit Solvation Toolbox (MOIST) [6], providing an accessible route toward robust quantum-chemical modeling in solution.

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P190

Simulating a bimetallic rotaxane with classical molecular dynamics

K. Zois (University of Vienna), L. González (University of Vienna)

Structural confinement is ubiquitous in nature and can lead to strong alteration of the physicochemical properties of the confined molecules. Previously, we have reported a photocatalytically active rotaxane, which is the product of confining a bimetallic, Ru-Rh, dyad inside the cavity of a cucurbit[7]uril ring. [1] This design principle leads to steric protection that overcomes degradation during catalytic conditions.
Our initial studies involved density functional theory (DFT) calculations in combination with continuum solvation models, to account for solvent effects. Our approach was also limited to the study of a few conformations. The limitations concerning solvation and geometry sampling can in principle be overcome by classical molecular dynamics (MD) simulations, where solvent molecules are treated explicitly and a vast number of geometries are sampled. However, MD simulations on our system were not possible due to the absence of force-field (FF) parameters for the description of the Rh-diimine moiety, which is part of the dyad.
Herein, we present such tailored FF parameters [2] and perform MD simulations by combining them with already existing ones for the other parts of the molecule. The FF is validated against DFT results, and the effects of confinement are studied, by comparing the behavior of the rotaxane against the 'naked' dyad. Moreover, we study the effect the different solvents exert on the dynamics of the dyad and the rotaxane, by performing the MD simulations in water, acetonitrile, and diethylene glycol. Key dihedral angles are identified, which enable a structural classification of the system. Our classification leads to a quick determination of a conformer's ability to allow for charge-transfer between the metal centers. We also determine lifetimes and corresponding energy barriers associated with important structural motions.

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P191

Small molecular ions as probes for variations of fundamental constants

C. Zülch (Philipps-Universität Marburg/DE), K. Gaul (Helmholtz-Institut Mainz/DE), R. Berger (Philipps-Universität Marburg/DE)

Molecules provide a well-established framework for investigating the laws of nature at low-energies [1]. One such test is a hypothetical variation of fundamental physical constants, such as the fine-structure constant or the electron-to-proton mass ratio [2]. Many theories that attempt to unify gravity with other known forces assume such variations. Accompanying energy-shifts can, in principle, be detected in laboratory experiments when clock transitions in atoms and molecules tend to drift [3]. Thus, progress in research on variations of fundamental constants also represents, indirectly, advances in time measurement.

One way of testing such variations is to measure two transitions starting from a common initial state. The influence of a potential variation in the fine-structure constant is then obtained from the difference between the sensitivity factors of these transitions, divided by the difference in energy. Transitions to quasi-degenerate vibronic states are therefore particularly well suited. The sensitivity factors are usually calculated using electronic structure theory by numerically varying the speed of light in relativistic electronic structure programs.

In this contribution, we discuss an analytical approach [4] for calculating the sensitivity factors. The formulas are derived both within the four-component Dirac–Coulomb framework and the two-component Zeroth Order Regular Approximation [5-7]. On the level of complex generalized Hartree–Fock, we investigate several small molecular ions for possible large energy-shifts due to variations in the fine-structure constant and the electron-to-proton mass ratio. Small molecules with a large charge have the appeal of a dense level structure [8], which gives rise to many quasi-degenerate levels and enhances thereby relative shifts of transitions energies.

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P192

Grid-Based Description of Molecular Association

H. Zupan (Freie Universität Berlin/DE), B. G. Keller (Freie Universität Berlin/DE)

We develop a sampling-free, grid-based approach as an alternative to Markov State Models (MSMs) to model molecular association processes. We use rigid body approximation to simplify association of two molecules down to a six-dimensional space of relative translation and orientation, where a grid-based discretization of space is computationally manageable and physically meaningful. Considering the total exchange of probability density between neighboring grid cells as the approximation of rate in the short-time limit, we provide expressions for rates that do not rely on sampling frequency; instead, a single energy evaluation per grid cell is required as well as geometric properties of the grid: cell surface area, distance between gridpoints and cell volumes. The resulting rate matrix is closely related to the transition matrix, offering insights into metastable states and association kinetics. The reduced number of energy evaluations compared to sampling approaches makes the method accessible not only to MD, but also DFT-based methods. We demonstrate our methodology on several systems of interests, including hydrogen bonding of water molecules, pi-pi stacking of guanidinium groups and diffusion of host-molecules through metal-organic frameworks. The software is made available as a python package MolGri.

