

# Bringing together rare event sampling, excited state dynamics and machine learning

Book of Abstracts

1<sup>st</sup> ViRAPID Workshop 2024

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# Program Overview

	Mon 26.	Tue 27.	Wed 28.	Thu 29.
9:00-9:40		Jörg Behler	Gerhard Hummer	Sapna Sarupria
9:45-10:25		Luigi Bonati	David Limmer	Roberto Covino
10:30-11:00		Coffee break	Coffee break	Coffee break
11:00-11:40		Chris Oostenbrink	Peter Bolhuis	Bettina Keller
11:45-12:00		Esther Heid	Rangsiman Ketkaew	Elena Betti
12:00-12:30	Registration	Discussion	Discussion	Discussion
12:30-		Lunch break	Lunch break	Lunch break
13:30-14:00	Opening			
14:00-14:40	Steven Lopez	Eric Vanden Eijnden	Basile Curchod	Jeremy Richardson
14:45-15:25	Nađa Došlić	Jutta Rogal	Federica Agostini	Caroline Lasser
15:30-16:00	Coffee break	Coffee break	Coffee break	Coffee break
16:00-16:15	Julia Westermayr	Juan P. Garrahan	Lea Ibele	Rafael Gómez-Bombarelli
16:15-16:40			Discussion	
16:45-17:00	Davide Avagliano	Ofir Blumer	Free time	Elisa Pieri
17:00-17:30	Discussion	Discussion		Discussion
18:00-	Reception	Poster session		Closing
19:00-			Social Dinner	

# Daily Program

Monday 26.		
12:00-13:30	Registration	
13:30-14:00	Opening	
	Session 1	Chair: Leticia González
14:00-14:40	Steven Lopez	Machine-learning-accelerated photodynamics simulations in complex environments towards new materials and medicines
14:45-15:25	Nada Došlić	Structure and wavelength dependence in organic photochemistry
15:30-16:00	Coffee break	
16:00-16:40	Julia Westermayr	Navigating Chemical Space: Deep Neural Networks and Reinforcement Learning for Excited States
16:45-17:00	Davide Avagliano	Wavefunction mapping: benefits for machine learning, excited states dynamics and time-resolved spectra
17:00-17:30	Discussion	
18:00-	Reception	

Tuesday 27.		
	Session 2	Chair: Maximilian X. Tiefenbacher
9:00-9:40	Jörg Behler	Atomistic Simulations of Complex Systems by High-Dimensional Neural Network Potentials
9:45-10:25	Luigi Bonati	Reactive potentials via machine learning and enhanced sampling: from methods to catalytic applications
10:30-11:00	Coffee break	
11:00-11:40	Chris Oostenbrink	BuRNN: polarizable QM/MM simulations with machine-learning
11:45-12:00	Esther Heid	Errors and uncertainty in machine learning models
12:00-12:30	Discussion	
12:30-14:00	Lunch break	
	Session 3	Chair: Christoph Dellago
14:00-14:40	Eric Vanden Eijnden	Deep learning probability flows and entropy production rates in active matter
14:45-15:25	Jutta Rogal	Exploring free energies with deep generative models
15:30-16:00	Coffee break	
16:00-16:40	Juan P. Garrahan	Discrete diffusion models and tensor networks
16:45-17:00	Ofir Blumer	Stochastic Resetting for Enhanced Sampling
17:00-17:30	Discussion	
18:00-	Poster session	





Wednesday 28.		
	<u>Session 4</u>	Chair: Brigitta Bachmair
9:00-9:40	Gerhard Hummer	Reaction mechanisms from AI-guided trajectory sampling
9:45-10:25	David Limmer	Reactive path ensembles out of equilibrium
10:30-11:00	Coffee break	
11:00-11:40	Peter Bolhuis	Learning reaction coordinates and finding optimal model parameters from sampled trajectory ensembles
11:45-12:00	Rangsiman Ketkaew	Unsupervised Collective Variables for Exploring Expanded Configurational Space of Chemical Reactions
12:00-12:30	Discussion	
12:30-14:00	Lunch break	
	<u>Session 5</u>	Chair: Ulisse Stefanelli
14:00-14:40	Basile Curchod	On the creation of a hierarchy of methods for nonadiabatic molecular dynamics
14:45-15:25	Federica Agostini	Theories and simulations of ultrafast processes in molecules
15:30-16:00	Coffee break	
16:00-16:15	Lea Ibele	CCT: Combined Coupled Trajectories - An equity-based method for kinetic energy distribution in surface hopping
16:15-16:45	Discussion	
16:45-19:00	Free time	
19:00-	Social Dinner	

Thursday 29.		
	<u>Session 6</u>	Chair: Johannes Dietschreit
9:00-9:40	Sapna Sarupria	Learning Pathways to Polymorphs
9:45-10:25	Roberto Covino	Molecular Free Energies, Rates, and Mechanisms from Data-Efficient Path Sampling Simulations
10:30-11:00	Coffee break	
11:00-11:40	Bettina Keller	Thermal isomerization of retinal: from transition state theory to simulations
11:45-12:00	Elena Betti	How machine learning enhances simulation of energy transfer in light-harvesting complex II
12:00-12:30	Discussion	
12:30-14:00	Lunch break	
	<u>Session 7</u>	Chair: Sebastian Mai
14:00-14:40	Jeremy Richardson	Nonadiabatic rate theory from the mapping approach to surface hopping (MASH)
14:45-15:25	Caroline Lasser	Numerical analysis for excited state dynamics
15:30-16:00	Coffee break	
16:00-16:40	Rafael Gómez-Bombarelli	Machine learning potentials for photoswitching and helicene photochemistry
16:45-17:00	Elisa Pieri	Can we automate in silico photoreaction discovery?
17:00-17:30	Discussion	
18:00-	Closing	

# Invited talks

## Machine-learning-accelerated photodynamics simulations in complex environments towards new materials and medicines

26. Feb  
14:00

Steven Lopez

*Northeastern University*

Photochemical reactions are increasingly important for constructing value-added, strained organic architectures. Direct excitation and photoredox reactions typically require mild conditions to access therapeutic gases (e.g., carbon monoxide) and new synthetic methodologies. A priori design of photochemical reactions is challenging because degenerate excited states often result in competing reaction mechanisms to undesired products. Further, a lack of experimental techniques that provide atomistic structural information on ultrafast timescales (10–15 – 10–12 s) has limited general rules about these reactions. Computations, however, provide a path forward. I will discuss how my group has leveraged multiconfigurational complete active space self consistent field (CASSCF) calculations, non-adiabatic molecular dynamics, and machine learning (ML) techniques to understand reaction mechanisms and enumerate new reaction pathways. I will introduce our new open-access machine learning tool, Python Rapid Artificial Intelligence Ab Initio Molecular Dynamics (PyRAI2MD), which enables 100,000-fold longer simulations than current NAMD simulations with multiconfigurational quantum chemical methods. I will describe how PyRAI2MD has enabled the first ML-NAMD simulations with QM/QM (CAS/HF) training data. The presentation will explain the origins of the reactivities and selectivities of photochemical pericyclic reactions and CO-evolving reactions in aqueous environments.



## Structure and wavelength dependence in organic photochemistry

26. Feb

14:45

Nada Došlić

*Ruder Bošković Institute*

Excited-state proton transfer reactions typically occur between a proton donor (e.g., NH or OH) and an electronegative heteroatom. Sometimes, however, the proton acceptor can be a carbon atom. These findings are at first sight somewhat surprising since the protonation of a carbon atom of an aromatic ring typically is a slow process in the ground state. Yet, why do some aromatic ring carbons gain basicity in the excited state? We consider ortho-, meta-, and para-aminobiphenyl isomers undergoing distinctly different photochemical reactions involving proton transfer and show that excited-state antiaromaticity relief can play important roles in these reactions.

Photoreactions taking place from higher excited states, known as anti-Kasha photochemistry, are rare since not many photochemical processes can compete with fast internal conversion to the first excited electronic state (S1). However, there is increasing evidence of violation of Kasha rule in the photochemistry and photophysics of organic compounds. In this talk, we discuss some common structural and electronic properties of molecules exhibiting wavelength-dependent photochemistry.

In the last part of this talk, I present a theoretical framework for the simulation of time-resolved UV pump X-ray probe spectra. Recently, the ability of X-ray photoelectron spectroscopy to probe the constituent atoms of a molecule was exploited to investigate the relaxation dynamics of UV-excited uracil. While O, N, and C 1s core level spectra provide complementary information, the interpretation of these spectra is notoriously difficult and requires considerable theoretical involvement. We show how a joint effort in nonadiabatic dynamics and electronic structure theory contributed to clarifying uracil's excited state dynamics.



# Navigating Chemical Space: Deep Neural Networks and Reinforcement Learning for Excited States

Julia Westermayr

*Leipzig University*

26. Feb  
16:00

Chemical reactions are fundamental to drive the transformation of matter and are pivotal across diverse domains like medicine, materials science, and energy generation. In this talk, we will explore the potential of machine learning algorithms to explore chemical structure space on ground and excited states. Specifically, we will illustrate the proficiency of deep neural networks in accelerating the prediction of excited-state properties, thereby enhancing our understanding of the photochemistry of organic molecules [1,2]. Additionally, we will showcase how this model can be used to guide reinforcement learning agents in exploring chemical structure space [3,4].

## References

- [1] J. Westermayr, P. Marquetand, Chem. Rev., 121, 9873-9926 (2020)
- [2] J. Westermayr, M. Gastegger, D. Vörös, L. Panzenboeck, F. Joerg, L. González, P. Marquetand, Nat. Chem., 14, 914-919 (2022)
- [3] R. Barrett and J. Westermayr, arXiv:2310.03511 (2023) (J. Phys. Chem. Lett.)
- [4] R. Barrett, S. Mausenberger, J. Westermayr, "Actor-Critic Reinforcement Learning for the Search of Critical Points on Excited-State Potentials: Towards Rapid Identification of Conical Intersections", submitted (2024).



# Atomistic Simulations of Complex Systems by High-Dimensional Neural Network Potentials

Jörg Behler

27. Feb  
9:00

*Ruhr-Universität Bochum*

In recent years there has been tremendous progress in the development of interatomic potentials employing machine learning. High-dimensional neural network potentials (HDNNP) are an important class of machine learning potentials, which allow to combine the accuracy of electronic structure calculations with the efficiency of simple empirical potentials enabling large-scale simulations. Depending on the types of systems and physical phenomena they are able to describe, HDNNPs can be classified into up to now four generations. In this talk, an overview about the methodical evolution of HDNNPs will be given along with typical example applications to condensed systems with a particular focus on chemical processes at interfaces.



# Reactive potentials via machine learning and enhanced sampling: from methods to catalytic applications

27. Feb  
9:45

Luigi Bonati

*Italian Institute of Technology*

Machine learning methods for learning potential energy surfaces offer an efficient alternative to bridge the gap between the accuracy of DFT calculations and the efficiency of empirical potentials. However, simulating reactive processes like chemical reactions and phase transitions poses challenges due to their inaccessible time scales, making it difficult to obtain reference configurations. To address this, we employ an active learning strategy accelerated by enhanced sampling methods such as metadynamics or OPES, which allows us to obtain reliable potentials along all the reaction pathways [1-3]. The fruitful combination of these techniques enables DFT-quality reactive simulations of rare events that otherwise fall outside the scope of classical and ab initio simulations. For instance, our study on the iron (111) surface at high temperatures influencing nitrogen decomposition in the Haber-Bosch process uncovers temperature-dependent behaviors, emphasizing the need for calculations that fully consider dynamics in assessing catalytic activity [1]. Furthermore, I will discuss recent developments in constructing data-efficient potentials and identifying relevant collective variables using machine learning methods.

[1] PNAS 120 50 e2313023120 (2023).

This research was supported by BMBF within the Ammoref project (03HY203A-F) and by the Italian Institute of Technology.



# BuRNN: polarizable QM/MM simulations with machine-learning

27. Feb  
11:00

Chris Oostenbrink

*University of Natural Resources and Life Sciences*

In hybrid quantum mechanics / molecular mechanics (QM/MM) approaches, the molecular system is partitioned into regions that are treated at different levels of theory. At the interfaces between these regions, artifacts may occur. Examples are an overpolarization of the QM region due to near partial charges in the MM region, the lack of polarization in the MM region or unbalanced interactions between particles in the different regions, leading to an intrusion of MM particles into the QM region, or an accumulation or depletion of QM particles if particles are allowed to change character.

We have recently introduced a buffered embedding scheme, in which a buffer region between the inner (QM) and outer (MM) region is defined for which the interactions are computed both at the QM and MM level. This comes at the cost of introducing a second QM-calculation at every timestep of the simulation. The use of neural networks to describe molecular potential energies, allows for an elegant solution to this problem. We train a neural network directly on the difference between the two QM calculations, ensuring that the network reproduces the QM-interactions of the inner region, with itself and with the buffer region as well as the polarization of the buffer region due to the inner region. Any remaining artifacts largely cancel in the trained differences and are far removed from the inner region of interest. The use of the Buffer Region Neural Network (BuRNN) approach, furthermore, allows us to apply alchemical free-energy calculations at the QM-level of theory. In this presentation, I will demonstrate our most recent advances with BuRNN.

