



HDQD

High-Dimensional Quantum Dynamics
Challenges and Applications

Hamburg
16-19 July, 2024

HDQD 2024

BOOK OF ABSTRACTS



Universität Hamburg
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High Dimensional Quantum Dynamics

Hamburg, Germany July 16-19, 2024

Invited Talks (IT)		Contributed Talks (CT)	
25 min + 5 min discussion		15 min + 5 min discussion	
Hamburg, Germany July 16-19, 2024			
TIME	TUESDAY	TIME	WEDNESDAY
from 8:00 on	Registration	Chair: <i>O. Vendrell</i>	
9:15 - 9:30	Welcome	9:00 - 9:30	IT9: <i>E. Narevicius</i> - Collisions with Cold Molecules: Tomography of Feshbach resonances
Chair:	<i>U. Manthe</i>	9:30 - 10:00	IT10: <i>H. Larsson</i> - High-Dimensional Quantum Dynamics Simulations using Tensor Network States
9:30 - 10:00	IT1: <i>M. Thoss</i> - Simulation of quantum dynamics and transport using the hierarchical equations of motion method	10:00 - 10:30	IT11: <i>G. Worth</i> - Non-Adiabatic Spectroscopy and Dynamics: The Linear Vibronic Coupling Model and Beyond
10:00 - 10:30	IT2: <i>H. Wang</i> - Dynamics of electron transfer and transport in complex glassy environment ^{††}	10:30 - 11:00	Coffee break
10:30 - 11:00	Coffee break	11:00 - 11:30	IT13: <i>I. Burghardt</i> - Vibronic quantum dynamics with multiplicative neural network potentials and multiconfigurational thermo-field wavefunctions
11:00 - 11:30	IT3: <i>F. Santoro</i> - Mixed Quantum-Classical Dynamical Approaches for Studying the Photophysics of Complex Systems	11:30 - 12:00	IT14: <i>D. Picconi</i> - HDQD... DD: Challenges and applications
11:30 - 12:00	IT4: <i>S. Gomez</i> - Blending non-adiabatic dynamics methods to describe tetraphenylpyrazine	12:00 - 14:00	At the beginning: Group foto, afterwards: Lunch break
12:00 - 14:00	Lunch break	Chair:	<i>M. Thoss</i>
Chair:	<i>G. Worth</i>	14:00 - 14:30	IT15: <i>H. Sadeghpour</i> - Universality class of a spinor BEC (really) far from equilibrium
14:00 - 14:30	IT5: <i>J. Küpper</i> - Ultrafast dynamics in microsolvated biomolecules	14:30 - 15:00	IT16: <i>P. Saalfrank</i> - Spectroscopy and dynamics of molecules strongly coupled to cavity photons
14:30 - 15:00	IT6: <i>D. Lauvergnat</i> - Solving time-(in)dependent Schrödinger equation with Smolyak scheme using a system-bath like partition	15:00 - 15:30	IT17: <i>O. Vendrell</i> - High-dimensional quantum dynamics with the ML-MCTDH method: a perspective on the applications to protonated water clusters
15:00 - 15:30	IT7: <i>C. Sanz</i> - Multi-state coupled driven photodissociation	15:30 - 16:00	Coffee break
15:30 - 16:00	Coffee break	16:00 - 16:30	IT18: <i>R. Santra</i> - Techniques for computing the dynamics of matter in strong x-ray fields
16:00 - 16:30	IT8: <i>T. Carrington</i> - An MCTDH collocation method with more points than basis functions: obviating integrals	16:30 - 16:50	CT4: <i>D. Gorelova</i> - Theoretical description of attosecond imaging and spectroscopy of electron dynamics with ultrashort x-ray pulses
16:30 - 16:50	CT1: <i>T. Niemann</i> - Multidimensional Hubbard models in the MCTDH framework	16:50 - 17:10	CT5: <i>N. Krupp</i> - Quantum Dynamics Simulation of Exciton-Polariton Transport in an organic microcavity
16:50 - 17:10	CT2: <i>X. Meng</i> - Quantum Dissipation with Minimally Extended State Space: A Universal Framework for Exact Time-Local Evolution Equations	17:10 - 17:30	CT6: <i>A. Freibert</i> - A fully dynamical quantum description of ultrafast X-ray spectroscopy of pyrazine
17:10 - 17:30	CT3: <i>N. Jamshidi</i> - Dynamics of Plasmonic Nanocavities Using a Linear Vibronic Coupling Hamiltonian	18:00 - 20:00	Poster Session
18:00 - 20:00	Welcome Reception		
TIME	THURSDAY	TIME	FRIDAY
Chair:	<i>I. Burghardt</i>	Chair:	<i>H. Larsson</i>
8:30-9:00	IT19: <i>U. Manthe</i> - Recent developments in the MCTDH approach	9:00 - 9:30	IT23: <i>M. Erakovic</i> - Molecular Quantum Dynamics with the Density Matrix Renormalization Group
9:00 - 9:30	IT20: <i>L. Cao</i> - Orbital entanglement between ultracold lattice atoms: A showcase of how ML-MCTDHX benefits quantum gas investigations	9:30 - 10:00	IT24: <i>L. Mathey</i> - Time crystals in an atom-cavity system
9:30 - 10:00	IT21: <i>S. Mistakidis</i> - Phases and correlated dynamics of droplet and bubble self-bound states of matter	10:00 - 10:30	IT25: <i>O. Christiansen</i> - Quantum molecular dynamics with coupled cluster and direct methods
10:00 - 10:30	IT22: <i>E. Matys</i> - Hyperfine and Zeeman effects in the high-resolution rovibrational spectrum of H ₃ ⁺	10:30 - 11:00	Coffee break
10:30 - 11:00	Coffee break	11:00 - 11:30	IT26: <i>O. Alon</i> - Coupled-cluster for trapped bosonic mixtures
11:00 - 11:20	CT7: <i>F. Theel</i> - Crossover from attractive to repulsive induced interactions and bound states of two distinguishable Bose polarons	11:30 - 11:50	CT10: <i>R. Cuenca</i> - Effect of attosecond electronic coherences on conical intersection dynamics in core-excited states
11:20 - 11:40	CT8: <i>H. Hoppe</i> - Quantum Dynamics of the Reaction of Chlorine with Methane	11:50 - 12:00	Concluding Remarks
11:40 - 12:00	CT9: <i>G. Koutentakis</i> - Optimizing Orbital Angular Momentum Transfer in Resonant Vibrational Spectroscopy of Diatomic Molecules	12:00 - 14:00	Lunch break
12:00 - 14:00	Lunch break		
14:00 - 17:30	Free Afternoon		
17:30	Meeting at Überseebrücke, 20459 Hamburg		
18:00 - 21:00	Dinner at Klein Fritzen		

- All talks, welcome and the concluding remarks take place at the [DESY lecture hall](#) (building 5, Room Auditorium)
- Welcome Reception and coffee breaks are in the [foyer of the DESY lecture hall](#) (building 5)
- Lunch is served in the [DESY Kantine](#) (building 9, next to the lecture hall)
- On Wednesday, the group photo is taken immediately at the start of the lunch break in front of building 5
- Poster session is in the [basement of the CFEL](#) (center for free electron laser science, building 99 on the DESY campus)

Scientific committee

Shirin Faraji (University of Groningen)

Fabien Gatti (University of Paris-Saclay)

Henrik Larsson (University of California at Merced)

Uwe Manthe (University of Bielefeld)

Peter Schmelcher (University of Hamburg)

Oriol Vendrell (University of Heidelberg)

Graham Worth (University College London)

Local organizing committee

André Becker (University of Hamburg)

Anja Cordes (University of Hamburg)

Dimitrios Diplaris (University of Hamburg)

Peter Schmelcher (University of Hamburg)

Friethjof Theel (University of Hamburg)

Talk abstracts

Tuesday — Morning Presentations

July 16th, 9:30 AM – 12:00 AM

Chair: U. Manthe

Simulation of quantum dynamics and transport using the hierarchical equations of motion method

[THOSS, Michael \(University of Freiburg\)](#)

The hierarchical equations of motion (HEOM) formalism is an accurate and efficient approach to simulate the dynamics of open quantum systems [1]. Formulated as a density matrix scheme, it generalizes perturbative quantum master equation methods by including higher-order contributions as well as non-Markovian memory and allows for the systematic convergence of the results. In this talk, recent extensions of the HEOM method are discussed, including open quantum systems with multiple bosonic and fermionic environments [2] and a matrix product state formulation in twin space [3]. While the former is important for applications in the areas of quantum thermodynamics and quantum transport, the latter allows the simulation of significantly larger systems. Applications of the method are discussed to simulate quantum transport in molecular junctions [4], nonequilibrium reaction rates [5], and molecule-surface scattering.