P193

Accelerating Conformer Reranking with Machine Learning Interatomic Potentials

Christopher Zurek (RWTH Aachen University/DE), Tomoya Shiota (University of Osaka/JP), Kenji Ishihara (University of Osaka/JP), Tuan Minh Do (University of Osaka/JP), Christoph Bannwarth (RWTH Aachen University/DE), Wataru Mizukami (University of Osaka/JP)

The foundation for most computational chemistry workflows is thorough conformational sampling. As the number of low-energy conformers grows rapidly with molecular flexibility, tools like CREST [1] and GOAT [2] are usually restricted to inexpensive molecular mechanics (GFN-FF [3]) or semi-empirical (GFN2-xTB [4]) methods. To make up for their rather inaccurate conformational energies, large energy windows need to be chosen to avoid discarding relevant structures. This leads to ensembles of hundreds of conformers, which makes reranking at DFT level the computational bottleneck.
In this context, we investigate whether machine learning interatomic potentials including MACE-POLAR-1 [5] and UMA [6] provide more accurate conformers, including structures that might be absent in GFN-FF- or GFN2-xTB-based ensembles. Furthermore, we evaluate to what extent MLIPs as well as the next-generation SQM method g-xTB [7] may accelerate the reranking workflow. Here, we tested the respective methods in the CENSO [8] multi-level framework.
For conformer search, using uma-s-1p2 with GOAT shows only marginal improvement in the final DFT ensembles compared to GFN2-xTB-based sampling, indicating limited practical benefit at a significantly higher cost. In contrast, for the subsequent reranking, optimizing conformer ensembles at MLIP level allows for much smaller energy windows, decreasing the number of candidate structures, and hence accelerating the reanking procedure significantly. In our benchmarks, MACE-POLAR-1 offers the best balance of accuracy and cost.

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P194

Computational discovery of the initial formation processes of the solid-electrolyte interface and the role of novel additives

Tom-Luka Zwarg (Heinrich-Heine University), Jan Meisner (Heinrich-Heine University)

Solid electrolyte interphase (SEI) formation in lithium-ion batteries is governed by the earliest reductive decomposition events of electrolyte components. Yet these events occur on different timescales, involve multiple competing and often multi-electron pathways, and are difficult to probe experimentally. Conventional mechanistic studies compound this problem: a pathway is typically proposed by chemical intuition and then characterized in isolation by density functional theory (DFT), an approach that can only ever describe the pathway it set out to test and therefore cannot detect competing, unanticipated chemistry. Our approach combines ab initio nanoreactor molecular dynamics with electron addition. Periodic mechanical compression drives the system into densely interacting configurations that accelerate reactive events, but SEI formation is inherently a reductive process, and mechanical driving forces alone cannot simulate the electron-transfer steps required to initiate it. Sequential electron injection therefore supplies the missing reducing environment, approximating the potential experienced at the electrode surface and allowing reduction-initiated SEI chemistry to be simulated alongside the compression-driven reactions. This approach grants unbiased access to both barrierless and activation-limited decomposition pathways beyond the reach of conventional AIMD. In ethylene carbonate (EC) and EC-based mixtures with vinylene carbonate (VC) or 1,3-propane sultone (PS), ab initio nanoreactor MD in combination with electron addition maps in a dense network of reductive decomposition pathways, revealing that EC, VC, and PS share a common kinetic bottleneck in EC ring-opening, while VC and PS become reducible at less negative potentials, allowing them to intercept electron flux and redirect decomposition before EC-dominated pathways can proceed. Building on this validated framework, we then turn the electron-addition nanoreactor on an actively debated additive, 1,3,6-hexanetricarbonitrile (HTCN), whose decomposition mechanism, reductive cyanide CN- release, has so far been examined only along this single proposed pathway. The resulting network is resolved into distinct mechanistic classes, bimolecular EC-addition, CN- release, and oligomerization, each kinetically and thermodynamically characterized.