1. Lier, B., Poliak, P., Marquetand, P., Westermayr, J., Oostenbrink, C. (2022) BuRNN: Buffer Region Neural Network Approach for Polarizable-Embedding Neural Network/Molecular Mechanics Simulations. J Phys Chem Lett 13, 3812-3818. doi: 10.1021/acs.jpcllett.2c00654



# Deep learning probability flows and entropy production rates in active matter

Eric Vanden-Eijnden

27. Feb  
14:00

*Courant Institute, NYU*

Active matter systems, from self-propelled colloids to motile bacteria, are characterized by the conversion of free energy into useful work at the microscopic scale. These systems generically involve physics beyond the reach of equilibrium statistical mechanics, and a persistent challenge has been to understand the nature of their nonequilibrium states. The entropy production rate and the magnitude of the steady-state probability current provide quantitative ways to do so by measuring the breakdown of time-reversal symmetry and the strength of nonequilibrium transport of measure. Yet, their efficient computation has remained elusive, as they depend on the system's unknown and high-dimensional probability density. In this talk, building upon recent advances in generative modeling, I will present a deep learning framework that estimates the score of this density. The score, together with the microscopic equations of motion, gives direct access to the entropy production rate, the probability current, and their decomposition into local contributions from individual particles, spatial regions, and degrees of freedom. The broad utility and scalability of the method will be illustrated by applying it to several high-dimensional systems of interacting active particles undergoing motility-induced phase separation (MIPS).

This is joint work with Nick Boffi.





# Exploring free energies with deep generative models

27. Feb

Jutta Rogal

14:45

*New York University*

Computing free energy differences is a computationally demanding task, requiring a rigorous sampling of the phase space. Here, we train a machine learning model based on normalizing flows to map between probability distributions of condensed phase systems at different thermodynamic conditions. Using the trained flow model, a large number of uncorrelated configurations can easily be generated to efficiently estimate ensemble averages. This allows us to assess free energy differences over a wide range of temperatures and pressure, needed to evaluate the relative stability of different phases and reconstruct phase diagrams.



# Discrete diffusion models and tensor networks

27. Feb  
16:00

Juan P. Garrahan

*School of Physics and Astronomy, University of Nottingham*

Diffusion models (DMs) refers to a class of generative machine learning methods for sampling a target (often empirical) distribution from samples of a trivial (typically Gaussian) distribution evolved with a de-noising dynamics that inverts the effect of adding diffusive noise to the distribution of interest. I will consider the generalisation of DMs to lattice systems with discrete degrees of freedom and Markov chain dynamics. I will show how to use tensor networks (efficient parametrisations of states and operators originally devised to study quantum many-body systems but increasingly also used for classical stochastic systems) to efficiently define and sample discrete DMs.



# Reaction mechanisms from AI-guided trajectory sampling

Gerhard Hummer

28. Feb  
9:00

*Max Planck Institute of Biophysics*

Enhanced sampling algorithms combined with machine learning techniques greatly speed up molecular dynamics simulations. My presentation will focus on AI-guided transition path sampling. By an iterative training of deep learning models on the sampled transition dynamics, we gain a mechanistic understanding of the reaction processes that we in turn use to increase the efficiency of the rare-event sampling. The general framework for autonomous trajectory sampling and mechanism learning will be illustrated with specific applications to a diverse set of (bio)molecular systems.



# Reactive path ensembles out of equilibrium

28. Feb

9:45

David Limmer

*UC Berkeley*

The modern theory of rare events is grounded in near equilibrium ideas, however many systems of modern interest are sufficiently far from equilibrium that traditional approaches do not apply. Using the recently developed variational path sampling, I will discuss some basic principles we have deduced for reactive events in systems evolving within nonequilibrium steady-states and relaxing following photoexcitation. These include a thermodynamic speed limit for the rate enhancement achievable out of equilibrium, and the conditions to coherently control photochemical yield.



# Learning reaction coordinates and finding optimal model parameters from sampled trajectory ensembles

28. Feb  
11:00

Peter Bolhuis

*University of Amsterdam*

The reaction coordinate (RC) is the principal collective variable or feature that determines the progress along an activated or reactive process. A good RC is crucial for generating sufficient statistics with enhanced sampling. Moreover, the RC provides invaluable atomistic insight in the process under study. The optimal RC is the committor, which can be computed with brute force MD, or more efficiently by e.g. Transition Path Sampling. Novel schemes for transition path sampling using reinforcement learning can now effectively map the committor function. The interpretability of the committor, being a high dimensional function, remains very low. Applying dimensionality reduction can reveal the RC in terms of low-dimensional human understandable molecular collective variables (CVs) or order parameters. In the first part, I discuss several methods to perform this dimensionality reduction, such as likelihood maximization or symbolic regression, but they usually require a preselection of these low-dimension CVs. In addition, we apply an extended auto-encoder that maps the input (many CVs) onto a lower-dimensional latent space, used for the reconstruction of the input as well as the prediction of the committor [1]. I illustrate the method on simple but nontrivial toy systems, as well as extensive molecular simulation data of methane hydrate nucleation. The extended autoencoder model can effectively extract the underlying mechanism of a reaction, make reliable predictions about the committor of a given configuration, and potentially even generate new paths representative for a reaction.

In the second part, I focus on a general framework of imposing known rate constants as constraints in molecular dynamics simulations, based on a combination of the maximum-entropy (MaxEnt) and maximum-caliber principles (MaxCal). Starting from an existing ensemble of (rare event) dynamical trajectories or paths, e.g. obtained from TPS, each path is reweighted in order to match the calculated and experimental interconversion rates of a molecular transition of interest, while minimally perturbing the prior path distribution [2]. This kinetically corrected ensemble of trajectories leads to improved structure, kinetics and thermodynamics. One also learns mechanistic insight that may not be readily evident directly from the experiments. This method does not alter the Hamiltonian directly, and therefore we recently proposed a novel MaxCal-based path-reweighting technique to optimize parameters in the molecular model itself, while constraining kinetic observables [3]. This opens up the possibility to design molecular models that lead to desired kinetic behaviour.

- [1] M. Frassek, A. Arjun, and P. G. Bolhuis, J. Chem. Phys. 155, 064103 (2021).
- [2] Z. F. Brotzakis, M. Vendruscolo, and P. G. Bolhuis, Proc. Natl. Acad. Sci. 118, (2021).
- [3] P. G. Bolhuis, Z. F. Brotzakis, and B. G. Keller, J. Chem. Phys. 159, 074102 (2023) .



# On the creation of a hierarchy of methods for nonadiabatic molecular dynamics

28. Feb  
14:00

Basile Curchod

*University of Bristol*

Different theoretical tools have been developed to simulate the photochemistry of molecules in their full dimensionality. Two examples of such methods include ab initio multiple spawning (AIMS) and trajectory surface hopping (TSH). AIMS describes the dynamics of nuclear wavepackets using adaptive linear combinations of traveling frozen Gaussians. TSH portrays the nuclear dynamics with a swarm of independent classical trajectories that can hop between potential energy surfaces for this task. In this talk, I intend to survey some of our recent work on the development of a hierarchy of methods for excited-state dynamics based on the AIMS framework. I will also spotlight challenges for the field of nonadiabatic molecular dynamics that were identified when simulating the photochemistry of atmospheric molecules.



# Theories and simulations of ultrafast processes in molecules

Federica Agostini

28. Feb

14:45

*University Paris-Saclay, Institut de Chimie Physique*

In this talk I will present various methodologies to simulate the excited-state dynamics in molecules, underlying ultrafast processes typically encountered in photochemistry. I will focus in particular on trajectory-based techniques, comparing those derived from the exact factorization [1], and thus based on coupled trajectories [2, 3], with those based on independent trajectories, as the well known Ehrenfest method and surface hopping.

After presenting the theory, I will give an overview on several applications ranging from isolated molecular models [4] and molecules [5, 6] undergoing ultrafast internal conversions and intersystem crossings [7], to systems in the presence of external time-dependent fields [8, 9].

- [1] Abedi, Maitra, Gross, Phys. Rev. Lett. (2010); Agostini, Gross, Eur. Phys. J. B (2021).
- [2] Min, Agostini, Gross, Phys. Rev. Lett. (2015).
- [3] Pieroni, Agostini, J. Chem. Theory Comput. (2021).
- [4] Marsili, Olivucci, Lauvergnat, Agostini, J. Chem. Theory Comput. (2020).
- [5] Min, Agostini, Tavernelli, Gross, J. Phys. Chem. Lett. (2017).
- [6] Sangiogo Gil, Persico, Granucci, Agostini, in preparation.
- [7] Talotta, Morisset, Rougeau, Lauvergnat, Agostini, Phys. Rev. Lett. (2020).
- [8] Ibele, Curchod, Agostini, J. Phys. Chem. A (2022).
- [9] Schirò, Eich, Agostini, J. Chem. Phys. (2021).



## Learning Pathways to Polymorphs

Sapna Sarupria

29. Feb  
9:00

*University of Minnesota Twin Cities*

Crystallization is consequential to many applications, including pharmaceutical production, flow assurance, and climate modeling. Effective control over crystallization relies on an understanding of the possible structures that can form during nucleation and growth. Molecular simulations allow a more fine-grained approach to discovering important, though possibly short-lived, intermediate structures, but their characterization from atomic coordinates is often difficult. We combine general features of the local atomic arrangements with a deep learning model to discover the unique structures that form during crystal nucleation. While many previous mechanistic studies have relied on features that describe the entire crystal nucleus, such as its size, shape, and composition, we focus on the evolution of the atoms involved in the formation of the nucleus in the feature space to describe nucleation processes. Through understanding the evolution of the local atomic environments, we can make predictions of polymorphs. This has been a long-standing problem in nucleation. Our studies thus provide methods that will enable control of nucleation processes, with applications in polymorph selection.





# Molecular Free Energies, Rates, and Mechanisms from Data-Efficient Path Sampling Simulations

29. Feb  
9:45

Roberto Covino

*Bayreuth University - Frankfurt Institute for Advanced Studies*

Understanding the physical mechanisms governing the formation of molecular complexes is critical to explaining how biomolecular function emerges from the interplay of structures, dynamics, and complexity. Physics-based simulations as molecular dynamics are potent instruments that enable us to investigate crucial molecular events inaccessible to experiments. However, straightforward use of these simulations can often not sample the time scales on which many key biomolecular processes occur. Path sampling tackles this limitation by biasing the initializing of trajectories to enhance the sampling of rare molecular events while keeping the dynamics unbiased. The integration of machine learning can further boost the sampling in an adaptive and data-driven way. At the same time, machine learning can also help in learning a quantitative representation of the sampled mechanisms. Still, the sampled trajectories are by construction non-Boltzmann-distributed, preventing the calculation of free energies and rates. I will discuss an algorithm to approximate the equilibrium path ensemble from machine-learning-guided path sampling simulations. At the same time, our algorithm provides efficient sampling, mechanisms, free energy, and rates of rare molecular events at a moderate computational cost. I will discuss some applications to biomolecular systems. Our algorithm is straightforward and data-efficient, opening the door to applications in many challenging molecular systems.



## Thermal isomerization of retinal: from transition state theory to simulations

Bettina Keller

29. Feb  
11:00

*Freie Universität Berlin*

Reaction dynamics are conventionally described by Eyring Transition State Theory (TST), a model well-suited for small molecules in the gas phase but constrained by its rigid assumptions. With modern potential energy surfaces, simulations that extend beyond the limitations of Eyring TST come within reach. This allows for modelling reactions with anharmonic reactants and transition states, as well as multiple subminima in the reactant state and/or transition states. However, two difficulties arise. First, simulations impose a classical description of the dynamics, neglecting the zero-point energies and modelling the high-temperature limit of the partition function. Second, enhanced sampling techniques are needed to overcome the reaction barrier and the choice of method for enhanced sampling and reweighting can significantly impact the rate estimate. Focussing on reaction-coordinate based methods, I will discuss the relative magnitude of these error sources. As a case study, I will examine the thermal cis-trans isomerization of retinal.

S. Ghysbrecht, B.G. Keller arXiv:2312.10520

S. Ghysbrecht, L. Donati, B.G. Keller arXiv:2312.12948



# Nonadiabatic rate theory from the mapping approach to surface hopping (MASH)

Jeremy Richardson

29. Feb  
14:00

*ETH Zurich*

The mapping approach to surface hopping [1] combines the best aspects of fewest-switches surface hopping (FSSH) with rigorous quasiclassical mapping methods. We show how it can be used to simulate rare events in systems with nonadiabatic reactions and capture the correct rate over a wide range of couplings [2]. In particular, we recover the Marcus behaviour in the golden-rule regime without requiring decoherence corrections (unlike FSSH). We explain the subtle differences between MASH and FSSH and explain why FSSH fails where MASH succeeds. Given the current popularity of using FSSH in ab initio simulations of chemical systems, our new algorithm has the potential for offering a more accurate and rigorous dynamical method for these applications, all at a comparable computational cost.

[1] Mannouch & Richardson, J. Chem. Phys., 158, 104111 (2023)

[2] Lawrence, Mannouch & Richardson, J. Phys. Chem. Lett., 15, 707 (2024)



## Numerical analysis for excited state dynamics

Caroline Lasser

29. Feb

14:45

*TUM*

In addition to high dimensions, the numerical simulation of excited state dynamics offers interesting challenges for numerical analysis: multi-scale behaviour, high frequency motion, singular potential energy surfaces, and more. The talk aims to investigate, how the popular surface hopping algorithm of the fewest switches addresses them and how its numerical time-integration could be improved. (This talks reports joint work with Leonardo Araujo.)



# Machine learning potentials for photoswitching and helicene photochemistry

Rafael Gomez-Bombarelli

29. Feb  
16:00

*MIT DMSE*

Helicenes are molecules whose synthesis involves the formation of a sigma chemical bond in the excited state from a (poly)aromatic stilbene derivative. The rules governing the reaction mechanism and thus the yield in synthetic experiments are not understood at all, preventing their scalable synthesis despite their interesting applications. The computational cost of running many non-adiabatic molecular dynamics trajectories at the quantum mechanical level is too expensive to analyze known chemistries, and even more so to prospectively explore new ones. Deep neural networks, trained as surrogates of the quantum mechanics, retain the accuracy but at a millionth of the computational cost, particularly through algorithmic developments like diabatic-neural network potentials that learn the smoother diabatic surface. Here, we will describe the training and utilization of DANN potentials trained on Mixed-Reference Spin Flip DFT energies, forces and couplings, to study the trans-cis isomerization of helicene precursors and the photo-assisted ring-closure Mallory reaction. The role of both enhanced sampling, and gradient-based adversarial attacks on uncertainty to create the training data will be highlighted, as well as the correlation between the NN-driven simulations and the experimental reaction yields of helicene synthesis.