References:

- [1] Y. Tanimura, J. Chem. Phys. 153, 020901 (2020).
- [2] J. Bätge, Y. Ke, C. Kaspar, and M. Thoss, Phys. Rev. B 103, 235413 (2021).
- [3] Y. Ke, R. Borrelli, M. Thoss, J. Chem. Phys. 156, 194102 (2022).
- [4] C. Schinabeck, A. Erpenbeck, R. Härtle, and M. Thoss, Phys. Rev. B 94, 201407(R) (2016); C. Kaspar, M. Thoss, Phys. Rev. B 105 195435 (2022); Y. Ke, J. Dvořák, M. Čížek, R. Borrelli, and M. Thoss, J. Chem. Phys. 159, 024703 (2023) .
- [5] Y. Ke, C. Kaspar, A. Erpenbeck, U. Peskin, and M. Thoss, J. Chem. Phys. 157, 034103 (2022).

Dynamics of electron transfer and transport in complex glassy environment

[WANG, Haobin \(University of Colorado Denver\)](#)

The dynamics of electron transfer and transport reactions in a complex environment are investigated in the context of the spin-boson model with a bath characterized by the Cole–Davidson spectral density. Using multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method, the reduced density dynamics of the subsystem has been investigated in a broad physical regime. Upon changing various parameters, the simulation results exhibit either weakly damped coherent motion, incoherent decay, or localization. Transitions between these regimes are discussed in terms of several important physical parameters. Comparison of the ML-MCTDH simulations with the non-interacting blip approximation (NIBA) shows that the latter performs quite well in the nonadiabatic regime despite the complex multiple time scales the bath exhibits, but fails in the adiabatic and intermediate regimes. The glassy environment also has a non-negligible impact on the current for bridge-mediated electron transport.

Mixed Quantum-Classical Dynamical Approaches for Studying the Photophysics of Complex Systems

[SANTORO, Fabrizio \(ICCOM-CNR\)](#)

The impressive efficiency of ML-MCTDH allows nowadays the quantum dynamical investigation of nonadiabatic processes even in large systems, especially if the diagonal and off-diagonal terms of the electronic Hamiltonian of the system can be expanded in low-order Taylor expansions of the nuclear degrees of freedom. In past years we have developed a flexible tool for the automatic parameterization of generalized Linear Vibronic Coupling (LVC) models that are able to describe the competition between intra-molecular (internal conversions) and inter-molecular (exciton and charge-transfer couplings) processes in multi-component systems, like multichromophoric systems or metal-cluster/dye aggregates. Our approach is based on a versatile fragment-based maximum-overlap diabaticization technique, combined with TD-DFT [1]. We have recently applied this strategy in several fields including the nonadiabatic prediction of resonance Raman and the investigation of the Charge-Transfer enhancement mechanism in Surface enhanced resonance Raman [2].

Model Hamiltonian approaches are usually well suited for rigid systems. However, most of the systems of practical interest are characterized by some flexible degrees of freedom, and/or are embedded in a fluctuating environment. In order to study photoinduced nonadiabatic dynamics in these systems, we introduced an approach that combines classical Molecular Dynamics (MD) and Quantum Dynamics (QD) propagation. It is based on an adiabatic separation of modes in which soft degrees of freedom are considered slow with respect to the photodynamical process. In this limit, sometimes known as static disorder, their effect on the photophysical properties can be described by sampling them with classical MD and then introducing their effect on the photodynamics by running QD propagations on specific model Hamiltonians along stiff modes, parameterized for each representative configuration of the slow modes. This approach is well suited to study multichromophoric systems, since the motions leading to the fluctuation of the solvent cavity and of the stacking geometry of the different dyes can be considered slow, with respect to the high-frequency modes coupled to the photodynamics in the ultrafast (100fs) timescale. We have applied this approach to study the excited-state dynamics of several multichromophoric systems, including different DNA stacks [3,4] in chloroform and water, NADH [5] in water and perylene diimides [6] or Zn-phtalocyanins aggregates [7] in different solvents. In this contribution, after a presentation of the main computational ingredients of our approach, some of the recently achieved results will be illustrated.

References:

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Blending non-adiabatic dynamics methods to describe tetraphenylpyrazine

[GOMEZ, Sandra](#) (*Universidad de Salamanca*), [MARTIN SANTA DARIA, Alberto](#) (*Universidad de Salamanca*), [HERNANDEZ-RODRIGUEZ, Javier](#) (*Universidad de Salamanca*)

Efforts within our research group have been recently directed towards understanding the behavior after photoexcitation of molecular crystals with potential photosensitizing applications, i.e., the capability to absorb light to create reactive species of oxygen to fight diseases. This work specifically focuses on tetraphenylpyrazine, known for their fluorescence enhancement due to aggregation in the form of molecular crystals. We explore the deactivation mechanisms leading to the emissive states of this system.

An initial study was conducted in the gas phase, employing non-adiabatic dynamics methods such as trajectory surface hopping and multilayer MCTDH to probe the photodeactivation of tetraphenylpyrazine. Surface hopping was used to validate precomputed potentials, assess the role of the electronic ground state, and determine the intersystem crossing rate. Following the benchmarking of these analytical potentials, long-time dynamics simulations were performed with the ML-MCTDH method to obtain timescales and electronic state yields.

The excited state dynamics of tetraphenylpyrazine, utilized as a photosensitizer and derived from tetraphenylethylene and pyrazine, was then compared to both parent compounds. This comparison highlighted the differences and similarities in their photophysical properties. By elucidating these deactivation mechanisms, we aim to enhance the understanding of tetraphenylpyrazine's photosensitizing capabilities and pave the way for the design of more efficient molecular photosensitizers.

Tuesday — Afternoon Presentations

July 16th, 2:00 PM – 6:00 PM

Chair: G. Worth

Ultrafast dynamics in microsolvated biomolecules

[KÜPPER, Jochen \(CFEL, DESY & UHH\)](#)

Interactions between proteins and their solvent environment can be studied in a bottom-up approach using hydrogen-bonded biomolecule-solvent clusters. The ultrafast dynamics following UV-light-induced electronic excitation of the biomolecular chromophores, potential radiation-damage, and their dependence on solvation are important open questions. Specific and precise studies of the microsolvation effect are challenging due to the inherent mix of the produced gas-phase aggregates.

We used the electric deflector [1] to spatially separate different molecular species in combination with pump-probe velocity-map-imaging experiments, including applications of 4D “cameras” based on Timepix3 [2, 3]. We demonstrated that this powerful experimental approach reveals intimate details, e.g., on the radiation damage of water-water [4] and pyrrole-water [5] dimers as well as on the UV-induced dynamics in the near-UV-absorbing prototypical biomolecular indole-water system [6].

We determined the time-dependent appearance of the different reaction products and disentangled the occurring ultrafast processes. This novel approach ensures that the reactants are well-known and that detailed characteristics of the specific reaction products are accessible – paving the way for the complete chemical-reactivity experiment.

References:

- [1] Y.-P. Chang, D. A. Horke, S. Trippel, and J. Küpper, *Int. Rev. Phys. Chem.* 34, 557 (2015), arXiv:1505.05632.
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Solving time-(in)dependent Schrödinger equation with Smolyak scheme using a system-bath like partition

[LAUVERGNAT, David \(CNRS and Université Paris-Saclay\)](#), [NAUTS, André \(Université Catholique de Louvain\)](#)

Solving the Schrödinger equation using method using a multidimensional grid such as DVR, FBR-DFR or pseudo-spectral approaches [1] is limited by the number of degrees of freedom, d , of the system. With these methods using direct-product, the numerical complexity grows exponentially with d and it is relatively easily to study four ($d = 6$) or five ($d = 9$) atomic systems. This limit can be pushed away using contraction techniques [2-4], pruned basis sets [5] or schemes with a basis function selection. [6]

Somehow, the Smolyak scheme [7-9] can be viewed as an approach with a selection of basis functions and a sparse grid adapted to that basis set. The parameter, L , controls the selection and thus the size of the basis set and the grid. With this scheme, the numerical complexity grows as a polynomial of degree L with d . Therefore, systems up to 12 degrees of freedom can be studied, [10-12] although larger systems ($d = 21$) are possible if few states are needed.[13]

This limit can be pushed away using a system-bath separation, and in our Smolyak scheme, three L parameters are required: [14] (i) L_s for the degrees of freedom associated with the system part. (ii) L_b associated with the bath modes. (iii) L_m a parameter controlling the coupling between the system and the bath.