P195

Automated Assembly and Characterization of Coordination Cages

J. Leodolter (Graz University of Technology/AT), A. Kondinski (Graz University of Technology/AT)

Coordination cages are self-assembling metal-ligand structures that feature nanoscale cavities utilized for sensing, encapsulation, and functional materials.[1] Expanding upon our previous frameworks for the automated rational design and assembly modelling of metal-organic polyhedra (MOPs),[2,3] we present the "Cageinator", a computational Python pipeline designed for the fast generation and preliminary screening of coordination cages. The "Cageinator" builds geometries directly from linker coordinates by positioning metal nodes across predefined topologies (such as octahedral, cuboctahedral, or lantern) and optimizing the orientation of the linkers so that donor atoms (N/O/S) align with these nodes. To enable quick screening of structures and properties, candidate architectures are initially optimized using force fields and subsequently refined via GFN2-xTB.[4] For validation purposes, we reconstruct a previously reported photoswitchable cage, successfully replicating the characteristic UV-Vis signatures of both its open- and closed-ring isomers.[5] Current efforts are focused on expanding this methodology to encompass a wider variety of cage families, alongside the implementation of automated property ranking.[6]

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P196

Thermodynamic Properties of Various Polymorphs of 2-Thiobarbituric Acid via Quasi-Harmonic Calculations

T.-E. Monz, N. Goncharova, J. Hoja, A.D. Boese(University of Graz/AT)

Polymorphism is a well-known phenonomen in molecular crystal systems and important for the development of active pharmaceutical ingredients (APIs). A particular variant, tautomeric polymorphism, occurs when the crystalline phases of a system contain different tautomeric forms. Although many APIs exhibit tautomerism, tautomeric polymorphs are rarely observed [1].
A prominent example of a system with a rich collection of tautomeric polymorphs is 2-thiobarbituric acid (TBA) as it is reported to exist in up to six different crystalline forms: one containing only the enol tautomer (II), four composed of the keto form (I, III, V and VI), and one containing a 50:50 mixture of both tautomers (IV) [2,3].
Here, we explore the thermodynamic properties of six polymorphs (II, III, IV, V, VI and VI_{trans}) of TBA by using a subtractive multimer embedding scheme — ME3(PBE0+MBD:PBE+MBD) — which approximates a full periodic density functional theory (DFT) calculation at the PBE0+MBD level by embedding multimers up to trimers into DFT calculations at the PBE+MDB level [4]. This approach was used for lattice optimizations and phonon calculations using the light species default settings in FHI-aims, with additional electronic lattice energies obtained using tight settings. All calculations were performed utilizing the MEmbed python package. To account for thermal effects, the quasi-harmonic approximation was used in conjunction with a fit to the Murnaghan equation of state.
Overall, polymorphs of the same tautomeric composition show similar values for the relative Helmholtz (ΔF) and Gibbs (ΔG) free energy per molecule both at 0 K and 300 K, allowing for a clear separation of all investigated polymorphs based on thermodynamic stability: form II is the thermodynamically most stable polymorph, followed by form IV, with the least stable group comprising the forms III, V, VI and VI_{trans}. Values for the heat capacity at constant pressure C_p at 300 K lie in the range of 128.1 to 132.0 J/mol·K per molecule for all polymorphs except form V, which exhibits a value of 123.2 J/mol·K per molecule. Thermal expansion coefficients β range from 0.5×10^{-5} K^{-1} per molecule (form IV) to 4.8×10^{-5} K^{-1} per molecule (form III).

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P197

Detailed Pathways of Chemical Reactions in Molecular Crystals Using MLFFs

O. Schweighofer, N. Goncharova, J. Hoja (University of Graz/AT)

Machine-learned force fields (MLFFs), which provide density functional theory (DFT)-level accuracy for nudged elastic band (NEB) and frequency calculations, enable the simulation of supercells that are otherwise computationally prohibitive [1]. Reaction pathways in molecular crystals frequently assume that all constituents within a unit cell react simultaneously, neglecting how sequential reaction orders impact energy barriers and internal mechanical stress. Building upon the Diels-Alder reaction in a bis(N-allylimino)-1,4-dithiin and 9-bromoanthracene cocrystal [2], we decouple these individual reactions and investigate a detailed sequential pathway. Although the minimum energy path (MEP) profiles yield comparable energies for both simultaneous and sequential mechanisms, the sequential route is physically more probable. Expanding this analysis from a single unit cell to 2x2x2 and 3x3x3 supercells further demonstrates that surrounding unreacted lattice environments significantly influence the overall MEP energy barrier.

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