# Hot topic contributed talks

## Wavefunction mapping: benefits for machine learning, excited states dynamics and time-resolved spectra

26. Feb  
16:45

Davide Avagliano

*University of Toronto*

A crucial component of simulating long-scale and rare events is the choice of the electronic structure method, especially when we want to simulate medium-to-large systems. Ideally, the dream electronic structure method would combine the high accuracy of multi-reference methods and the computational efficiency of TD-DFT, but single or multireference methods are always unbalanced either in one or the other directions. However, by mapping the results and the properties obtained at two different levels of theory it is possible to exploit their strengths and overcome the limitation along the computational workflow. In this talk, I want to show the theory behind mapping two calculations at two different levels of theory by calculating the overlap of their transition density matrices or their electronic wavefunction. The same concept can be exploited in different steps of the computational workflow to simulate excited states dynamics. First, it allows the design of a scoring system to have a quantitative and numerical definition of the quality of a calculation against a higher-quality reference one. Transforming the complicated task of evaluating at the same time energies, characters, and oscillator strengths of a manifold of excitations into a numerical task, allowed us to efficiently train a graph attention neural network that can recommend the best density functional to be used for TD-DFT calculations of molecules without the need of a functionals benchmark [1]. When we want to simulate the dynamics, our recently proposed algorithm to compute CIS-like wavefunction overlap, based on the unitary transformation of the orbitals of one of the two sets of molecular orbitals, allows us to additionally speed up the simulation of excited states dynamics with TD-DFT [2]. Last, I want to show how our algorithm can be extended to mapping again excited states calculations at different levels, to diagnostic dynamics at TD-DFT level, and to obtain simulations of stimulated emission and excited states absorption spectra at the efficiency of TD-DFT, but at the quality of CASPT2 [3], offering a new appealing playground for the application of machine learning in excited states dynamics.

[1] D. Avagliano, M. Skreta, S. Arellano-Rubach, A. Aspuru-Guzik, "DELFI: A computer oracle for recommending density functionals for excited states calculations", in revision in Chemical Science, preprint: DOI:10.26434/chemrxiv-2023-v9841

[2] D. Avagliano, M. Bonfanti, A. Nenov, M. Garavelli, "Automatized Protocol and Interface to Simulate QM/MM Time-Resolved Transient Absorption at TD-DFT Level with COBRAMM", J. Comput. Chem. 2022, 43(24)

[3] A. Loreti, V. M. Freixas Lemus, D. Avagliano, F. Segatta, S. Mukamel, M. Garavelli, N. Govind, A. Nenov, manuscript in preparation



## Errors and uncertainty in machine learning models

27. Feb

Esther Heid

11:45

*TU Wien*

Machine learning models have become very successful for chemical applications, such as the prediction of molecular or reaction properties, or as surrogate models of the interatomic potential. But how certain is a specific prediction? Can an uncertainty estimation via mean-variance prediction or ensembling really relate to the actual model error? In this work, we present general rules how to identify aleatoric and epistemic contributions to the uncertainty of a model, further divide epistemic error into model bias and variance, and discuss means to critically assess the applicability of common uncertainty metrics to a range of different prediction tasks on various datasets.



# Stochastic Resetting for Enhanced Sampling

Ofir Blumer

27. Feb

16:45

*School of Chemistry, Tel Aviv University*

We present a new approach for enhanced sampling of Molecular Dynamics (MD) simulations using stochastic resetting (SR). MD simulations is a powerful tool, used for the study of physical and chemical systems at the microscopic level. However, due to their atomic resolution, MD simulations are limited to processes shorter than a few microseconds. Longer processes, such as protein folding, or crystal nucleation and growth, cannot be sampled by standard MD simulations.

SR is the procedure of stopping random processes and restarting them, resampling independent and identically distributed initial conditions. It was shown to expedite different kinds of stochastic processes, ranging from queuing systems to diffusion of colloidal particles. Here, we employ it to enhance MD simulations for the first time, leading to speedups of up to an order of magnitude. We also present an inference procedure, to obtain the unbiased kinetics from simulations with SR.

Next, we demonstrate that SR can be combined with existing enhanced sampling methods, such as Metadynamics (MetaD). For a simple model system, we show that this combination may lead to higher speedups than either approach independently. In another model, we show that restarting MetaD simulations with suboptimal collective variables (CVs) gives comparable accelerations to using the optimal CV, suggesting resetting can be an easy alternative to improving CVs. We apply the combined approach to the folding of chignolin in water, showing that SR expedites simulations with a suboptimal CV by an order of magnitude. Lastly, we present an inference procedure of unbiased kinetics for the combined MetaD and SR method.





# Unsupervised Collective Variables for Exploring Expanded Configurational Space of Chemical Reactions

Rangsiman Ketkaew

*University of Zurich*

28. Feb  
11:45

We develop a machine learning algorithm called a deep learning autoencoder neural network (DAENN) to generalize collective variables (CVs) for enhanced sampling. The essential novelties of the DAENN are a self-learning engine that applies a specific-purpose loss function using the min-max technique and eXtended Social PeRmutation INvariantT (xSPRINT) representation. To train a model, the DAENN requires only a trajectory of reactant conformers as input and no intermediate or product structures. Carefully manifested by primitive organic reactions such as the Diels-Alder reaction, DAENN-generated CVs can identify transitions between rare-event metastable states on the expanded configurational space. The results show that the adopted CVs give accurate computed free energy that is in line with those obtained by previously developed CVs and experimental results. In addition, the proposed method is implemented in Deep Learning for Collective Variables (DeepCV), a computer code that provides an efficient and customizable implementation of the DAENN, which can communicate with other molecular dynamics software, namely CP2K and PLUMED.



# CCT: Combined Coupled Trajectories - An equity-based method for kinetic energy distribution in surface hopping

28. Feb  
16:00

Lea Ibele

*CNRS/University Paris-Saclay*

The exact factorization of the electron-nuclear wavefunction proposes to represent the dynamics of a molecule in the excited state as a single time-dependent nuclear wavefunction, evolving under the action of a single time-dependent potential energy surface and a single time-dependent vector potential [1].

These time-dependent scalar and vector potentials provide a ready framework for describing the nuclear dynamics through trajectories. Coupled trajectory formalisms (coupled trajectories mixed quantum classical – CT-MQC[2], and coupled trajectories Tully surface hopping – CT-TSH[3]) have been derived that can be applied to accurately describe the nonadiabatic dynamics of molecular systems.

However, in both formalisms the question of energy conservation is not trivial. Recently, a new formalism for energy conservation within the ensemble of trajectories in CT-MQC has been proposed.[4,5] In CT-TSH, by default, energy conservation is enforced along each trajectory by rescaling the momentum following a surface hop. Due to the coupled nature of the trajectories, such a strict criterium can lead to a too high number of frustrated hops and therefore affect the internal consistency of the method.

Therefore, we propose a new formalism, coined Combined Coupled Trajectories (CCT), which allows the trajectories to "borrow" energy from each other and thereby, reduce the number of frustrated hops. On two model systems, a three dimensional model of the photoisomerization of the Retinal chromophore and a two dimensional, three state model of the photodissociation of Phenole, we show the advantages of energy sharing between the trajectories and evaluate different hopping formalisms that are more suited for CCT-TSH.

- [1] Abedi, A.; Maitra, N. T.; Gross, E. K. U. Phys. Rev. Lett. 2010, 105, 123002.
- [2] Min, S. K.; Agostini, F.; Tavernelli, I.; Gross, E. K. U. J. Phys. Chem. Lett. 2017, 8, 3048–3055.
- [3] Pieroni, C.; Agostini, F. J. Chem. Theory Comput. 2021, 17, 5969–5991.
- [4] Arribas, E. V.; Ibele, L. M.; Lauvergnat, D.; Maitra, N. T.; Agostini, F. Journal of Chemical Theory and Computation 2023, 19, 7787–7800.
- [5] Villaseco Arribas, E.; Maitra, N. T. The Journal of Chemical Physics 2023, 158.



## How machine learning enhances simulation of energy transfer in light-harvesting complex II

Elena Betti

*University of Pisa*

29. Feb  
11:45

In plant photosynthesis, the harvesting of solar energy is made possible by aggregate of pigments embedded in specialized membrane proteins, called light-harvesting complexes (LHCs)[1]. Specific interactions with the protein and electronic couplings with other chromophores alter the optical properties of individual pigments, and light absorption in the aggregate is followed by a cascade of energy transfer processes. Because of the complex nature of LHCs, the simulation of such excited state dynamics is challenging and requires expensive multiscale methods[2] to estimate all the involved parameters. Structural disorder adds on top, requiring calculations to be repeated over many configurations of the system.

Machine learning (ML) can represent a valuable alternative to traditional approaches in the simulation of energy transfer events. Here, we show that a ML strategy[3] can be applied to estimate excitonic quantities of LHCII of higher plants with accuracy comparable to standard multiscale methods, with the advantage of an extremely higher speed which allows wide sampling of the configurational space of the system when coupled to molecular dynamics. The resulting estimated parameters are robust and allow simulation of the excited state dynamics which closely reproduces the experimental one, as demonstrated by comparison of transient absorption spectra[4]. New insights on the most relevant pathways and associated characteristic times are achieved through this integrated model.

[1] Croce et al., Nat. Chem. Biol. 10, 492–501 (2014). doi: 10.1038/nchembio.1555

[2] Cupellini et al., Biochim. Biophys. Acta - Bioenerg. 1861, 148049 (2020).

doi: 10.1016/j.bbabi.2019.07.004

[3] Cignoni et al., J. Chem. Theory Comput. 19, 965–977 (2023). doi: 10.1021/acs.jctc.2c01044

[4] Akhtar et al., J. Phy. Chem. B 123, 6765–6775 (2019). doi:10.1021/acs.jpcc.9b05421



## Can we automate in silico photoreaction discovery?

29. Feb

16:45

Elisa Pieri

*UNC Chapel Hill*

In the field of photochemistry, the role of theoretical chemistry in designing new photoactive molecules is increasingly significant, driven by enhanced computational capabilities and the data science revolution. Consequently, grasping the mechanisms governing photochemistry is critical for effective theoretical molecular design. While nonadiabatic molecular dynamics is the technique of election for predicting photochemical outcomes, its computational demands can be substantial, often necessitating prior knowledge of the photochemistry under investigation. Addressing this challenge, we present and discuss the Nonadiabatic Nanoreactor, a novel tool that autonomously reveals a molecule's photoproducts without relying on prior reaction information. Our method extensively samples the intersection space between two electronic states via seam-constrained metadynamics, pinpointing key conical intersections, which are then linked to accessible photoproducts. We demonstrate the tool's efficacy on benzene and cyclopentenones, identifying both common and rare photoproducts. Consequently, the tool serves as a valuable diagnostic and supplementary resource to nonadiabatic dynamics. Furthermore, it paves the way for high-throughput screening of molecules and substituents, offering insights into novel photosynthetic pathways and the design of light-driven molecular systems.

# Posters

Poster Number	Name
P1	Antoine Aerts
P2	Ebru Akkus
P3	Amanda Arcidiacono
P4	Kasra Asnaashari
P5	Brigitta Bachmair
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P10	Hyeonsik Choi and Jiho Son
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P36	Chithra Mohan Jayakumari
P37	Mátyás Pápai
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P39	Salvatore Romano



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P43	Christian Schmidt
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P56	Richard Jacobi
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P58	Michael Sahre
P59	Dóra Vörös



## Computation of adsorption and desorption rate coefficients to/from amorphous ice

P1

Antoine Aerts

*Université libre de Bruxelles*

An accurate description of the desorption of small molecules from amorphous surfaces is desirable. For instance, the interaction of O<sub>2</sub> with amorphous ice is of particular interest to astrochemistry.[1] Indeed, desorption processes from the grain surfaces to the gas phase included in astrochemical models are associated with large uncertainties. More accurate modeling, assisted by computational chemistry methods, can contribute toward a better understanding of the origin of O<sub>2</sub> in the interstellar medium. A possibility is that a significant part originates from exchanges between the gas phase and the icy mantles of dust grains in molecular clouds. A slab of amorphous ice is generated from molecular dynamics simulations following a procedure developed in-house.[2] We have developed an end-to-end methodology based on ab initio simulations to contribute to the computation of adsorption and desorption rate coefficients of various atomic species to/from amorphous ice.

[1] Maggilo, R., et al., (2019). *Astrophys. J.*, 882(2), 131.

[2] Gibbons, A. (2019). Abundance and icy grain surface chemistry of O<sub>2</sub> in comet 67P/Churyumov-Gerasimenko: through ROSINA/DFMS measurements and molecular and kinetic modelling. (Doctoral dissertation, Université libre de Bruxelles, Brussels, Belgium). Retrieved from: <https://dipot.ulb.ac.be/dspace/bitstream/2013/292895/3/thesis.pdf>



## Elucidating the exciton transfer mechanism in LHCII through ML P2

Ebru Akkus

*Karlsruhe Institute of Technology*

A deep understanding of the exciton transfer mechanism in the major antenna trimer Light Harvesting Complex II (LHCII) is necessary to comprehend the complex mechanism of photosynthesis in plants. For this, we will simulate LHCII classically and perform DFTB+ calculations to get crucial informations on the exciton transfer via the system's Hamiltonian which includes excitation energies (site energies) and interactions between chlorophylls (couplings) through the extensive trajectories. To obtain the exciton transfer dynamics, machine learning (ML) techniques will be utilized to speed up the most costly part of the study.