This system-bath separation has no limitation with respect to the form of the Hamiltonian and it works well when the coupling between the system and the bath is weak and typically: $L_s \gg L_b$ and $L_m > L_s$ ($L_m = L_s + 1$ or $L_s + 2$ can be used).

To illustrate the advantages and the limitations of this approach, time-independent and time-dependent applications are presented:

- The effect of the rotation-translation motions (bath modes, up to 120) of the water shell on the rotation-translation H2 motions (system modes, 5) in clathrate hydrate. [14]
- The photoisomerization of a retinal chromophore model with 2 active modes (system) and 23 modes (bath). [15]

References:

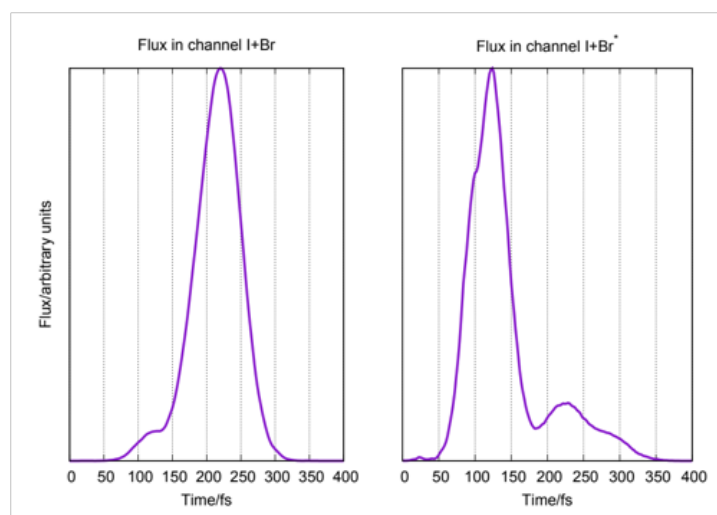
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- [4] O. Vendrell, H.-D. Meyer, *J Chem Phys* 2011, 134, 044135.
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Multi-state coupled driven photodissociation

SANZ-SANZ, Cristina (Autonoma University Madrid), WORTH, Graham A. (University College London)

One of the primary goals in chemistry is to control chemical reactions. Over the years, laser pulses have been employed as a strategy to guide reactions along various pathways. The control of photodissociation through the application of a time-delayed, non-resonant control pulse has been both experimentally and theoretically studied, resulting in the inversion of the branching ratio of dissociation into different channels. The IBr system exhibits an avoided crossing among excited states, leading to dissociation into two distinct channels. These states are coupled by spin-orbit interactions. The experimental procedure involves a sequence of two pulses: the first (pump) pulse excites the system into the upper manifold of states, while the second (control) pulse, non-resonant with the states involved in the avoided crossing, modifies the potential curves near the crossing, thereby enhancing dissociation into the upper channel.

We have simulated the experiment using time-dependent wavepacket propagations across a comprehensive set of new potential energy surfaces that depend on the strength and orientation of an external electric field. The photodissociation into the $I + Br$ and $I + Br^*$ channels is analysed by measuring the flux through a surface placed in each channel. The flux analysis indicates that the system takes longer to reach the lower channel compared to the upper channel (see Figure below), consistent with experimental results. However, the timescale of our simulations differs from the experiments, regardless of the control pulse's time delay. Further analysis of the propagations suggests that the enhanced flux in the upper channel might result from a late excitation of the wavepacket, occurring after the system has already traversed the avoided crossing.



References:

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An MCTDH collocation method with more points than basis functions: obviating integrals

[WODRASZKA, Robert \(Queen's University\)](#), [SIMMONS, Jesse \(Queen's University\)](#), [CARRINGTON, Tucker \(Queen's University\)](#)

It is common to use variational methods to solve the Schrödinger equation to study the motion of nuclei in a molecule or a reacting system. MCTDH is a variational method that uses optimized basis functions. When using a variational method, one must confront the problem of computing the matrices that are fed into whatever method is used to solve the Schrödinger equation, e.g. MCTDH. Many variational methods therefore require that the PES has a simple form that facilitates the calculation of the potential matrix. Most MCTDH calculations are done with a sum-of-products PES. In this talk, I shall present collocation ideas that obviate the need to compute the matrices required in a variational method. Like a variational method, a collocation method represents solutions as linear combinations of basis functions. Unlike a variational method, collocation determines basis function coefficients by demanding that the Schrödinger equation be satisfied at points: there are no integrals and no quadratures. In our calculations, collocation points are the points on a "sparse" grid. When using polynomial basis functions in a variational method, it is common to systematically reduce quadrature error by using more quadrature points than basis functions. Using more points than functions is unfortunately not straightforward in a MCTDH calculation. I shall discuss collocation methods that use more points than functions in order to systematically approach variational accuracy. To extract the best possible solutions from a given basis by using more points than basis functions means using rectangular matrices. Because the MCTDH basis is excellent, it is important to use rectangular collocation with MCTDH. This requires deriving new equations because the original MCTDH equations were derived with a variational approach. Excellent results are obtained for molecules with as many as six atoms without any need to optimize points.

Multidimensional Hubbard models in the MCTDH framework

[NIERMANN, Tristan \(Universität Bielefeld\)](#), [MANTHE, Uwe \(Universität Bielefeld\)](#)

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

While the simulation of the quantum dynamics on one-dimensional lattices can be routinely performed using tensor contraction schemes as, e.g., DMRG, simulations on two and three-dimensional lattices pose a challenge.

The present work addresses the problem by employing the tree structure of the multi-layer MCTDH approach and a self-similar mapping of the lattice structure onto a one-dimensional sequence.

Specifically, the multi-layer MCTDH approach in second quantization representation is used to study two-dimensional Bose-Hubbard models with up to 64x64 sites. The free energy and the condensate fraction are studied as a function of temperature.

A statistical sampling approach specifically designed for application in the MCTDH framework facilitates these calculations.

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

Quantum Dissipation with Minimally Extended State Space: A Universal Framework for Exact Time-Local Evolution Equations

XU, Meng (ICQ & IQST, Ulm University), ANKERHOLD, Joachim (ICQ & IQST, Ulm University)

The dynamics of open quantum systems is formulated in a minimally extended state space comprising the degrees of freedom of a system of interest and a finite set of non-unitary, pure-state reservoir modes. This formal structure, derived from the Feynman-Vernon path integral for the reduced density, is shown to lead to an exact time-local evolution equation in a mixed Liouville-Fock space. The crucial ingredient is a mathematically consistent decomposition of the reservoir auto-correlation in terms of harmonic modes with complex-valued frequencies and amplitudes, which are obtained from any given spectral noise power of the physical reservoir. This formulation provides a universal framework to obtain a family of equivalent representations which are directly related to new and established schemes for efficient numerical simulations. By restricting some of the complex-valued mode parameters and performing linear transformations, we make connections to previous approaches, whose auxiliary degrees of freedom are thus revealed as restricted versions of the minimally extended state space presented here. From a practical perspective, the new framework offers a computational tool which combines numerical efficiency and accuracy with long time stability and broad applicability over the whole temperature range and also for strongly structured reservoir mode densities. It can thus deliver high precision data with modest computational resources and simulation times for actual quantum technological devices.

Dynamics of Plasmonic Nanocavities Using a Linear Vibronic Coupling Hamiltonian

JAMSHIDI, Zahra (Associate Professor Sharif University of Technology)

Plasmonic nanoparticles with strong and tunable absorption can concentrate the electromagnetic field in sub-wavelength volumes, significantly enhancing it. This property makes plasmonic nanoparticle cavities attractive for quantum optical applications, facilitating strong light-matter interactions with few or even single emitters at room temperature. The multipolar resonances of the plasmonic cavity facilitate short-range multipolar coupling between the electronic states of the cavity and the emitters. Despite the strong coupling of these sub-diffraction limiting mode volumes, plasmonic cavities typically suffer from short lifetimes due to the inherent large losses of metal nanoparticles. In this presentation, we introduce a theoretical model that accounts for the quantum nature of plasmonic structures and their lossy dynamics within the framework of linear vibronic coupling Hamiltonian. Our Hermitian formalism, integrating parameters from first-principles electronic structure calculations, can accurately characterize the ultra-confined electromagnetic field and the nonradiative dynamics of small and medium-sized metal nanocavities. The coupling between plasmonic and emitter electronic states is examined using the dipolar coupling Hamiltonian. In this model, we investigate the influence of the relative distance and orientation of emitters on the strength of coupling and the splitting of polaritonic states. Quantum dynamics simulations are performed using the multiconfiguration time-dependent Hartree (MCTDH) approach, specifically its multilayer generalization, implemented with the Heidelberg MCTDH package.