## The photochemical mechanism of the activation of Orange Carotenoid Protein

P3

Amanda Arcidiacono

*University of Pisa*

Orange Carotenoid Protein (OCP) [1] is a photo-responsive protein found in cyanobacteria, responsible for their photoprotection. OCP activates in response to light absorption, going from the dark-adapted form (OCPO) to the light-adapted one (OCPR). Once in the active conformation, OCP is able to bind the phycobilisome (PBS), the light-harvesting apparatus of cyanobacteria, and quench the excess of energy in a process known as non-photochemical quenching (NPQ). The series of conformational changes of OCP in its activation cycle is triggered by the light-absorption and consequent excited state evolution of the chromophore bound to OCP, a ketocarotenoid named canthaxanthin (CAN). The photochemistry following the initial excitation of the carotenoid is still unclear, and there is debate on how light absorption can trigger the conformational changes of OCP. In particular, there is no clear evidence of the molecular mechanism constituting the very first step of this process [2]. In this work, QM/MM nonadiabatic dynamics were employed to simulate the excited state decay of CAN bound to OCP [3]. We found that the  $S_1 \rightarrow S_0$  conversion is characterized by multiple timescales, related to the ground-state conformational heterogeneity of the ketocarotenoid, particularly regarding the puckering conformation of the 1 ring [4]. Our simulations also revealed a hula-twist isomerization observed in a small portion of the trajectories, which could be the atomistic mechanism of the initial trigger to the photoactivation of OCP [5].

- [1] C. Kerfeld, et al., *Structure*, 11, 55–65 (2003).
- [2] P. Konold, et al., *J. Am. Chem. Soc.*, 141, 520–530 (2018).
- [3] G. Granucci, et al., *J. Chem. Phys.*, 114, 10608–10615 (2001).
- [4] M. Bondanza, et al., *J. Am. Chem. Soc.*, 142, 21829 (2020).
- [5] A. Arcidiacono, et al., *Chem. Sci.*, 14, 11158–11169 (2023).



## Reaction rates with MASH: the quest for a nonadiabatic transition state theory

P4

Kasra Asnaashari

*ETH Zurich*

We demonstrate the effectiveness of a novel nonadiabatic trajectory method, the mapping approach to surface hopping (MASH), in describing reaction rates model systems with a range of diabatic coupling. Remarkably, MASH accurately reproduces the results of Marcus theory in the golden-rule limit, without the need for a decoherence correction, for which fewest-switches surface hopping is known to fail.

Additionally, as MASH dynamics are inherently deterministic, we investigate the prospect of a high-temperature nonadiabatic transition state theory (TST) based on MASH and a low-temperature nonadiabatic TST through a ring-polymer extension of MASH.



# **Illuminating Rare Pathways in Electronically Excited States: The Use of Nonadiabatic Forward Flux Sampling for Ammonia Photodissociation**

P5

Brigitta Bachmair,<sup>ab\*</sup> Madlen Maria Reiner,<sup>ac</sup> Christoph Dellago,<sup>ad</sup> and Leticia González<sup>ae</sup>

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We present the application of our recently developed nonadiabatic forward flux sampling (NAFFS) algorithm, which is an enhanced sampling method that allows to efficiently obtain reactive surface hopping trajectories which include rare events such as high energy barriers in coupled electronic excited states.[1]

We discuss the use of the NAFFS methodology to investigate the rare  $\text{NH}_3 \rightarrow \text{NH} + \text{H}_2$  photodissociation channel of the ammonia molecule, using a neural network representation of its lowest three excited-state potential energy surfaces[2,3]. In this context, we further accentuate aspects concerning the application of NAFFS in practice.

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# Optimisation of Enzymatic Reactivity via Graph Neural Network Embedded Screening of Small Molecules

P6

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The chemical space of drug-like small molecules and fragments is gargantuan. Searching this space is one of the fundamental problems of drug discovery efforts. We develop a computational screening methodology, combining the insight of QM/MM enhanced sampling simulations, experimental information and a graph neural network (GNN) architecture into an iterative pipeline to select promising candidates in a cost-effective manner.

Our prototype target is the oncogenic G12D Ras GTPase, the goal is to find small molecule cofactors to lower the barrier of GTP hydrolysis, impaired by the G12D mutation. The representation of ligands in their bound poses by the GNN enables the extension of few thousands of reactivity calculations to hundreds of thousands of docked compounds, while iteratively enriching the pool of ligands with hits.



## Statistical identification of important factors for the singlet-triplet gap in blue TADF emitters

P7

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In a world of technology, futuristic-looking, transparent and foldable displays are of great interest. Organic light-emitting diodes (OLEDs) make this possible but while there are efficient and cost effective red and green ones, the blue light emitters still develop at slower pace. A major direction of research aims at enhancing the lighting capacity of blue OLEDs. One of the strategies to improve luminescence performance is to develop organic dyes, which have the potential for thermally activated delayed fluorescence (TADF) [1]. To observe this effect, compounds with energy difference between the lowest triplet (T1) and the lowest singlet (S1) excited states smaller than ca. 0.2 eV are sought.

The molecules of such compounds can be constructed by combining electron-donor and electron-acceptor fragments [2], which could be separated by a spacer [3]. However, the correlation between the optical properties of the composite emitter and those of the fragments it is built of is often not straightforward. The aim of the current work is to derive QSPR models to help understand the importance of different factors for the singlet-triplet gap of the combined compounds and to search for a relation to characteristics of their building blocks. The structures and optical properties of a series of new organic TADF blue emitters are computed with (TD)DFT and the electron densities are post-processed in order to obtain descriptors for multiple linear regression (MLR) and principal component analysis (PCA) models.

The MLR highlights the importance of the electron-donor as well as the degree of charge transfer for the singlet-triplet gap. The electron-hole overlap, the amount of electron on the donor and the charge transfer from the acceptor to the spacer in particular are leading factors for the S1-T1 energy difference.

The PCA underlines the complexity of the excited states energetics. All descriptors have similar weights in the process, thus delineating it as highly cooperative. The principal component regression model has better predictive quality than the MLR one.

The QSPR modelling provides valuable guidelines, which might be used to focus the future design of blue organic TADF emitters complying with the donor-spacer-acceptor molecular framework.

The research is funded by the Bulgarian National Scientific Fund, Project № KP-06-N49/3 from 26. 11. 2020.

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# Enhanced Artificial Intelligence Molecular Mechanism Discovery of Reaction Paths in Complex Systems

P8

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Self-organization of molecules into ordered structures is crucial for both living and non-living matter. AIMMD is an autonomous transition path sampling algorithm that uses deep learning to discover the underlying reaction mechanism of such molecular self-organizing phenomena. The algorithm uses the outcome of unbiased dynamical trajectories to construct, validate and update the quantitative mechanistic model. With the learned mechanistic model, the sampling of mechanistic trajectories or rare events can be enhanced, completing the cycle. Here, we enhance the method by including all potentially possible configurations in the reweighted path ensemble. We illustrate the novel methodology on simple potentials and a more complex molecular system.



# The design of transition metal based molecular spin state switches by ligand substitution

P9

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*Wigner RCP*

Octahedral iron metal complexes have long been recognised as candidates for molecular data storage devices and switches [1]. However, reversible switching between the singlet and the quintet state of the Fe(II) complexes could only be achieved at low temperature [2,3].

It was shown that deeper understanding on the stability of the quintet state can be achieved by theoretical methods [4]. In our earlier study, we examined how the potential energy surfaces of  $[\text{Fe}(\text{terpy})_2]^{2+}$  (Figure 1, terpy = 2,2':6',2''-terpyridine) can be modified upon substitution with electron donating (ED) or withdrawing (EW) groups on the central pyridine ring in the 4' position. Our conclusions were also supported experimentally with transition optical absorption spectroscopy (TOAS). Recently, we expanded this project by applying a larger, thoroughly chosen set of substituents and various theoretical and experimental approaches.

We found that the substitution has minor effect on the geometry of the structures, while the gradual change in the electron density of the iron and the axial N atoms can be observed by different methods. Moreover, the quintet potential energy surfaces turned out to be sensitive to the electronic effect of EW and ED groups, while the singlet and triplet energies do not significantly change upon substitution. It is known that the singlet-quintet energy gap is highly related to the lifetime of the quintet state, thus new molecules were synthesized, and almost one magnitude of quintet lifetime lengthening could be achieved, based on TOAS results. In highly electron donated and withdrawn systems, the previously applied theoretical approaches based on the energy barrier between the quintet and the singlet state turned out to be highly inaccurate in the estimation of the quintet lifetime. However, calculations based on single configuration coordinate model [5] with the inclusion of tunneling processes can result in accurate results, possibly due to the high similarity of the investigated structures.

As the adequately chosen theoretical methods show high similarity to the experimental results, it can be concluded that quantum chemistry based calculations can definitely lead to the rational design of functional molecules.

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## Multiscale Computer Simulation of Charge Transport in Organic Light-Emitting Diodes

P10

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Organic Light-Emitting Diodes (OLEDs) have garnered significant attention over the last few decades due to their flexibility, transparency and diverse applications. While OLEDs are already widely utilized in the display industry, the search for novel materials remains crucial for enhancing charge mobility, efficiency and device lifetime. Despite the necessity of finding new candidate molecules, the current screening process is time-consuming and resource-intensive, involving repetitive synthesis and performance validation. In this study, we present a computational approach that not only significantly reduces real-world efforts but also provides a microscopic understanding of the charge transport phenomenon. Our multiscale simulation method commences from a single molecular structure. Through a molecular dynamics simulation that mimics physical vapor deposition schemes, we generated the amorphous state of OLED candidate material. Deposited morphology reveals distinctive structures and properties compared to traditional glass-making methods involving fast quenching. To assess charge transport, we computed charge hopping rates between molecules using the Marcus theory. Needed parameters such as reorganization energy, transfer integral and site energy differences were computed via DFT calculations. Charge carrier mobility values were then obtained through kinetic Monte Carlo simulations. Applying this computational approach to several known OLED compounds, we achieved charge mobility values on a scale comparable to experimental measurements.

Joint work with Jaeyoung Gil, Yoonki Kim, Jay-Hak Lee and YounJoon Jung (Department of Chemistry, Seoul National University).





# Simulating Nonadiabatic Dynamics Using the Meyer-Miller-Stock-Thoss Hamiltonian: A Comparison of Algorithms

P11

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Mixed quantum-classical models are commonly used to simulate nonadiabatic dynamics. Often, these approaches use a mapping to describe the electronic dynamics by time-propagating a set of classical variables, where averaging over many trajectories allows the approximation of thermal equilibrium properties through correlation functions. Many integration algorithms exist to propagate the dynamics, but a thorough performance comparison appears to be lacking. Here, we compare three time-propagation algorithms for the Meyer-Miller-Stock-Thoss Hamiltonian: [1] the MInt, Split-Liouvillian (SL), and Degenerate Eigenvalue (DE) algorithms. [2–4] We determine that the MInt is the most accurate algorithm based on the symplecticity, energy conservation, computational cost, and accuracy of correlation functions. Despite not being symplectic, the SL algorithm obtains similar results for a lower computational cost and in some cases, better energy conservation. Approximations within the DE algorithm results in inaccurate dynamics, poor energy conservation and a higher computational expense for systems with weak electronic coupling. These results should guide future simulations utilising mapping variable approaches.

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# Normalizing Flows for Statistical Mechanics: Transition Path Sampling and Equilibrium Configurations of Liquid Systems

P12

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In the framework of deep learning, generative models are getting increasing attention due to their ability of generating independent samples starting from a set of training examples. The use of these tools in statistical mechanics is promising considering the difficulty of generating decorrelated samples from physical distributions. This idea has been followed in recent publications to produce physical configurations and to compute free energy differences using a particular network architecture called normalizing flows with very interesting results for biophysical and many-body systems. The standard approach of these models consists in training a network to transform samples from an easy-to-sample distribution (e.g. a Gaussian or a uniform distribution) to samples obtained from the correct physical probability. In particular, normalizing flows are built in such a way so that it is possible to reweight the network-generated density to obtain samples that are exactly distributed according to the desired distribution. Yet, the training process of such networks can be painful, in particular for disordered systems, where source and target distributions are very different from each other. We show two novel approaches in which normalizing flows can be fruitfully used in statistical mechanics: transition paths and liquid systems. In the first case we show how to condition the normalizing flow to generate shooting points on the top of an energy barrier. This, in addition of improving the acceptance ratio of the transition path algorithm, removes correlations between subsequently sampled paths which are challenging when different transition channels are present in the system. In the second case we explore different choices for the source distribution which are closer, from a physical point of view, to the target one. This can lead on the one hand to an efficient exploration of the space of thermodynamics variables for a given model and, on the other, to the possibility of transforming between configurations obtained using different representations of the same physical system. The approach turns out to be particularly efficient to decorrelate configurations of very expensive interaction models such as the ones used in ab-initio MD.



# Nonadiabatic dynamics simulations in periodic condensed phase systems at the time-dependent density functional level of theory with CP2K

P13

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Almost all nonadiabatic (NA) processes encountered in nature happen in the presence of the condensed phase. City smog is a direct consequence of various nitrogen oxides and hydroxides generated by solar light photodecomposition of various manmade pollutants, such as nitrophenols, in the atmosphere with the presence of water droplets. In technological applications like CO<sub>2</sub> photocatalytic reduction, the attachment of a photocatalyst to a solid surface can enhance its absorbance, increase its photostability, and use the surface as a direct sacrificial electrode, to name a few benefits.

In silico accurate modelling of NA processes of photoexcited systems with the presence of condensed phase, however, represents a significant theoretical and computational challenge. Not only does the system increase its size due to additional environment molecules that have to be taken into account, but the number of electronic states and the number of potential nonradiative deactivation (NRD) pathways, all increase. We simulate two such systems including a photoexcited system with a condensed phase environment by means of NA molecular dynamics (MD) simulations with electronic structure of all the atoms at the same level of time-dependent density functional theory (TDDFT), incorporating periodic boundary conditions for a sophisticated description of the condensed phase. All simulations were performed by our in-house modified version of the CP2K code.[1]

NRD mechanisms of ortho- and para-nitrophenol initiated from the brightest  $\pi$  to  $\pi^*$  singlet excited electronic state have been investigated with trajectory surface hopping NA MD simulations on a manifold including several (up to twelve in total) singlet and triplet excited electronic states, mutually coupled by the spin-orbit coupling elements computed at the linear response TDDFT level of theory. By careful analysis between such NRD pathways obtained on isolated and in water-solvated nitrophenols, the cage effect exhibited by the surrounding water molecules on electronically excited nitrophenol reduces the number of inter-system crossings and facilitates its NRD deactivation from the first singlet excited electronic states. When the water solvent was modelled at a force field level as usually performed when applying the computationally cheaper molecular mechanics/quantum mechanics (QM/MM) approach, the NRD mechanisms resemble more those of the isolated system than when the whole solvent was treated at the same level of theory as the chromophore.[2]

An ultrafast excitation transfer from a localized Re-photoreduction catalyst to a TiO<sub>2</sub> anatase (101) surface was simulated with Ehrenfest NA MD utilizing the real-time TDDFT propagation of the initially  $\Delta$ SCF generated excited electronic state density. In a subfemtosecond time scale, the metal-to-ligand charge transfer excitation localized on the Re-photoreduction catalyst transfers through the ligand frame and its phosphate groups, anchoring it to the anatase (101) surface, to the anatase (101) surface and suddenly polarizes all its layers.[3]

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# Stabilized coupled trajectory mixed quantum–classical algorithm with improved energy conservation: CTMQC-EDI

P14

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Coupled trajectory mixed quantum–classical (CTMQC) dynamics is a rigorous approach to trajectory-based non-adiabatic dynamics, which has recently seen an improvement to energy conservation via the introduction of the CTMQC-E algorithm. Despite this, the method’s two key quantities distinguishing it from Ehrenfest dynamics, the modified Born–Oppenheimer momentum and the quantum momentum, require regularization procedures in certain circumstances. Such procedures in the latter can cause instabilities, leading to undesirable effects, such as energy drift and spurious population transfer, which is expected to become increasingly prevalent when the system gets larger as such events would happen more frequently. We propose a further modification to CTMQC-E, which includes a redefinition of the quantum momentum,

CTMQC-EDI (double intercept), such that it has no formal divergences. We then show for Tully models I–III and the double arch model that the algorithm has greatly improved total energy conservation and negligible spurious population transfer at all times, in particular in regions of strong non-adiabatic coupling. CTMQC-EDI, therefore, shows promise as a numerically robust non-adiabatic dynamics technique that accounts for decoherence from first principles and that is scalable to large molecular systems and materials.



## Tuning the optical properties of TADF blue light emitters via TD-DFT

P15

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Nowadays, organic light-emitting diodes (OLEDs) gradually overtake their predecessors – the phosphorescent LEDs, due to being more cost efficient and eco-friendly. Recently, a lot of interest has been directed towards devices that operate on the principle of thermally activated delayed fluorescence (TADF). At the core of this process lies the upconversion from triplet to singlet excited state, which aims to enhance the performance of an OLED. Another line of development is the finding of more stable and efficient blue light emitting diodes.

The present work summarizes the results of (TD)DFT calculations in toluene solution performed on organic compounds with potential for blue light emission enhanced by TADF. The molecules belong to two groups – one containing triphenylamine and the other one indolocarbazole as electron-donors combined either with a cyano, or with an oxadiazole acceptor. Their geometries in the ground and the relevant excited states are optimized with PBE0/6-31G\*, while absorption and emission spectra are obtained with TD-PBE0/6-31+G\*. The possibility of TADF in different molecules and their capability of emitting blue light are evaluated. Each group features one very promising representative with clear blue emission and singlet-triplet splitting lower than 0.5 eV. These most promising candidates are further analyzed by calculating kinetic parameters for the process reverse intersystem crossing (rISC) to estimate characteristic rates for TADF.



## Learning Dynamics from Trajectories

P16

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The computer simulation of many molecular processes is complicated by long time scales caused by rare transitions between long-lived states. These processes include fundamental phenomena in soft matter statistical physics such as nucleation, chemical reactions and biomolecular reorganization. Enhanced sampling techniques have been developed to bias the simulation towards transition regions with the drawback of distorting the dynamics of the system. In contrast, for obtaining true dynamic reactive trajectories, path sampling schemes were proposed that restrict the simulation time to the transition region. However, extracting information on the thermodynamics and kinetics of complex processes based on trajectories from path sampling schemes can be non-trivial. Here, we present approaches such as shooting point exchanges, committor learning and free energy prediction from a set of trajectories.



## Nonadiabatic dynamics of molecular upconversion

P17

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Photon upconversion (shifting light from red to blue) via triplet-triplet annihilation in molecular materials is a technology which could massively increase photovoltaic (solar cell) efficiency. Current examples do not have sufficient quantum efficiency to be useful. Rational design of new molecular upconverters is limited by poor understanding of the upconversion process.

Here we have focused on the 2021 report by Izawa and Hiramoto of an efficient solid-state upconverting interface made out of a bilayer of the Y6 non fullerene acceptor and rubrene. We model the non-adiabatic photoexcitation dynamics of this system with a combination of real-time path integral and hierarchal equations of motion approaches.

Izawa, S., Hiramoto, M. (2021). Efficient solid-state photon upconversion enabled by triplet formation at an organic semiconductor interface. *Nature Photonics*, 15(12), 895–900.  
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## Efficient Methods for Multi-Scale Simulation of Charge and Exciton Transfer Properties in Organic Semi-Conductors (OSCs)

P18

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Organic semiconductors, known for their potential in optoelectronic applications, demand advanced computational approaches for atomistic-level understanding of their properties. Our study addresses this by developing a multi-scale simulation method, integrating the Fewest Switches Surface Hopping (FSSH) with classical Molecular Dynamics (MD) simulations. This novel approach utilizes a Fragment Orbital (FO) technique and Density Functional Tight-Binding (DFTB) methods to efficiently model charge and exciton transfer phenomena in non-covalently bonded organic semiconductor structures. Emphasizing on a range of organic semiconductor crystals (OSCs), our method demonstrates strong agreement with experimental data in assessing charge mobility and exciton diffusion constants. Additionally, we incorporate neural networks for predicting crucial Hamiltonian elements and Non-Adiabatic Coupling Elements (NACEs), enhancing the simulation's efficiency. This comprehensive approach not only elucidates the charge transfer mechanisms in complex materials like Metal-Organic Frameworks (MOFs) but also pinpoints 'Killer Modes'—the specific motions predominantly contributing to dynamic disorder, paving the way for tailored enhancements in organic electronic materials.





## Accelerating Rare-Earth Metal Separation Through Machine Learning

P19

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Rare-earth metals are important for use in clean energy technologies. However, since their properties are comparable, separation from one another is challenging. The extraction process often consists of attaching ligands to the lanthanide metal and is largely dependent on trial and error. A powerful method to speed up the prediction of suitable ligands is therefore needed. Even though quantum chemistry methods can be used, achieving a good prediction with high accuracy is both time-consuming and computationally expensive. In this work, we have built an efficient machine learning (ML) model that can both quickly and accurately predict properties of lanthanide-ligand complexes. We achieved a good correlation between the ground truth and predicted ML values, even with a small dataset. In this way, our model has the potential to accelerate the discovery of suitable ligands for rare-earth metal separation.



## Exciton transfer simulations in light harvesting complexes LH2 and FMO

P20

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In the course of photosynthetic evolution, nature has developed highly efficient photosynthetic units. Light-harvesting (LH) complexes collect and transfer sunlight energy in the form of excitons with an extremely high quantum efficiency. The motion of the exciton was simulated using the non-adiabatic molecular dynamics (NAMD) method of surface hopping. The rate-limiting step, the calculation of the transfer Hamiltonian elements (energies and couplings) of the photoactive pigments, is accelerated by machine learning. In this way, a statistically meaningful number of trajectories could be sampled for several picoseconds.



## Highly excited bound states of NS molecule

P21

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Electron scattering by the  $NS^+$  molecular cation leading to the formation of highly excited Rydberg states is discussed.

The interstellar medium provides a vantage point for the chemistry that takes place there and the analysis is done with the R-matrix method.



## Computational design of efficient organic TADF blue emitters

P22

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Organic light emitting diodes (OLEDs) are among the optoelectronic devices for which research is employed intensively to enhance their performance [1]. Blue OLEDs suffer from relatively short lifetimes and comparatively low lighting efficiency. One of the approaches to improve their characteristics is the development of luminophores with potential for thermally activated delayed fluorescence (TADF). In the current study, (TD)DFT [2] computations are applied to design a series of new organic donor-spacer-acceptor compounds, which may emit blue light and have feasible TADF. Energy and oscillator strength of the fluorescence and energy separation of the singlet and triplet excited states are used to assess the capacity for blue TADF-assisted emission. The rate constants of the various excited state deactivation processes are evaluated. The relative importance of several molecular factors for accomplishing the desired luminescence characteristics is tracked. Meta-binding to the spacer is found essential for a high-energy triplet excited state. To ensure non-zero oscillator strength of the fluorescence transition, the donor and the acceptor should close an angle lower than 75 degrees in S1 and their frontier orbitals should overlap partially on the spacer. The pi-conjugation length of the chromophore should not exceed three rings for blue fluorescence to take place. Following the derived molecular guidelines, several compounds are put forward as promising blue emitters for organic light-emitting diodes. Characteristic times for delayed fluorescence in the microsecond to millisecond time range are predicted for them.

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# Nanoscale Simulation of Thermoelectric Transport in Organic Semiconductors with Atomistic Non-Adiabatic Dynamics

P23

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The application of a temperature gradient across thermoelectric materials results in a voltage. Although the Seebeck effect has long been acknowledged in organic semiconductors, its understanding in these materials is relatively limited. The strong electron-phonon coupling in these systems results in partially delocalised charge carriers, whose non-adiabatic transitions to excited states cause them to undergo dynamical localisation and delocalisation. This places the charge transport regime of these materials in-between traditional theories applicable to common wide and narrow-band semiconductors. In past work, we have used the Fragment Orbital-Based Surface Hopping method (FOB-SH) to simulate charge transport in organic crystals, without a priori assumptions regarding the transport regime of the charge carriers. We now introduce a novel methodology that combines FOB-SH with explicit temperature gradients to simulate thermoelectric transport in crystalline rubrene. Our low-cost approach enables us to simulate thermoelectric transport in atomistic detail, on a (picosecond) timescale long enough to fully capture the movement of charge across the nano-scale. We consequently observe a net migration of charge from the system's hot region to its cold region, in line with experiment and indicative of the Seebeck effect. It is shown that the effect of temperature on the local electronic structure along the temperature gradient has a crucial impact on thermoelectric transport in these systems, with the charge carrier becoming more delocalised towards the cold region. In addition to providing an unprecedented insight into how thermoelectric transport in organic semiconductors involves excited-state dynamics, this opens new routes for the design of organic semiconductors with improved thermoelectric properties.



## Batch mode active learning a neural-network force field with nested sampling: A case study on silicon

P24

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In a recent published study, Unglert et al. [1] showed that the silicon phase diagram can be predicted accurately by combining the nested sampling algorithm with the MLFF NeuralIL [2] trained on an already existing hand-crafted silicon database [3]. However, the design of the training database was performed by using advanced domain knowledge and intuition which makes this approach impractical for general systems.

In this work it will be illustrated that it is possible to construct the training database solely by applying an active learning strategy. On top of that, different iterations of the active-learned MLFF will be analyzed and learned lessons will be discussed.

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# Transition Path Sampling For Run-and-Tumble Particles

P25

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Active particles or microswimmers often have to solve *target search* problems, possibly including crossing energy barriers.

When the energy barrier is high with respect to thermal fluctuations, a successful target search becomes a *rare event*.

Brute force simulations solving the equations of motion are inefficient.

Transition Path Sampling (TPS), initially developed for rare transitions of passive systems, is an advanced sampling algorithm with the advantage of being simple and providing a rigorous sampling of the reactive path ensemble. TPS has been recently generalized to active Brownian particles (ABPs). Here, we further extend it to Run-and-Tumble particles (RTPs).



## Probing photoreactions with multipulse spectroscopy and the prospective role of machine learning

P26

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Light controls multiple developmental and metabolic processes in plants, algae, and some non-photosynthetic organisms. The conversion of the absorbed photon energy into molecular rearrangements initiates signal transduction by photosensory proteins. The light triggers different types of excited-state chemistry (e.g., photoisomerization or proton transfer) inside proteins and initiates a cascade of downstream reactions that affect the biological processes of the protein surroundings.

Phytochromes, as photoactive protein receptors, present optimal model samples. They are extremely viable samples for the type of studies proposed, as they are easily expressed and amenable to modification. They are photostable, and their reversible photoswitching properties are easy to control between two states by absorption of red (Pr) or far-red (Pfr) light with intermediate meta-stable states in between. The isomerization of the chromophore between its Pr and Pfr forms is accompanied by structural changes in the phytochrome protein, which affect its biological functions and activity. A variety of such proteins and the diversity of their structures present a need for the advancement of methods to study the mechanisms that underlie their complex behavior, together with technologies that make use of these findings. Time-resolved spectroscopic techniques have been successfully applied to elucidate the chromophore-protein interactions, photoinduced signal transduction, and other fast changes in the field of photosensors. One particularly promising method is multipulse spectroscopy, which extends the capabilities of traditional transient absorption spectroscopy. While pump-probe setups monitor changes in the absorption signal after the excitation of molecules, multipulse spectroscopy allows controlling excited state population and drives it into higher excited states, back to the ground state, or to form new photoproducts. We are currently applying this method to study the photoreaction of phytochromes monitoring the branching ratios among relaxation pathways.