References:

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Wednesday — Morning Presentations

July 17th, 8:30 AM – 12:00 AM

Chair: O. Vendrell

Collisions with Cold Molecules: Tomography of Feshbach resonances

[NAREVICIUS, Edvardas \(TU Dortmund\)](#)

During collisions coupling between relative and internal atomic and molecular degrees of freedom leads to the formation of Feshbach resonances. The large phase space volume that particles explore in this metastable scattering state supports interference between many different quantum pathways that include inelastic and reactive processes. We present a new method that allows us to measure simultaneously all the quantum channels for Feshbach resonances that appear in collisions between vibrationally excited H_2^+ ion and noble gas atoms. Our quantum state mapping is based on ion-electron coincidence velocity map imaging spectroscopy.

High-Dimensional Quantum Dynamics Simulations using Tensor Network States

[LARSSON, Henrik \(University of California, Merced\)](#)

The fields of electronic structure and vibrational quantum dynamics have independently developed powerful methods to accurately solve the Schrödinger equation. These methods focus on decomposing the high-dimensional wavefunction as a complicated contraction over smaller dimensional functions, leading to impressive applications for challenging quantum systems in both fields. While the underlying wavefunction representations, known as tensor network states, are very similar, the algorithms used to solve the Schrödinger equation for electronic and vibrational motions are very different. Here, I present an attempt to make a systematic comparison of the strengths and weaknesses of the different approaches in order to gain a better understanding and to promote useful cross-fertilization of ideas [1,2,3].

In particular, I will show how to use a method from electronic structure theory, the density matrix renormalization group (DMRG), for vibrational simulations. I will compare the DMRG to the main algorithm used for vibrational dynamics, the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method. I will show how the DMRG can compute eigenstates at least an order of magnitude faster than the ML-MCTDH method. I will present applications of the DMRG for computing vibrational spectra of challenging systems such as protonated water clusters and molecules with large vibronic coupling. For these systems, the DMRG enabled the computation of more than 1000 high-dimensional eigenstates quickly with high accuracy. Finally, I will show how time-dependent versions of the DMRG can be used successfully in vastly different situations, namely electronic ionization dynamics.

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Non-Adiabatic Spectroscopy and Dynamics: The Linear Vibronic Coupling Model and Beyond

[WORTH, Graham \(UCL\)](#)

The Linear Vibronic Coupling (LVC) Hamiltonian is a standard model used to describe a manifold of coupled electronic states [1]. It has been used with great success to simulate the absorption spectrum and underlying nuclear dynamics of a number of problems. On top of its simple descriptive power, one of its strengths lies in its mathematical form that allows it to be used for accurate solutions of the time-dependent Schrödinger equation (TDSE). However, while it is well suited for describing short-time dynamics, it is not able to treat long-range motion, such as found in photochemical change. For this reason, it is sometimes necessary to go to higher order potentials, or to find other strategies to solve the TDSE. In this presentation, examples of calculations beyond the simple LVC model will be presented. These include the photo-excited dynamics of maleimide [2] and thiophene [3], along with the photoionisation dynamics of cyclobutadiene[4].

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Quantum dynamics of atoms and molecules on surfaces : CH₄/Ni (13D), H/Graphene (72D)

[SHI, Lei \(Université Paris-Saclay\), NADOVESA, Natasa \(CNRS University paris-Saclay\), \[GATTI, Fabien \\(CNRS University paris-Saclay\\)\]\(#\)](#)

Many molecular processes, ranging from fundamental to applied problems, are known today to be impacted by strong nuclear quantum mechanical effects, including phenomena like tunneling, zero point energy effects, or non-adiabatic transitions. Recent success in helping to understand experimental observations in fields like heterogeneous catalysis, photochemistry, reactive scattering, optical spectroscopy, or femto- and attosecond chemistry and spectroscopy underlines that nuclear quantum mechanical effects affect many areas of chemical and physical research. The correct theory to describe the corresponding dynamics is Molecular Quantum Dynamics [1,2]. In contrast to standard quantum chemistry calculations, where the nuclei are treated classically, molecular quantum dynamics can cover quantum mechanical effects in their motion. New strategies have been developed to extend the studies to systems of increasing size. In particular, we present here several applications of the MultiConfiguration Time-Dependent Hartree method (MCTDH) [3,4,5] to the understanding and the control of molecular processes involving quantum effects. MCTDH can be seen as a time dependent MCSCF approach for the nuclei where wavepackets are propagated on one or several potential energy surfaces. Its Multi-Layer variant allows one to treat up to thousands of degrees of freedom. Here, we will present applications of the quantum dynamics of molecules on surfaces such as the formation of a C-H bond (H on Graphene) or the breaking of a chemical bond (CH₄ on Nickel surface) in 72 D highlighting the quantum effects. We will also present cross sections of the breaking of the C-H bond of CH₄ on a surface of Nickel in 13D.

References :

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- [2] Quantum Physics, Applications to Chemistry, F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts, Lectures Notes in Chemistry, Springer, 2017.
- [3] H.-D. Meyer, U. Manthe, and L.S. Cederbaum, The multi-configurational time-dependent Hartree approach. Chem. Phys. Lett. 165 (1990), 73.
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Vibronic quantum dynamics with multiplicative neural network potentials and multiconfigurational thermo-field wavefunctions

BURGHARDT, Irene (Goethe University Frankfurt)

Vibronic quantum dynamics in high-dimensional systems including environmental effects necessitates both accurate diabatic potential energy surfaces and a realistic description of time-evolving system-environment correlations at finite temperature. Here, we illustrate how these requirements can be accommodated by combining hierarchical tensor schemes of ML-MCTDH type and analogous Gaussian-based ML-GMCTDH methods, with machine learning approaches and the thermo-field dynamics representation. Specifically, we focus on multiplicative neural network potentials that match the sum-of-products form of the wavefunction ansatz and can be made to include state-specific system-environment interactions. Applications are shown for vibronic absorption spectra and ultrafast photoinduced isomerization dynamics at conical intersections, along with extensions to lattice Hamiltonians for molecular aggregates.

HDQD... DD: Challenges and applications

PICCONI, David (Heinrich-Heine-Universität Duesseldorf)

Modelling high-dimensional quantum systems in contact with an environment that induces dissipation and decoherence is crucial for many applications in chemical dynamics, photophysics and photochemistry. The most common non-stochastic approaches developed in the field of open quantum systems [1] rely on the determination of the energy levels of the quantum subsystem, that can be done exactly only for low-dimensional problems.

One possibility to model large open quantum systems is to treat the system and the environment at the same level using powerful wavefunction methods such as the multilayer version of the multi-configurational time-dependent Hartree approach. However, the computational time for these calculations might become large for complex problems, where too accurate description of the environment might not even be needed.

In this contribution, alternative, hierarchical strategies are presented, whereby the full-dimensional problem is partitioned into different layers, described with different levels of theory. In these schemes a primary and secondary layers of coordinates are treated using the hybrid Gaussian/MCTDH approach, which describes a small set of coordinates (primary modes) using fully flexible single-particle functions, whereas a larger set of secondary modes is treated with Gaussian wave packets.

Different approximate methods will be discussed to account for the effect of the residual environmental degrees of freedom: (i) an implicit approach based on quantum master equations, solved using non-stochastic open-system Schrödinger equations (NOSSE) [2,3]; (ii) explicit perturbative descriptions; (iii) mixed quantum-classical methods.

The limitations of the different methods are illustrated on prototypical models for chemical dynamics involving vibrational or electronic relaxation.