Here, we will present a series of experiments on different mutants of bacteriophytochrome from *Deinococcus radiodurans*. Site-selective mutagenesis in photosensory module constructs has allowed the alteration of the spectroscopic properties of the ground state population. We have applied multipulse spectroscopy to study protonated and deprotonated populations in the excited states. The results have shown that there is potential to modulate the reaction yield of photoproducts, thus changing the branching ratios of relaxation processes by laser manipulation.

The next goal lies in the establishment of the working mechanisms to manipulate protein reaction pathways by applying machine learning. We will work on developing machine-learning models for the acquired data to distinguish meta-stable states within many samples at different experimental conditions. The analysis will be used to determine the hidden meta-states and their photophysical properties, and it will further be used to predict experimental conditions for the next experiments.





## Unsupervised identification of local atomic environment from atomistic potential descriptors

P27

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Machine learning potentials greatly accelerate molecular dynamics simulations, allowing access to longer time spans and larger systems. However, post-analysis poses a challenge for specific types of simulations, such as investigating defect mobility or phase growth. Due to the lengthy simulation times, visual analysis is impractical. Instead, it is common to develop tailored analyses accompanied by additional calculations of order parameters. However, designing order parameters can be complex and computationally intensive. A simpler alternative is to utilize atomistic potential descriptors, already computed for energy and force predictions.

Using the PaCMAP dimensional reduction algorithm, I will illustrate how atomistic potential descriptors can provide insights into the local atomic environment. We can track monovacancy diffusion in phosphorene and unequivocally determine the hopping mechanism. Additionally, PaCMAP demonstrates superior clustering compared to the commonly used PCA in distinguishing silicon structures and phases. All of these capabilities can be achieved in an unsupervised manner, without requiring prior knowledge and with minimal hyperparameter tuning.



# Dynamical phase transition of spin-lattice models using double-bias trajectory ensemble methodology

P28

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In this poster, we investigate dynamical phase transitions in spin-lattice models, specifically focusing on the 1D Ising model and the kinetically constrained model (KCM), employing the trajectory ensemble method. A double bias ensemble is introduced, incorporating conjugate fields denoted as  $s$  and  $g$ , corresponding to dynamical activity and trajectory energy, respectively. From the analytical calculation and the multistate Bennett acceptance ratio (MBAR), we obtain the dynamical free energy and explore the behaviors of the dynamical phase transition in the  $(s, g, T)$  parameter space. Notably, an anti-ferromagnetic phase appeared which is due to energy-activity decoupling through the introduction of an additional  $g$ -field in the 1D Ising model. This decoupling exhibits anomalous phase behaviors, including the freezing-by-heating and permanent liquid phase phenomena. Conversely in KCM, we observe the equality of the low-energy by  $g$  and the inactive phase by  $s$ . Additionally, by analyzing trajectory profiles, we interpret the strong energy-activity correlation that appears in both models and explain the equivalence of low-energy/inactive phases.



# Comprehensive Molecular Representation from Equivariant Transformer

P29

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The tradeoff between precision and performance in molecular simulations can nowadays be addressed by machine-learned force fields (MLFF), which combine *ab initio* accuracy with force field numerical efficiency. Different from conventional force fields however, incorporating relevant electronic degrees of freedom into MLFFs becomes important. Here, we implement an equivariant transformer that embeds molecular net charge and spin state without additional neural network parameters. The model trained on a singlet/triplet non-correlated CH<sub>2</sub> dataset can identify different spin states and shows state-of-the-art extrapolation capability. Therein, self-attention sensibly captures non-local effects, which, as we show, can be finely tuned over the network hyper-parameters. We indeed found that Softmax activation function utilised in the self-attention mechanism of graph networks outperformed ReLU-like functions in prediction accuracy. Additionally, increasing the attention temperature from  $\tau = \sqrt{d}$  to  $\sqrt{2d}$  further improved the extrapolation capability, indicating a weighty role of nonlocality. We also purposed a weight initialisation method that sensibly accelerated the training process.



## Vibrational strong coupling in liquid water from cavity molecular dynamics

P30

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We assess the cavity molecular dynamics method for the calculation of vibrational polariton spectra using liquid water as a specific example. We begin by disputing a recent suggestion that nuclear quantum effects may lead to a broadening of polariton bands, finding instead that they merely result in anharmonic red shifts in the polariton frequencies. We go on to show that our simulated cavity spectra can be reproduced to graphical accuracy with a harmonic model that uses just the cavity-free spectrum and the geometry of the cavity as input. We end by showing that this harmonic model can be combined with the experimental cavity-free spectrum to give results in good agreement with optical cavity measurements. Since the input to our harmonic model is equivalent to the input to the transfer matrix method of applied optics, we conclude that cavity molecular dynamics cannot provide any more insight into the effect of vibrational strong coupling on the absorption spectrum than this transfer matrix method, which is already widely used by experimentalists to corroborate their cavity results.

# Nonadiabatic processes in condensed phase systems with $\Delta$ SCF

P31

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Nonadiabatic molecular dynamics (NA-MD) enables direct insight into processes taking place after photoexcitation by elucidating mechanistic details at the atomic scale, explaining photoproducts' branching ratios, and mapping all the relevant excited electronic states along the time-evolving NA-MD trajectories. Computing the appropriate observables for the latter, spectroscopic data can be directly obtained, for example, for the time-resolved transient absorption spectra by determining the absorbance of all electronic states along the NA-MD trajectories. Accurate calculation of excited electronic state properties in the condensed phase systems represents the main bottleneck for efficient application of NA-MD methods for investigation of nonadiabatic processes in the condensed phase systems. A variational delta self-consistent field ( $\Delta$ SCF) density functional theory (DFT) based method [1,2] represents a potential approach to address the aforementioned constraints in addition to perturbative time-dependent density functional theory (TD-DFT). We applied a restricted-open Kohn-Sham (KS) formulation of  $\Delta$ SCF with constrained occupation numbers for the direct construction of singlet and triplet excited electronic states.[3] A direct energy minimization method based on the molecular orbital (MO) rotation technique aids in convergence of excited electronic states[4] while a projection procedure removes the contribution of the ground electronic state from the excited state KS MOs enabling the calculation of excited electronic state properties (transition dipole moments, NA couplings) as well as the spin-orbit coupling terms between singlet and triplet electronic states at the  $\Delta$ SCF level of theory.[3] By utilizing the combined Gaussian and plane waves approach with periodic boundary conditions the method is easily applicable to full atomistic DFT simulations of condensed phase and it can be combined with subsystem density embedding to further expand its capabilities.[5] We applied our methodology for the investigation of nonradiative deactivation mechanisms in a number of solvated systems, emphasizing the details of chromophore-environment interactions and their influence on photochemical processes in condensed phase systems.[1,6]

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## Improved excited-state ab initio dynamics simulations with the mapping approach to surface hopping

P32

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The mapping approach to surface hopping (MASH) is a recently derived independent trajectory approach that is ideally suited to performing practical yet accurate ab initio simulations of photoexcited processes in molecules. Through a series of benchmark simulations of paradigmatic molecular systems, I will demonstrate the superior accuracy of MASH over well-established methods such as fewest switches surface hopping (FSSH) and even ab initio multiple spawning (AIMS), a Gaussian wavepacket technique. Finally, I will show how MASH gives rise to new and improved momentum rescaling schemes for dynamics involving explicit light pulses and spin-orbit coupling, paving the way for more accurate and realistic simulations of molecular experiments in the future.



# BRINGING EQUIVARIANCE TO NEURAL NETWORKS FOR EXCITED STATES

P33

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Understanding photo-chemical processes in molecules can help with the development of new light-emitting or photovoltaic materials, it is also useful to investigate the mechanisms of radiation damage in materials and bio-molecules. Accurate simulations of the processes that happen when a photon hits a molecule are quite expensive and limited to very small molecules. Therefore approximate methods like trajectory surface hopping were developed to speed up the simulations at the cost of less accuracy. Surface hopping is a mixed quantum-classical method where the nuclei are propagated with classical mechanics and the electronic structure is treated quantum mechanically. To further reduce the cost of electronic structure computations, the SchNarc [1] approach was introduced in 2020. Here, the expensive quantum chemical treatment of the electronic structure was replaced by an invariant neural network. In this work the invariant neural network is replaced by an equivariant neural network to improve the prediction of equivariant properties.

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# A Fast Method for Polarizable QM/MM Excited-State Dynamics in Complex Systems

P34

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Observing a photoinduced mechanism in complex systems is still a challenging goal. To this aim, molecular dynamics has been coupled with hybrid quantum mechanics/molecular mechanics (QM/MM) models to produce simulations on the excited-state potential energy surface [1]. However, the computational cost associated with these methodologies, such as Time-Dependent Density Functional Theory (TD-DFT) or Complete Active Space Self-Consistent Field (CASSCF), remains prohibitively high. Therefore, the study of complex systems is impeded by the challenges of obtaining statistically significant results.

In this contribution, we present the development of a fast strategy to perform QM/MM excited-state simulations, which combines a SCF description of the excited state (SCF) with the AMOEBA forcefield [2,3,4]. The integration of SCF with a polarizable embedding environment is highly intriguing due to the inherent inclusion of state-specific environmental effect on the excited state [3]. Consequently, this methodology proves to be more accurate than conventional TD-DFT methods when describing excited states with a significant charge-transfer (CT) character. Additionally, we enhance this algorithm by incorporating an extrapolation technique for the excited-state density matrix. Extrapolation addresses two crucial challenges associated with these simulations: maintaining the dynamics on the excited state and reducing the high number of SCF iterations necessary for convergence. This straightforward yet effective approach was applied to the investigation of the photoinduced activation of the AppA Blue-Light Using Flavin (BLUF) photoreceptor. We propagated the dynamics on the CT state and we successfully observed the expected proton transfers, showing that the Proton-Coupled Electron Transfer (PCET)-based mechanism that characterizes other BLUF proteins [5,6] is valid also for AppA.

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## Computational Insights into the Photochromic Behaviour of Iminothioindoxyls

P35

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Ideal photochromic systems for biological and medicinal applications need to be responsive to visible light, show large separation of absorption bands and are functional in water. Recently, a new class of fully-visible-light-operated molecular photoswitches called iminothioindoxyls (ITIs) which meet these requirements was successfully designed. ITIs show an unprecedented band separation of over 100 nm, isomerize on ps time scale and thermally relax on ms time scale. In addition, they exhibit acidochromism, which makes them multi-responsive functional systems. By combining advanced spectroscopic techniques and computational methods, we elucidated the photoswitching behavior and acidochromism of ITIs. Using state-of-the-art computational tools, we also addressed the nature of excited states involved in the photoactinic step of the switching process and the dynamics of the photo-excited system from the Franck-Condon region to a conical intersection.

## Effect of Lewis acid complexation on the excited-state chemistry of chromophores

P36

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Lewis acids are frequently used as photocatalysts in C-C bond forming reactions.<sup>1</sup> The availability of chiral Lewis acids has aroused interest in this research field, given their ability to facilitate enantioselective catalysis in specific reactions.<sup>2,3</sup> This makes it necessary to understand how the Lewis acid can affect the photophysical and photochemical properties of a chromophore.

The coordination of a Lewis acid on a chromophore may substantially alter the excited-state behavior of the chromophore.<sup>4,5</sup> The binding of the Lewis acid can either result in the activation of the chromophore<sup>6</sup> or the activation of the Lewis acid.<sup>7</sup> It affects the energetics and the dynamics of the excited-states and also opens up reaction pathways which were inaccessible to the free chromophore.

The present work explores the photochemical and photophysical changes upon the coordination of BCl<sub>3</sub> on pyridine. Nonadiabatic dynamics simulations are performed using the Surface Hopping including ARbitrary Coupling (SHARC) approach.<sup>8</sup> The simulations predict the mode of action of the Lewis acid upon photoexcitation and provide insights into the relaxation pathways. The obtained results are compared to previously reported photochemical behavior of Lewis acid complexes.<sup>4,7</sup> The proposed mechanism motivates synthetic applications without the use of heavy transition metal complexes with carbonyl compounds. Further studies involve exploring the effect of a chiral Lewis acid in the enantioselective photocycloaddition reaction of a naphthylethanone derivative using multireference approach.

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## Simulation of Ultrafast Excited-State Dynamics in Functional Fe(II) Complexes

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Photofunctional Fe(II) complexes have a great potential in several applicational areas such as molecular data storage, solar energy conversion, and photocatalysis. In order to design and optimize the performance of advanced materials, it is vital to gain a profound mechanistic understanding of the ultrafast excited-state dynamics. Pump-probe femtosecond experiments have delivered invaluable insights, however, interpretations are often controversial and consistency is still lacking. Herein, we demonstrate for photofunctional Fe(II) complexes how dynamical excited-state simulations can be exploited to guide and complement ultrafast experiments. We develop a synergistic methodology taking advantage of the complementary power of quantum dynamics (QD) and trajectory surface hopping (TSH) [1,2]. We utilize a hybrid approach based on the combination of time-dependent density functional theory (TD-DFT) potential energy surfaces and multiconfigurational second-order perturbation theory (CASPT2) spin-orbit couplings; crucially, this enables access to the entire singlet-triplet-quintet dynamics. Using this methodology in conjunction with full-D TSH, we offer decision to the decade-long debate on Fe(II) polypyridines: we show that the quintet HS state is populated on a sub-ps timescale via a sequential mechanism involving the two  $^3\text{MC}$  components (with no direct  $^3\text{MLCT} \rightarrow ^5\text{MC}$  contribution), non-exponential dynamics, and coherent Fe-N breathing oscillations [3]. Furthermore, using full-D TSH, we fully resolve the  $^3\text{MLCT}$ - $^3\text{MC}$  branching mechanism in the first-discovered Fe-carbene photosensitizer  $[\text{Fe}(\text{bmip})_2]^{2+}$  (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)-pyridine) [4].