References:

- [1] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, New York, 2002)
- [2] L. Joubert-Doriol, I. G. Ryabinkin, and A. F. Izmaylov, *J. Chem. Phys.* 141, 234112 (2014)
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Wednesday — Afternoon Presentations

July 17th, 2:00 PM – 6:00 PM

Chair: M. Thoss

Universality class of a spinor BEC (really) far from equilibrium

[SADEGHPOUR, Hossein R. \(ITAMP, Harvard University\)](#)

Universality in equilibrium systems is an established concept. How or if a quantum system exhibits universal behavior, when driven out of equilibrium, is not. I will describe a joint collaboration which establishes universality in a driven 2D ferromagnetic superfluid (^7Li spinor gas) by studying the long time coarsening (merging) dynamics of patterns (topological defects and domain walls) in the spinor fluids, and show that critical exponents become dependent on the symmetry of the Hamiltonian, i. e. whether post quench, the ground state of the system has spin inversion or spin-rotation symmetry [1]. This work establishes how out of equilibrium systems approach equilibrium.

References:

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Spectroscopy and dynamics of molecules strongly coupled to cavity photons

[SAALFRANK, Peter \(University of Potsdam\), FISCHER, Eric \(Humboldt University, Berlin\)](#)

The strong coupling of photons in a cavity to molecular vibrations modifies the molecular spectroscopic response and chemical reactivity. In this talk, vibrational strong coupling (VSC) phenomena will be considered from a quantum dynamical point of view, based on Pauli-Fierz Hamiltonians. The following issues shall be addressed:

- (i) The formation of vibro- and rovibro-polaritons and their signatures in (ro-)vibrational spectra. For small systems, spectra will be calculated non-perturbatively by solving a time-dependent Schrödinger equation [1,2], or, for multi-mode molecules, perturbatively in linear-response double-harmonic approximation [3].
- (ii) The influence of VSC on rates and yields of chemical reactions and their possible control [4,5,6].
- (iii) Finally, the validity of the Born-Oppenheimer approximation in VSC will be addressed. [7].

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High-dimensional quantum dynamics with the ML-MCTDH method: a perspective on the applications to protonated water clusters

[VENDRELL, Oriol](#) (*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg*)

Protonated water clusters in the gas phase provide finite realizations of the solvated proton. As their size increases, these realizations become increasingly closer to the solvated proton in the condensed phase. Hence, they have been the target of multiple experimental and theoretical investigations over the years.

In this talk I will review the application of the (ML-)MCTDH method to the spectroscopy and dynamics of protonated water clusters, starting with the 15-D Zundel cation $H_5O_2^+$, covering the Eigen cation $H_9O_4^+$, and finishing with the 51-D extended Zundel cation $H_{13}O_6^+$. In passing, I will mention the various technical and methodological challenges faced by these investigations, and how they were overcome.

Techniques for computing the dynamics of matter in strong x-ray fields

[SANTRA, Robin](#) (*Deutsches Elektronen-Synchrotron DESY and Universität Hamburg*)

For certain applications of x-ray free-electron lasers, such as the European XFEL in the Hamburg metropolitan area, the x-ray beams have to be so tightly focused that individual atoms in matter may absorb several photons during a single x-ray pulse. X-ray multiphoton absorption, combined with inner-shell decay cascades, gives rise to ultrafast electronic ionization dynamics. In order to account for and, when needed, correct for the associated electronic damage, we are developing theoretical models and associated software that undergo testing and validation against experimental data collected at x-ray free-electron lasers (see Refs. [1-4] for recent examples). In this presentation, I will focus on gas-phase atoms and discuss the latest developments in how we handle the corresponding nonstationary quantum-mechanical electronic-structure problem, in which atoms can lose a considerable fraction, or even all, of their electrons on femtosecond time scales.

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- [4] A. Rörig *et al.*, *Nature Commun.* **14**, 5738 (2023).

Theoretical description of attosecond imaging and spectroscopy of electron dynamics with ultrashort x-ray pulses

[GORELOVA, Daria \(University of Hamburg\)](#)

We explore how attosecond x-ray and extreme ultraviolet pulses can be employed for imaging electron dynamics in real time. In the first part of my talk, I will present our ab initio description of experiments, in which x-ray pulses probe materials during the time they are driven by an optical light. Namely, we show how attosecond x-ray diffraction and x-ray absorption spectroscopy can reveal microscopic details about laser-dressed materials. In the second part of my talk, I will review our theoretical developments to describe pump-probe experiments, in which a pump and a probe pulses are time delayed. We describe ultrafast imaging by means of photoelectron momentum microscopy with extreme ultraviolet pulses. I will talk about attosecond momentum-resolved resonant x-ray scattering that is another imaging technique to follow electron dynamics in materials. We developed an ab initio scheme based on the Bethe-Salpeter equation and the full-potential linearized augmented-plane-wave method to treat optical-pump – resonant x-ray probe-techniques and will demonstrate our results for x-ray absorption spectroscopy of optically-excited excitons in 4H-SiC.

Quantum Dynamics Simulation of Exciton-Polariton Transport in an organic microcavity

[KRUPP, Niclas \(Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg\)](#), [VENDRELL, Oriol \(Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg\)](#)

Hybrid light-matter systems offer high control and tunability of material properties through strong coupling between cavity photons and material excitations. Potential applications encompass optoelectronic devices such as ultrafast switches, transistors, gates and photovoltaic cells. In particular, quasiparticles consisting of excitons and photons – termed exciton-polaritons (EPs) – display long-range and long-lived propagation at velocities reaching significant fractions of the speed of light. Recent experimental progress in ultrafast microscopy enables to observe EP propagation with high spatiotemporal resolution in organic semiconductors [1, 2]. Crucially, organic condensed-phase cavities exhibit static and dynamic disorder, connected to the inhomogeneous broadening of the excitonic resonance and vibronic motion, respectively. Both lead to elastic and inelastic scattering of EPs [1-3], but a thorough understanding of their impact on polariton transport is still lacking. Here, we address these questions with quantum dynamical simulations, treating cavity photons, molecular electronic and vibrational degrees of freedom fully quantum-mechanically. Our model includes more than 200 electro-magnetic modes coupled to an array of more than 200 vibrating molecules. To meet the challenge of such high-dimensional systems, we employ the Multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method. Our results help to disentangle the impact of static and dynamic disorder, providing mechanistic insight into EP transport in perfect and lossy organic microcavities. Beyond that, our simulations showcase ML-MCTDH's powerful abilities in tackling the quantum dynamics of correlated light-matter systems in the many-molecule, many-mode regime.

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A fully dynamical quantum description of ultrafast X-ray spectroscopy of pyrazine

FREIBERT, Antonia (University of Hamburg), MENDIVE-TAPIA, David (Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg), HUSE, Nils (Universität Hamburg), VENDRELL, Oriol (Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg)

Recent developments of short-pulse X-ray sources have enabled the extension of ultrafast pump-probe techniques into the X-ray domain allowing to measure not only equilibrium X-ray spectra but also to track dynamical processes in transient species. The combination of element-specific core-level probing with unprecedented femtosecond time resolution revolutionized the ability to observe photoinduced electronic and structural changes. Due to the complex nature of detecting structural dynamics on ultrafast time scales, detailed theoretical studies are required to link the spectroscopic observables to the underlying dynamics and thereby access the high information content contained in ultrafast X-ray spectra. In this context, a substantial influence of nuclear dynamics is expected in nonlinear spectroscopy, demanding a time-dependent framework capable of describing non-adiabatic phenomena. I will present full time domain approaches for calculating transient X-ray absorption [1] and resonant inelastic X-ray scattering.[2,3] To exemplify these approaches, I will showcase ultrafast X-ray spectroscopy simulations of pyrazine at the nitrogen K-edge, incorporating wavepacket dynamics in both valence- and core-excited state manifolds. The validity of the widely used short-time (or Lorentzian limit) approximation which neglects the nuclear dynamics following the X-ray interrogation will be discussed. Furthermore, the impact of an explicit description of the external electric field will be demonstrated providing a foundation for state-of-the-art time-resolved experiments with pulsed coherent light sources.

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Thursday — Morning Presentations

July 18th, 8:30 AM – 12:00 AM

Chair: I. Burghardt

Recent developments in the MCTDH approach

[MANTHE, Uwe \(Bielefeld University\)](#)

Recent methodological work on the (multi-layer) multi-configurational time-dependent Hartree (MCTDH) approach frequently relied on a systematic analysis of the underlying tree tensor network structure. It also highlighted common aspects present in the MCTDH and density matrix renormalization group (DMRG) or matrix product state (MPS) approaches. If the dynamics of molecular systems is studied on realistic ab-initio based potential energy surfaces (PES), the representation of the Hamiltonian in a form suitable for MCTDH or DMRG calculations is a key problem to be addressed. Two different types of strategies have been successfully applied in large scale applications to address the issue: either the PES is refitted in a sum of product form (using the POTFIT scheme or related approaches) or a time-dependent grid representation, the correlation discrete variable representation (CDVR), is used to efficiently evaluate the potential energy matrix elements. In this talk, the ideas underlying the CDVR approach are reviewed and a new version of the CDVR approach is introduced. This new version, the non-hierarchical CDVR, takes full advantage of the symmetries present in the tree tensor network. In addition, an extension of the CDVR approach that facilitates numerically exact quadrature is discussed. 24-dimensional wavepacket dynamics calculations studying the non-adiabatic dynamics in pyrazine illustrate the properties of the new CDVR scheme. It is shown that correct results can be obtained with a remarkably small number of quadrature points. Furthermore, the CDVR scheme enables the efficient calculation of adiabatic electronic populations and related observables based on existing wavefunction data. Depending on availability and time available, further results or methodological aspects of the MCTDH approach in second quantization will be discussed.

Orbital entanglement between ultracold lattice atoms: A showcase of how ML-MCTDHX benefits quantum gas investigations

[CAO, Lushuai \(Huazhong University of Science and Technology\)](#)

In this talk, I will present our theoretical investigation on preparing determined entangled states on the orbital degree of freedom (DoF) of ultracold atoms confined in the double-well superlattice. The orbital DoF refers to the single-particle energy levels in each site, and is normally treated with the extended Hubbard model, which is constructed by the multi-band Wannier function. The multi-band Wannier function is, however, time-independent, and cannot thoroughly capture the temporal modification of the lattice potential, which has become a key tool in lattice atom manipulation. ML-MCTDHX inherits the time-dependent SPF from MCTDH family, which bears the ability to spontaneously adapt to the temporal modification of the optical lattice. Moreover, the SPF also helps to uncover a hidden symmetry with respect to the orbital DoF, which guarantees the selective excitation of entangled states in degeneration. Our work, in general, highlights the flexibility of ML-MCTDHX in dealing with time-dependent Hamiltonians.

Phases and correlated dynamics of droplet and bubble self-bound states of matter

[*MISTAKIDIS, Simeon \(Missouri University of Science and Technology\)*](#)

We will discuss the formation of quantum droplet and bubble phases of matter arising in two-component attractively interacting bosonic mixtures. Insights regarding the interplay of atom and interaction imbalance as well as the impact of dimensionality will be elucidated. These phases are analyzed within the extended Gross-Pitaevskii framework and the ab-initio ML-MCTDHF method which allows to identify beyond Lee-Huang-Yang correlations. A simplified effective model based on the established Lee-Huang-Yang theory is constructed and found to provide qualitative analytical predictions. For instance, it is explicated that for moderate particle imbalance each component maintains its droplet flat-top or Gaussian type character depending on the intercomponent attraction. Interestingly, an increasing intercomponent imbalance leads to a flat-top shape of the majority component with the minority exhibiting spatially localized configurations. The latter imprint modulations on the majority component which become more pronounced for increasing interspecies attraction. The underlying two-body correlation patterns of the above-mentioned structural transitions will be also explicated. Further applications to vortex structures, kink configurations and dispersive shock-waves will be provided.

Hyperfine and Zeeman effects in the high-resolution rovibrational spectrum of H₃⁺

[*MATYUS, Edit \(ELTE, Eotvos Lorand University\)*](#)

In this talk, I will present our recent work on modelling magnetic effects in the high-resolution rovibrational spectrum of the H₃⁺ molecular ion.

Crossover from attractive to repulsive induced interactions and bound states of two distinguishable Bose polarons

[THEEL, Friethjof](#) (*Center for Optical Quantum Technologies, Department of Physics, University of Hamburg*)

We study the impact of induced correlations and quasiparticle properties by immersing two distinguishable impurities in a harmonically trapped bosonic medium. It is found that when the impurities couple both either repulsively or attractively to their host, the latter mediates a two-body correlated behavior between them. In the reverse case, namely the impurities interact oppositely with the host, they feature anti-bunching. Monitoring the impurities relative distance and constructing an effective two-body model to be compared with the full many-body calculations, we are able to associate the induced (anti-) correlated behavior of the impurities with the presence of attractive (repulsive) induced interactions. Furthermore, we capture the formation of a bipolaron and a trimer state in the strongly attractive regime. The trimer refers to the correlated behavior of two impurities and a representative atom of the bosonic medium and it is characterized by an ellipsoidal shape of the three-body correlation function. Our results open the way for controlling polaron induced correlations and creating relevant bound states.

Quantum Dynamics of the Reaction of Chlorine with Methane

[HOPPE, Hannes](#) (*Bielefeld University*), [MANTHE, Uwe](#) (*Bielefeld University*)

Full-dimensional quantum mechanical studies employing these reactions are very challenging. Thermal rate constants as well as quantum-state resolved reaction probabilities were calculated employing the ML-MCTDH (multi-layer multi-configurational time-dependent Hartree) approach in full dimensionality for the $\text{H} + \text{CH}_4$ reaction and its isotopic analogues. These calculations employ an intuitive and rigorously correct quantum transition state concept. Within this approach, flux correlation functions are employed to obtain thermal rate constants.

This work reports a full-dimensional quantum dynamics simulation of the $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$, $\text{Cl} + \text{CHD}_3 \rightarrow \text{HCl} + \text{CD}_3$ and $\text{Cl} + \text{CD}_4 \rightarrow \text{DCl} + \text{CD}_3$ reactions based on first principles. The resulting thermal rate constants are in great agreement with experimental data. Comparisons to approximative theories show deviations up to significant amounts for the reaction of Cl with CH_4 , but not for the reactions of Cl with CHD_3 or CD_4 .

Optimizing Orbital Angular Momentum Transfer in Ro-Vibrational Spectroscopy of Diatomic Molecules

KOUTENTAKIS, Georgios (Institute of Science and Technology Austria (ISTA)), HRAST, Mateja (Institute of Science and Technology Austria (ISTA)), LEMESHKO, Mikhail (Institute of Science and Technology Austria (ISTA)), MASLOV, Mikhail (Institute of Science and Technology Austria (ISTA)), BAHL, Monika (University of Vienna), HECKL, Oliver H. (University of Vienna), JUNGNICKELE, Tom (University of Vienna)

Optical vortex beams have intrigued researchers since Allen's seminal 1992 paper. Each photon in these beams carries orbital angular momentum in addition to spin momentum. These beams have diverse applications, including optical tweezers and quantum information processing. Recently, we have shown that the non-zero vorticity of such helical beams can significantly enhance certain ro-vibrational transitions that are otherwise forbidden in non-helical light spectroscopy. In particular, we have found that electric field interacts with the multipole moments of the molecule through its spherical gradients, thus enabling orbital momentum transfer via quadrupole or higher order transitions.

Building on this concept, we aim to optimize the electric field distribution to maximize the interaction between photons and molecules. By analyzing the incident and scattered light by quadrupolar diatomic molecular media, we unveil the field configurations that increase the orbital angular momentum transfer among the light and molecule. Optical vortex lattice configurations, either resulting from either multiple scalar beam interference or vortex beam diffraction, are found to be an ideal platform to observe and control the orbital angular momentum transfer. This method highlights the synergistic interplay between the number, size, and charge of vortex cores, leading to improved interaction efficiency for spectroscopic applications. Harnessing the potential of such structured optical fields, paves the way for significant advances in molecular spectroscopy.

Friday— Morning Presentations

July 19th, 9:00 AM – 11:50 AM

Chair: O. Vendrell

Molecular Quantum Dynamics with the Density Matrix Renormalization Group

[ERAKOVIC, Mihael \(ETH Zurich\)](#), [REIHER, Markus \(ETH Zurich\)](#)

Accurate methods for the description of the quantum dynamics in molecular systems provide an invaluable insight into a variety of physical processes and molecular properties. Examples include the calculation of molecular spectra, the simulation of nonadiabatic dynamics, and light-matter interaction. Simulation of molecular quantum dynamics has become an invaluable tool for both the interpretation of a wide range of experimental data and for the design of experimental setups. For an accurate description of most molecular systems, a large number of degrees of freedom must be included in the quantum dynamics simulation, which can quickly increase the computational cost beyond the available resources. It is therefore essential to develop new approximate, yet accurate computational methods that can cope with the quantum dynamics of large molecular systems.