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# Excitonic Configuration Interaction Method: Energies and Transition Dipole Moments

P38

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Fragment-based electronic-structure methods are very common choice for the treatment of the large, multifragment molecular systems. More specifically, when it comes to the treatment of the excited states of multichromophoric systems, the most popular approach is to employ a certain molecular exciton model,[1] such as Frenkel-Davidov model.[2] However, most of the exciton models employ non-complete excitonic basis of antisymmetrized products of the site states (e.g. only local-excitation products) and no or suboptimal point-charge embedding in the site-state calculations, which results in suboptimal excitonic basis.

In this work we present the Excitonic Configuration Interaction (ECI) method,[3] a fragment-based analogue of the CI method that (i) allows inclusion of the antisymmetrized products with arbitrary number of excited site states (only local excitations – ECIS, local and double-local excitations ECISD, etc.), (ii) allows the embedding via arbitrary point charges in the site-state calculations, and (iii) calculates the full-system Hamiltonian matrix in the ECI basis exactly within the strong-orthogonality assumption. We present the performance of the method on the calculation of the electronic absorption spectra of two multichromophoric systems, one having only hydrogen bonds between chromophores and the other additionally having strong metal-ligand bonds. The results show that the ECI method, depending on the employed ECI expansion and the choice of the embedding charges, is capable of reproducing the electronic states of multichromophoric systems with error being in range 0.02-0.1 eV. Hence, it represents a promising starting point for further development of general ab-initio method for the calculation of both static and dynamic photochemical properties of the multichromophoric molecular systems.

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## Neural Network Potential for the Magnetite/Water Interface

P39

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Interfaces between magnetite and water occur commonly in nature and their properties could significantly impact many technological applications. Despite their relevance, our understanding of the structure of the magnetite and the water at the interface and of the associated processes remains limited. Molecular Dynamic (MD) simulations, grounded in accurate Density Functional Theory (DFT) calculations, offer valuable microscopic insights. However, the computational expense of DFT restricts its application to small systems and short timescales, posing a challenge for the study of material interfaces that may involve long range reconstructions as well as a diverse range of timescales. Furthermore, the intrinsic magnetism of magnetite comes out to introduce instability in DFT calculations, leading to convergence issues and inaccurate energy and force predictions even after achieving convergence. To overcome these challenges we have developed a Neural Network Potential (NNP). The use of the NNP is twofold beneficial: it enables the simulations of bigger system for longer times and it allows to get around the instability problem by cleaning the training dataset excluding the erroneous DFT structure. Multiple MD simulations of systems containing the magnetite/water interface have been conducted, varying in sizes, water coverages and at different temperatures. The analysis of the trajectories of these magnetite/water simulations provide new detailed information about the structure and the dynamics at the interface.



## The Spectroscopy and Dynamics of Cations of Adamantane and Derivatives

P40

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Diamondoids are the carbon cage molecular entities which are quite popular in interstellar chemistry and in medicinal chemistry and industry. The molecular units of these are adamantane ( $C_{10}H_{16}$ ) which has been quite frequently studied in the scientific community. Having these various applications in different fields, the derivatives of these molecules are triggering interest in the scientific community. In our work, we have studied the cations of adamantane and two of its derivatives : amantadine ( $C_{10}H_{15}NH_2$ ) and cyanoadamantane ( $C_{10}H_{15}CN$ ). We have extended earlier theoretical work on vibrationally resolved electronic spectroscopy by accounting for the higher lying electronically excited states of the adamantane cation in the absorption and photoelectron spectra for adamantane. We also performed adiabatic and nonadiabatic (surface hopping) molecular dynamics simulations to study (fast) fragmentation processes and electronic relaxation of  $C_{10}H_{16}^+$  and the derivatives. For the SH calculations, Thiel's semiempirical configuration interaction method (OM3/CISD) was adopted. Using various excitation energies and a large swarm of trajectories, we found that fragmentation (H loss) is possible already at low excitation energies, (for all the molecules) in accordance with experimental findings. In case of adamantane, our simulations reveal that after excitation with near-infrared ultraviolet photons, the adamantane cation undergoes an ultrafast internal conversion to the ground (doublet) state (on a time scale of 10-100 fs depending on initial excitation energy for adamantane and for amantadine, the timescale is similar while it takes relatively more time (200 fs) in case of cyanoadamantane to populate the ground state) which can be followed by a fast fragmentation predominantly a hydrogen loss. In the end, we will compare the fragmentation pattern and the chemical differences between the adamantane and its derivatives.



# Branching mechanism of photoswitching in $[\text{Fe}(\text{terpy})_2]^{2+}$ explained by full singlet-triplet-quintet dynamics

P41

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It has long been known that irradiation with visible light converts Fe(II) polypyridines from their low-spin (singlet) to high-spin (quintet) state, yet mechanistic interpretation of the photorelaxation remains controversial. Herein, we simulate the full singlet-triplet-quintet dynamics of the  $[\text{Fe}(\text{terpy})_2]^{2+}$  (terpy = 2,2':6',2''-terpyridine) complex in full dimension by trajectory surface hopping method in conjunction with a linear vibronic coupling (LVC) model, in order to clarify the complex photodynamics.[1]

We report a branching mechanism involving two sequential processes: a dominant  $^3\text{MLCT} \rightarrow ^3\text{MC}(^3\text{T}_{2g}) \rightarrow ^3\text{MC}(^3\text{T}_{1g}) \rightarrow ^5\text{MC}$ , and a minor  $^3\text{MLCT} \rightarrow ^3\text{MC}(^3\text{T}_{2g}) \rightarrow ^5\text{MC}$  component. (MLCT = metal-to-ligand charge transfer, MC = metal-centered) and show that the direct  $^3\text{MLCT} \rightarrow ^5\text{MC}$  mechanism could have only been operative, and thus lead to competing pathways, in the absence of  $^3\text{MC}$  states. The quintet state is populated on the sub-picosecond timescale involving non-exponential dynamics and coherent oscillations along the Fe-N breathing mode. The results are in agreement with the available time-resolved experimental data on Fe(II) polypyridines [2], and fully describe the photorelaxation dynamics.

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## Multi-state mapping approach to surface hopping: an excellent way to simulate exciton energy transfer in photosynthetic systems

P42

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One of the most popular methods for excited-state dynamics is fewest-switches surface hopping (FSSH), which involves stochastic hops of classical nuclear trajectories between adiabatic electronic states. This method can be used with *ab initio* potentials and is widely applied in photochemistry. However, it suffers from long-standing problems such as overcoherence and violation of detailed balance. A new “mapping approach to surface hopping” (MASH) [1] appears to resolve many of these issues: it avoids *ad hoc decoherence corrections* and provably relaxes to the correct quantum–classical equilibrium. Although originally developed for two states, we have extended the method to any number of states and applied it to a variety of problems, including gas-phase photochemistry, spin-boson models, and exciton transfer in photosynthetic systems [2]. In all cases, we find MASH to be both more accurate and more numerically tractable than FSSH. The talk will summarize this development and in addition show how a simple trick to incorporate quantum vibrations leads to full quantum accuracy in large light-harvesting complexes for a fraction of the usual computational cost.

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# Fluorescence Analysis of a Dye in Complex Environments with Quantum Mechanical and Machine Learning Approaches

P43

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The emission spectrum provides a unique identifier for molecules, and fluorophores play a crucial role by emitting light upon excitation, making them valuable molecular probes in scientific and medical applications. Despite the significance of density function tight binding (DFTB) approaches, their limitations arise in determining the emission spectrum of fluorophores due to state label switching near conical intersections.

In this work, we propose a solution utilizing a machine learning approach integrated with molecular mechanical simulations to overcome the challenges associated with state crossing. Our method involves training neural networks with sampled data from excited states simulations, combining the strengths of machine learning and molecular mechanics simulations. Through this integrated approach, we aim to establish a reliable means of qualitatively determining the emission spectrum. We demonstrate the efficacy of our method by applying it to the fluorophore FR0 in diverse solvent environments.



## Electron-Passing Neural Networks

P44

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While neural-network force fields already make the construction of highly accurate and fast-to-evaluate potential energy hypersurface representations possible, there still remain open challenges. Among these is the inclusion of long-range interactions and the modelling of forces due to externally applied electric fields. We present an investigation of electron-passing neural networks (EPNN) as an option to tackle these challenges. Emphasis is put on finding physically well-defined target quantities for prediction.



## Excited States and Machine Learning: A Love-Hate Story

P45

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The performance of machine learning algorithms for electronically excited states is far behind ground-state applications.[1] The problem lies in the high complexity of reference electronic-structure calculations, subtle dependencies among densities of electronic states and insufficient smoothness of the modelled properties in the vicinity of state crossings and conical intersections. We proposed several machine-learning approaches to overcome these limitations allowing us to efficiently model excited-state properties.[2,3]

Electronic-structure codes provide us with energy-ordered adiabatic states. However, adiabatic states are usually not smooth in the whole configuration space as they form conical intersections. Therefore, it is advantageous to switch to a smooth diabatic basis via a geometry-dependent unitary transformation. Unfortunately, diabaticization itself is also an outstanding problem. We have found a solution by tackling both problems at once.[3] We use an iterative machine learning procedure to obtain diabatic states which provide us in return with smooth properties that can be easily fitted. We need only a very small amount of training data and we observe the increase in prediction accuracy by up to two orders of magnitude.

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## Estimating thermal isomerization half-lives of arylazopyrazole photoswitches using neural network potentials

P46

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Photoswitches are a class of molecules with the ability to change between two distinct configurations by absorbing light. This property gives them a broad range of applications such as energy storage, nanomachines, or photodrugs. A switch back can also occur via excitation but also from thermal effects. This thermal isomerization can span from milliseconds to years, and thus, the possible application of a specific photoswitch is conditioned by its thermal rate.

In this contribution, we focus on arylazopyrazole photoswitches. Our aim is to understand how chemical alterations change the thermal switching rate between the cis and trans isomers. Previous research on the reaction rate of this compound group [1] investigated the thermal isomerization mechanism of the parent compound and a few derivatives by means of quantum chemical methods and experiments. Here we use machine learning to explore approximately 31 000 derivatives and estimate their thermal isomerization half-lives. To this aim, we used the well-established neural network PaiNN [2] to predict the potential energy surfaces necessary to investigate thermal relaxation. We obtained the training data for those potentials with time dependent density functional theory calculations. Because of the chemical similarity between the compounds, we were able to reduce the amount of data points needed for the training set by a large fraction. This allowed us to obtain a neural network capable of predicting the energy of several electronic states. The neural network is able to interpolate between similar chemical species and understand relevant information that they share. Therefore, only a subset of all investigated molecules is sufficient as a basis for the training set. This is relevant since the number of molecules makes it impossible to obtain a large amount of data from every single molecule. In addition, we relied on a process called active learning [3], which enables us to find new, highly informative data points. This ML-assisted process promises a faster way to predict reaction rates of arylazopyrazoles.

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## Recommendations for velocity adjustment in Surface Hopping

P47

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Surface hopping simulates nonadiabatic dynamics by evolving a swarm of independent trajectories involving multiple electronic states. Trajectories are propagated on a single surface, and hops between them are based on a stochastic algorithm. This surface change occurs at small but finite potential energy gaps, when the potential energy instantaneously changes. Therefore, to ensure total energy conservation during the dynamics, the nuclear kinetic energy must be changed to compensate for the potential energy variation. The proper way to change the kinetic energy is by rescaling the nuclear velocities in the direction of the nonadiabatic coupling vector. However, in many cases, those vectors are not available. Thus, what is the next best direction to rescale velocities? A common choice is the momentum direction, but this can induce an abnormal amount of back hopping, leading to wrong dynamics. In this work,<sup>1</sup> we investigate the effect of using different velocity adjustment directions after hoppings on the dynamics of fulvene and a protonated Schiff base (PSB4): nonadiabatic coupling (h), gradient difference (g), or momentum directions (using the conventional algorithm (p-fullKE) and a reduced kinetic energy reservoir approach (p-redKE2). Our results show that the dynamics of fulvene is susceptible to the adjustment approach but cis-PSB4 is not. We correlate this result to the topographies near the conical intersections. When nonadiabatic coupling vectors are unavailable, the g direction is the best adjustment option. When this direction is also not available, the use of the momentum direction with a reduced kinetic energy reservoir (p-redKE) becomes an excellent option to prevent an artificial excess of back shopping. Overall, the precise velocity adjustment direction is less crucial for describing the nonadiabatic dynamics than the kinetic energy reservoir's size. Therefore, the most important thing to consider is to reduce the amount of kinetic energy, especially in large molecular systems, in order to avoid artificial back hoppings.

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## Retrieving polarizability tensor of chiral molecules from real-time ab-initio calculations

P48

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The dynamic polarizability tensor of chiral molecules is an essential parameter in the calculation of enantioselective optical forces, as it connects the response of a molecular system in terms of electric and magnetic dipole moment, to the external electromagnetic field. Here we propose an approach based on real-time Time Dependent Density Functional Theory (rt-TDDFT) calculations to estimate the frequency-dependent tensorial polarizability of molecules. Indeed, our method enables the direct calculation of the time-dependence of electric and magnetic dipole moments of a molecular system, upon interaction with a shape-customizable external electromagnetic field. We retrieve the dynamic polarizability tensor by Fourier transforming those time-dependent quantities and normalizing the results with respect to the intensity of the external electric or magnetic field.

We test our method on various notable systems i.e., iodine, water and p-hexahelicene. We find a good agreement with what reported in the literature. We further validate our numerical protocol against other measurable optical quantities such as the absorption and electronic circular dichroism (ECD) spectra.



## Multipole Expansion in the Density-Functional Tight-Binding Method

P49

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Density-functional tight-binding (DFTB) is a well-established semiempirical quantum mechanical approach. However, its capability to accurately describe noncovalent interactions and proton transfer processes is limited due to the use of a monopole approximation. To address this limitation, we extended the method to incorporate multipole interactions, including atomic dipole and quadrupole moments. In our benchmarks, the extended DFTB methods demonstrate superior accuracy over their predecessors, even with existing electronic parameters. This development elevates the capability of DFTB in accurately capturing noncovalent interactions and proton transfer processes.