The density matrix renormalization group (DMRG) exploits the matrix product state (MPS) form of the electronic wave function to efficiently encode and compress wavefunctions with many degrees of freedom. Moreover, the tangent-space time-dependent DMRG (TD-DMRG) method provides an efficient time propagation algorithm in which propagation step of the entire many-dimensional wavefunction is reduced to a series of propagations of smaller tensors along the MPS, resulting in a sweep-based algorithm for time evolution. Consequently, TD-DMRG is an ideal method for tackling the problem of large-scale molecular dynamics.

We present a robust and versatile framework for tangent-space TD-DMRG simulations of vibrational [1,2] and vibronic dynamics [3] as a part of our QCMAquis software [4]. We utilize this method to obtain IR and vibronic spectra of selected molecules, as well as to obtain nonadiabatic relaxation dynamics of pyrazine. Furthermore, we demonstrate the applicability of TD-DMRG to the systems with time-dependent Hamiltonians and use it to simulate interaction of molecules with electromagnetic radiation [5]. Finally, we combine TD-DMRG method with the laser pulse optimization algorithm to tackle the problem of quantum optimal control. [6]

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Time crystals in an atom-cavity system

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Quantum molecular dynamics with coupled cluster and direct methods

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Quantum molecular dynamics is important for understanding many phenomena in nature and in the laboratory, but explicitly simulating this dynamics presents many theoretical and practical challenges. These challenges include (i) obtaining potential energy surfaces (PESs) in a suitable format and (ii) describing nuclear motion with time-dependent wave functions. The cost of both parts scales steeply with the number of degrees of freedom, making computations on all but the smallest systems difficult. I will describe our current work on developing a range of new theories and computational methods that aim at providing efficient and accurate quantum dynamical computations on large systems.

I will describe our exploration into the possibilities of using coupled cluster methods for quantum dynamics. Time-dependent vibrational coupled cluster (TDVCC) (static basis set) is introduced along with time-dependent modals vibrational coupled cluster (TDMVCC) (adaptive basis set). Using the non-variational coupled cluster ansatz to describe dynamics presents a number of challenges in terms of fundamental theory and practical realization. I will give an overview of specific challenges and solutions that we found during the development of an efficient, accurate and stable theory. This includes the usage of biorthonormal basis sets, parametrization of single-particle basis functions (including linear, polar and exponential parameterization), and considerations for obtaining theories and codes with attractive computational scaling with respect to the number of degrees of freedom.

There can be no dynamics simulation without a potential energy surface. I will outline our newest initiatives towards a time-dependent adaptive density-guided approach (TD-ADGA) for constructing the PES on the fly while the wave packet evolves.

Coupled-cluster for trapped bosonic mixtures

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A coupled-cluster theory for bosonic mixtures of binary species in external traps is developed, providing a promising theoretical approach to demonstrate highly accurately the many-body physics of mixtures of Bose-Einstein condensates. The coupled-cluster wavefunction for the binary species is obtained when an exponential cluster operator e^T , where $T = T(1) + T(2) + T(12)$ and $T(1)$ accounts for excitations in species-1 bosons, $T(2)$ for excitations in species-2 bosons, and $T(12)$ for combined excitations in both species, acts on the ground state configuration prepared by accumulating all bosons in a single orbital for each species. The working equations for bosonic mixtures are derived by truncating the cluster operator upto the single and double excitations and using an arbitrary sets of orthonormal orbitals for each of the species. Further, the comparatively simplified version of the working equations are formulated using the Fock-like operators. Finally, using an exactly solvable many-body model for bosonic mixtures that exists in the literature allows us to implement and test the performance and accuracy of the coupled-cluster theory for situations with balanced as well as imbalanced boson numbers and for weak to moderately strong intraspecies and interspecies interaction strengths. The comparison between the computed results using coupled-cluster theory with the respective analytical exact results displays remarkable agreement exhibiting excellent success of the coupled-cluster theory for bosonic mixtures. All in all, the correlation exhaustive coupled-cluster theory shows encouraging results and it could be a promising approach in paving the way for high-accuracy modelling of various bosonic mixture systems.

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

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

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Poster abstracts

P01: A Molecular Dynamics/Quantum Vibronic Approach for Unrevealing the Contributions to the Spectral Shape and Fluorescence Quenching of Zinc Phthalocyanine Dyes Upon Aggregation

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Self-assembly strongly affects the photochemical and photophysics of molecules and results in optical properties that are largely structure-dependent. While Kasha's theory is capable of interpreting some general spectral changes observed in aggregates, a comprehensive understanding of the structure-(optical)-property relations requires more sophisticated computational modeling since other effects such as charge-transfer (CT) excitations, vibronic couplings, and nuclear motions due to the interaction with the environment generally play a fundamental role. In the specific case of the Zinc-Phthalocyanine (ZnPc) dyes, two lowest excited states show near-degeneracy, undergoing Jahn-Teller (JT)-like distortions. This calls for an accurate computational modeling by going beyond Kasha's model, taking into account all these effects. Here, we developed a quantum-classical protocol to investigate the interplay of intra-molecular (JT) and intermolecular (exciton-exciton and exciton-charge transfer) vibronic coupling effects together with thermal dynamical fluctuations on the spectroscopy and ultrafast photoinduced dynamics of ZnPc dyes upon aggregation in solution. According to this protocol, the solute and solvent nuclear degrees of freedom of the system are adiabatically separated into the so-called stiff and soft modes. The fast stiff modes, i.e., the intra-molecular vibrations of the monomers, are described at the quantum dynamical (QD) level through ML-MCTDH wavepacket propagation on the coupled electronic states described with a generalized linear vibronic coupling model, parametrized with a maximum-overlap diabaticization. On the contrary, the slow soft modes, describing the solvent and the relative arrangement of the monomers, are treated classically by molecular dynamics (MD) simulations. The proposed protocol accurately reproduces the change in experimental spectral features upon aggregation, clarifies that the blue-shift associated to ZnPc aggregation in aqueous solutions is mainly driven by excitonic interactions among local excitation (LE) states, while their couplings with CT states are responsible for the modulation of relative intensities and lineshape broadening of the vibronic bands. Moreover, MD simulations reveal that thermal fluctuations of dye aggregates are responsible for the modulation of the band intensity and broadening of the low-energy band. The ML-MCTDH quantum dynamics simulations exhibit an effective ultrafast population transfer to the dark CT states, suggesting a mechanism for the fluorescence quenching of ZnPc dyes in water solution, typical for H-type aggregates.

P02: Defy the Curse of Dimensionality in Potential Energy Surfaces with Sparse Grids and Local Polynomial Interpolation

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The Potential Energy Surface (PES) provides the potential energy as a function of the nuclear configurations and thereby governs nuclear dynamics. It is thus a crucial ingredient for simulations and the understanding of the spectroscopic and dynamics properties of molecular systems. In general, there are several reasons why it is preferable to pre-construct a PES rather than to use "on-the-fly" methods. Modeled potentials are several orders of magnitude faster to evaluate than electronic structure computations and may be constructed to provide a level of accuracy not affordable with "on-the-fly" methods.

Sampling is a key issue, a "curse", in high dimensional model fitting. Indeed, sampling should be simultaneously homogeneous to avoid a disbalance in the distribution of training data, but each computed point should provide as much information as possible about the function to be fitted. For this purpose, we compute points on sparse grids to mitigate the impact of the high dimensionality. Sparse grids are adaptively selected combinations of lower-dimensional grids, which alleviate the sampling problems. They are intended to leave out subspaces within the full grid that provide minor contributions to the sampled function in a similar spirit that n-body functions contribute incrementally less as n increases.

We obtain a smooth interpolation between the computed points from local polynomial primitive functions. Doing so allows for a systematical improvement of the PES expressions, which are in sum-of-product form by design. Therefore, such PESs can take full advantage of quantum dynamics software packages such as the Heidelberg implementation of the Multiconfigurational Time Dependent Hartree (MCTDH) method. The methodology is illustrated by comparison of computed vibrational states of the nitrous acid molecule (HONO) and available experimental data. HONO is a benchmark for this purpose and exhibits a two minima potential in its ground electronic state. We explore the extension of the methodology to (1) obtain a global PES from local ones stitched together and (2) multi-fidelity models, where low-level PESs are elevated to higher-level quality by corrections obtained from sparser data sets.