## ConsAMPHemo: A two-stage framework for efficient calculation of antimicrobial peptide hemolysis based on machine learning and deep learning

P50

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In the assessment of drug safety, the identification of hemolytic activity of antimicrobial peptides is crucial. This activity, primarily manifesting as the ability to disrupt cell membranes, is essential for their antimicrobial efficacy but also poses potential toxicity risks to human cells. Given that traditional experimental methods for hemolysis evaluation are resource-intensive, computational approaches for predicting the hemolytic properties of antimicrobial peptides have become a focal point of research. This study introduces a two-stage framework based on deep learning, named ConsAMPHemo. This framework not only performs conventional binary classification analysis of the hemolytic properties of antimicrobial peptides but also innovatively uses handcrafted features extracted from peptide sequences for regression analysis of hemolytic concentration. The experimental results demonstrate that our model achieved exemplary performance in the classification stage of antimicrobial peptides' hemolysis, attaining the best performance on three distinct datasets with accuracies of 99.54%, 82.57%, and 88.04% respectively. Notably, in the second stage, we present a interpretative regression analysis of the hemolytic properties of antimicrobial peptides, a first in this field of research. The trends identified in this regression analysis are not only useful for the safety identification and design of antimicrobial peptides but also elucidate the reasons behind their hemolytic nature. We believe this study will significantly contribute to the design of new, safer antimicrobial peptides and offer new insights for other drug safety analyses.





## Active learning for excited states dynamics simulations to discover molecular degradation pathways

P51

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The demand for precise, data-efficient, and cost-effective exploration of chemical space has ignited growing interest in machine learning (ML), which exhibits remarkable capabilities in accelerating atomistic simulations of large systems over long time scales. Active learning is a technique widely used to reduce the cost of acquiring relevant ML training data. Here we present a modular, transferrable, and broadly applicable, parallel active learning orchestrator. Our workflow enables data and task parallelism for data generation, model training, and ML-enhanced simulations. We demonstrate its use in efficiently exploring multiple excited state potential energy surfaces and possible degradation pathways of an organic semiconductor used in organic light-emitting diodes. With our modular and adaptable workflow architecture, we expect our parallel active learning approach to be readily extended to explore other materials using state-of-the-art ML models, opening ways to AI-guided design and a better understanding of molecules and materials relevant to various applications, such as organic semiconductors or photocatalysts.



## Effects of a surrounding environment during the coalescence of AuPd nanoparticles

P52

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The optimal design of nanoparticles and nanoalloys hinges on meticulous control of their morphology, encompassing size, shape, chemical composition, and ordering. Nanoalloy morphology is largely contingent upon the specific synthesis process employed. Coalescence, acknowledged as a prevalent growth mechanism, manifests in both liquid and gas phases. This phenomenon entails the collision and amalgamation of two existing nanoseeds into a larger entity, typically adopting a compact, often spherical structure.

However, the resulting nanoalloy can be far from the equilibrium isomer, the global minimum of the potential energy surface. The morphology of coalesced nanoparticles depends likely on the surrounding environment. In particular, understanding how the surface chemical composition is affected is paramount to designing bimetallic nanocatalysts. In this study, we employ Molecular Dynamics simulations to investigate the coalescence of Au and Pd nanoparticles. We compare the initial stages of the coalescence in the vacuum and the presence of an interacting environment, acting on Au and Pd atoms differently. Our findings reveal that the kinetics of coalescence are environment-dependent, and we demonstrate the partial tunability of the resulting nanoalloy's surface chemical composition by manipulating the interaction of the two chemical species with their surroundings

## Characterizing Palmatine-Induced Oxidative Stress in DNA

P53

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The formation of DNA lesions by certain compounds poses a significant risk to genome stability and various biological processes.[1] Palmatine, a protoberberine alkaloid, has shown potential as a DNA phototherapy drug due to its selective production of singlet oxygen ( $^1O_2$ ) in the presence of DNA.[2] However, the underlying mechanisms responsible for this selective behavior and the complex photophysics of palmatine are yet to be fully understood. In this study, we employed a hybrid quantum mechanics/molecular mechanics (QM/MM) approach to investigate the formation of DNA lesions induced by palmatine.

Through state-of-the-art QM/MM techniques combined with molecular dynamics simulations, we examined the structural and electronic aspects of palmatine's interaction with DNA. Two stable interaction modes exist between palmatine and B-DNA: insertion and minor groove binding. These modes exhibited similar UV-vis signatures and estimated binding free energies, suggesting their coexistence within the complex.[3] Furthermore, we characterized the excited state properties of palmatine in both aqueous solution and during its interaction with DNA, shedding light on the environmental factors that may influence the production of  $^1O_2$ . The competition between local and charge-transfer excited states was analyzed, highlighting the impact of the DNA molecular environment on the photophysical behavior of palmatine.

Additionally, this study emphasizes the importance of explicit molecular dynamics simulations to capture the dynamic nature of the palmatine-DNA aggregate, considering DNA's flexibility as a highly dynamic macromolecule. By utilizing a customized QM/MM protocol, we gained valuable insights into the potential energy landscape of palmatine in its ground and excited states within the heterogeneous DNA environment.

Overall, our findings contribute to the understanding of DNA lesions induced by palmatine, providing valuable insights into the structural and electronic features of the palmatine-DNA interaction.

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## Enzymatic and Non-Enzymatic Crosslinks in Collagen

P54

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Collagen is a force-bearing, hierarchical structural protein essential to all connective tissue and therefore vital for living organism. Among the 28 different types of collagen, type I is the most abundant in the human body, contributing to about 90% of the total collagen content. The type I collagen chain contains around 1000 amino acids and is involved in the formation of complex structural networks. These networks are stabilized by covalent cross-links, which can originate from both enzymatic and non-enzymatic processes; the latter are also known as Advanced Glycation End Products (AGEs). In the first case, the cross-links are beneficial for the integrity of the collagen structure, while in the latter case, they are associated with several diseases, such as diabetes, osteoporosis, cancer, cardiovascular diseases, retinopathy and Alzheimer's.

In this poster we address the current effort in modeling and understanding the effect of cross-links on mechanical properties of collagen.

First, we started with the parametrization of cross-links to develop a fully atomistic, crosslinked collagen model ( $\approx 67.5$  nm). Then, by using the G4(MP2)-6X composite method, we determined the Bond Dissociation Energies (BDEs) of each cross-link. Subsequently, by employing a Kinetic Monte Carlo/Molecular Dynamics (KIMMDY) approach, which requires BDEs as input, during constant velocity Steered Molecular Dynamics (SMD) simulations, we aim to investigate the distribution of forces within our model. This allows us to achieve a detailed understanding of how various cross-links influence the mechanical properties of collagen type I.



# Non-adiabatic Molecular Dynamics Coupled to External Electromagnetic Field Simulations

P55

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Optical spectroscopy of atoms and molecules allows retrieving information about electronic state energies and the transition strengths between different electronic energy levels. Conventional optical spectroscopic schemes, however, only rarely provide information about various “dark” electronic transitions, such as  $d \rightarrow d$  or  $f \rightarrow f$  transitions in metal complexes, or  $n\pi^*$  states in organic chromophores. These transitions are dark because they cannot be excited via electric field (EF)–electric dipole (ED) interactions, but could be accessed by other terms, e.g., magnetic field (MF)–magnetic dipole (MD) interactions. Unfortunately, the absorption spectrum of MD-allowed transitions is typically not directly measurable. This is because ED transitions are typically orders of magnitude stronger and conceal MD-governed transitions. However, even in the absence of ED transitions, electric quadrupole transitions both are of similar intensity and have similar selection rules [1]. Hence, they would obscure MD transitions as well.

A more elaborate approach for an “MD-only spectroscopy” could be based on the spatial (sub-wavelength) separation of the EFs and MFs. Within one recently proposed scheme [2], ultra-short azimuthally polarized laser beams (APBs) are directed on metallic nanoantennas, which generates isolated and substantially enhanced MFs, which oscillate at optical frequencies, along the beam axis.

Considering that EFs and MFs can be isolated and enhanced in such nontrivial ways, it would be of great interest to study the excited-state dynamics of molecules induced by such fields. In contrast to most investigations in the context of nonadiabatic molecular dynamics simulations, that focused on the EF–ED interaction term, we are particularly interested in the dynamics of dark states that could be selectively probed with MFs. Thus, in this contribution, we present a new multiscale protocol combining finite-differences time-domain (FDTD) simulations of EFs and MFs [3] of a “MD-only spectroscopy” setup [2] with nonadiabatic molecular dynamics simulations in the SHARC (Surface Hopping including ARbitrary Couplings) package [4].

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## Molecular dynamics simulations of a three-way DNA junction

P56

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Translating complex molecular systems into computational models can at times be a challenging task. Once an initial structure is generated, it is not guaranteed that the whole conformational space can be accessed from this structure within the simulation time periods feasible using modern methods. In our particular case, we are generating a three-way DNA junction to be used as a structural scaffold in a molecular light-harvesting array. Constructing this junction by linking three individual double strand leads to some ambiguity in the manner of how these strands are connected.

Here, we perform and analyze unconstrained molecular simulations of three distinct starting structures in order to unravel what conformations there are and with which descriptors they can be classified. Indeed, each simulation produces unique conformations, but it appears that these can interchange. We identify that the base pairs closest to the junction are in an equilibrium between the bonded and unbonded states, while base pairs at greater distance to the junction remain bonded throughout our simulations. It appears that the binding state of these base pairs closer to the junction determine to some extent the shape of the entire DNA scaffold. Thus, controlling these might allow to convert one conformation into another in potential metadynamic simulations, which could help unraveling the energetic landscape, thus allowing to judge which are the more stable conformations. This data will help to select a molecular model that is truly representative of the physical properties of the system.

## Elucidating time-dependent nonadiabatic three-dimensional solute—solvent dynamics via surface hopping simulations

P57

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Nonadiabatic dynamics in solution are subject to mutual solute–solvent interactions. Understanding these interactions fully requires the simulation of the solute’s nonadiabatic dynamics together with the three-dimensional solvent distributions. However, the widely used combination of trajectory surface hopping (TSH) with hybrid quantum mechanical/molecular mechanical (QM/MM) methods is too expensive to resolve the solvent distribution dynamics with sub-Ångstrom and femtosecond accuracy. For this reason, we recently combined efficient linear vibronic coupling models and MM (LVC/MM) using electrostatic embedding [Polonius et al., JCTC 2023, 19, 7171–7186]. This gives access to solvent-embedded, nonadiabatically coupled potential energy surfaces and computational cost similarly to MM force fields. In this work, TSH with LVC/MM is applied to the nonadiabatic dynamics of two small thiocarbonyls in water. Additionally, we establish a robust way to estimate the number of trajectories required to produce nearly noise-free three-dimensional solvent distribution functions. Afterwards, we show the analysis of about 10,000 trajectories propagated for 3 ps. In the ground state, both molecules show in-plane hydrogen bonds to the sulfur atom. After excitation, these hydrogen bonds are broken shortly after excitation and reform perpendicular to the molecular plane at different time scales (about 100 fs and 1000 fs) due to steric effects. We also analyze the coupled solvent relaxation and electronic dynamics, including to intersystem crossing. Our findings are not only interesting for the simulation and analysis of nonadiabatic dynamics in solution but the result on the thiocarbonyls are also relevant to thionated biological compounds.



## Transferability of atomic energies from alchemical decomposition

P58

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We study alchemical atomic energy partitioning as a method to estimate atomisation energies from atomic contributions which are defined in physically rigorous and general ways through use of the uniform electron gas as a joint reference. We analyze quantitatively the relation between atomic energies and their local environment using a dataset of 1325 organic molecules. The atomic energies are transferable across various molecules, enabling the prediction of atomisation energies with a mean absolute error of 23 kcal/mol - comparable to simple statistical estimates but potentially more robust given their grounding in the physics-based decomposition scheme. A comparative analysis with other decomposition methods highlights its sensitivity to electrostatic variations, underlining its potential as representation of the environment as well as in studying processes like diffusion in solids characterized by significant electrostatic shifts.



## Glass-Induced Photophysical Changes on a Push-Pull Functionalized Stilbene

P59

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In our research, we explore how amorphous silica surfaces influence the photophysical and photochemical properties of 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS), a stilbene derivate known for its photoisomerization and notable fluorescence emission. Changing the environment, like the introduction of different solvents, can affect its absorption spectra and even modify the ratio between photoisomerization and fluorescence. Previous studies have demonstrated that how the interaction with microplastics can lead to significant changes in the fluorescence emission. [1] The goal of this study is to understand the interactions between DANS and the glass surface and investigate the changes in the photophysical and photochemical properties of DANS due to that interaction. In the initial phase, we conducted optimization calculations with plane wave density functional theory on different orientations on the glass surface. [2] Following this, we assessed the interaction energies and examined the optimized geometries to determine the most favorable orientations. In order to gain a better understanding of the various orientations, we applied a range of techniques including analyzing charge density differences, clustering, and employing multiple linear regression. The results suggest that the hydrogen bonds between the nitro group of DANS and the OH group of the surface is very important. Furthermore, the involvement of the  $\pi$ -system plays a surprisingly significant role in the energy interaction, thereby enhancing the stability of the molecule on the surface. To gain insights into light-induced phenomena, we conducted calculations with time dependent density functional theory in the excited states and analyzed the absorption spectra of the gas phase as well as various orientations on the silica surface. We applied wave function analysis methods to observe changes in excitation in comparison to DANS in gas phase. Additionally, we utilize wave function overlap calculations to gain a deeper understanding of the similarities and differences between the wave function of DANS on glass and the wave function of DANS in the gas phase. Through an examination of the acquired absorption spectra, it was discovered that the hydrogen bond with the nitro group also leads to the most significant changes in the absorption spectra.

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