P03: Anharmonic vibration-translation-rotation of diatomic molecule encapsulated in hydrated clathrate cages

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Hydrate clathrates are crystalline compounds composed of water molecules that form cages in which small molecules are encapsulated, depending on the thermodynamic conditions of formation [1]. Two systems are studied: (i) Carbon monoxide hydrate, which can be considered an important component of the carbon cycle in the solar system, since CO gas is one of the predominant forms of carbon [1]. (ii) The H₂ clathrate hydrate, which is of great interest because of its potential as a hydrogen storage material [2].

The aim of this work is to solve the time-independent Schrödinger equation, to calculate the anharmonic Vibration-Translation-Rotation (VTR) levels of diatomic molecules trapped in the clathrate hydrates. We will then calculate the vibrational shift of the diatomic molecules resulting from its encapsulation in the water cage.

In our calculations, we use a quantum dynamics code, EIVibRot [3], and two recent potentials [2,4]. (fitted with a neural network and derived from ab initio calculations at CCSD(T)-F12a) to evaluate the interactions between the trapped molecule (CO or H₂) and H₂O molecules. We will present our results of quantum calculations of the anharmonic levels of the VTR motions of H₂ and CO trapped in H₂O cages. We will then deduce the order of magnitude of the vibrational shift of them that has been measured experimentally [5] and also the influence of the 3-body contributions on the VTR levels.

KEYWORDS: Diatomic; clathrate; vibration; translation; rotation; anharmonic.

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P04: Advanced HHG spectra with the TD-CI method

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High-harmonics generation (HHG) is central to the field of ultrafast, attosecond pulses and electron dynamics. Its description demands high accuracy in large-amplitude electron motion, the representation of ionization and other underlying electronic effects.

We employ the time-dependent configuration interaction method (TD-CI) using Gaussian-type orbitals to model this process and simulate HHG spectra. But as most current calculations are limited to the unperturbed, fixed-nuclei approximation, we present extensions to handle complex environments beyond that. In this context, we will discuss, among others, nuclear motion (Albrecht, Witzorky, Saalfrank and Klamroth *J. Phys. Chem. A* **2023**, 127, 28, 5942–5955).

P05: Cationic Phosphorous Hydrides: PH^+ and PH_2^+ molecules

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The astrochemical studies of the P-bearing molecules have attracted great interest in the latest years, since the increase of observations of these kind of molecules in several astrophysical objects. However, the chemistry of the P atom is neither very well-known nor well understood, making it difficult to develop chemical models to understand the origin of these molecules.[1] One of the possible triggers for the chemistry of the P atom are the phosphorous hydride molecules, supported by the great abundance of the H_2 molecules.[2] The simplest hydride is the PH^+ , which could be formed by the reaction of $\text{P} + \text{H}_2 \rightarrow \text{PH} + \text{H}$, reaction that may yield to the formation of the intermediate structure PH_2^+ . Due to the open-shell of both reaction channels (being P^+ (^3P) and PH^+ ($X^2\text{II}$)), several electronic states will be needed to correctly describe the dynamics of the reaction. In addition, for the correct description of reactants and products, we would need to correctly characterize the electronic states of H_2 and PH^+ .

Since the H_2 molecule is well characterized and the energy between its electronic states is much higher than for the PH^+ radical, in this study we will focus on the latter. To check the accuracy of the Potential Energy Curves (PECs) of PH^+ , we will study the fluorescence lifetime of several rovibrational levels of the electronic excited state $A^2\Delta$ to the ground state $X^2\text{II}$ and we will compare it with the experiments. Moreover, there are experimental evidences of competition between the fluorescence and the predissociation through the 1^4II excited dissociative state,[3] which we will also be investigating.

Finally, we will present the preliminary results on the Potential Energy Surfaces (PES) of the two first triplet states of the PH_2^+ system. The presence of conical intersections and the strategies employed to describe them properly will be discussed.

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P06: A system-bath model to investigate the quantum dynamics of complex or interacting molecular systems

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Addressing the dynamics of molecular systems coupled to an environment is a challenging task, especially when considering finite-size environments that can be affected by their interactions with the smaller system. In such cases, the usual open quantum system methods and approximations might fail as they assume that the environment (or “bath”) is infinite, always at thermodynamical equilibrium, and not perturbed by the system [1]. In particular, they do not take into account the fact that finite environments can be heated by the excitation of the system and evolve out of equilibrium. Such situations may occur when studying molecules in clusters or matrices [2], or when probing small molecules trapped in fullerenes [3], for example.

In this context, we are developing a new theoretical model based on a system-bath approach where we consider a one-dimensional system (e.g., one vibrational mode) interacting with a large harmonic bath (~100-1000 modes). The system and its coupling to individual bath modes are treated as rigorously as possible, but the bath part of the Hamiltonian is simplified, with its modes being replaced by a single ladder of effective bath states that describe the energy stored inside the bath. This model allows us to study the relaxation dynamics of the system at finite temperature and to analyze the response of the bath to the system’s excitation.

In this contribution, we will present this Effective Bath State (EBS) model as well as the first results obtained by using this method on a model system taken from [4], where an O-H stretching mode interacts with a bath of 40 to 600 harmonic oscillators. We will also discuss our current efforts to generalize this method in order to obtain finite-temperature infrared spectra of complex molecules.

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P07: Using n-mode expansion-based kinetic energy operators in vibrationally correlated calculations

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The investigation of chemical properties and processes of sizable molecular compounds at the quantum chemical level is significantly impeded by the inherent exponential scaling of the computations' numerical cost with the system size. It is thus of great importance to find theoretical and numerical approaches that increase the efficiency of quantum chemical calculations, such that they become accurate and affordable for systems of interest.

The foundation of a quantum chemical simulation of molecular motion is laid by the coordinate system that is selected to parameterize the investigated compound's degrees of freedom. A beneficial choice of the coordinate system typically corresponds to a set of strongly decoupled coordinates that naturally represents the investigated processes. One commonly employed type of coordinates is rectilinear normal coordinates, which are very suitable for the description of small amplitude motion, for example when studying low-lying vibrational excitations in a molecule or generally small displacements around a reference structure. In the case of large amplitude motion, which occurs in highly excited vibrations, torsional motion as well as dissociation reactions, employing general curvilinear coordinate systems is typically more adequate. This type of coordinates has been shown to yield reduced coupling in the potential energy surfaces (PES) and nuclear wave functions, but often at the cost of more involved kinetic energy operators (KEO).

In this work, we present time-independent vibrationally correlated calculations using polyspherical curvilinear coordinate systems, which we combine with truncated n-mode expansion-based representations of the kinetic energy operator (and the potential energy surface). The resulting KEO approximations produce accurate results in our test calculations, with the added benefits of increased control over the intermode coupling in the KEO and the option to apply further schemes to reduce the numerical cost, such as coefficient screening. This bodes well for applications of vibrational coupled cluster methods in combination with general coordinate systems to larger molecular systems. Moreover, we demonstrate a workflow to build up accurate n-mode expansion-based KEO and PES representations from low-level KEO approximations.

P08: Inter-particle Coulombic electron capture: Coupled electron-nuclear dynamics model calculations on the NeHe⁺ dimer

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Inter-particle Coulombic electron capture (ICEC) is a process in which a free electron can efficiently attach to an acceptor A (i.e. ion, atom, molecule, quantum dot, etc). The excess attachment energy is transferred to a neighbouring system B which gets ionized (or excited), $e(\epsilon) + A + B \rightarrow A^- + B^+ + e(\epsilon')$ where an eventual nuclear displacement is possible.

The proposed model system for an incoming electron colliding with NeHe⁺ consists of two electronic degrees of freedom in one dimension (x_1 and x_2) and one nuclear degree of freedom (R) which describes the distance between the atoms and allows us to analyse the role played by nuclear dissociation in the ICEC process. In the full Hamiltonian the potential terms were parametrized to reproduce atomic parameters of He and Ne. This Hamiltonian was previously employed to calculate the full dynamics time propagation of the system with appropriate initial conditions, namely an incoming electron as a Gaussian wavepacket and NeHe⁺ in the ground state. This was done with the multiconfigurational time dependent Hartree method (MCTDH-Heidelberg Package).

An extended Born-Oppenheimer approximation was later applied in order to reduce the dimensionality of the system and explore its validity. This approximation consists of solving the static fixed-nuclei NeHe⁺ system with a single electron coordinate. The resulting electronic eigenstates $\varphi_n(x; R)$ were used in the Born representation for the total wavefunction $\Psi(x_1, x_2, R, t) = \sum_i \chi_i(R, x_1, t) \varphi_i(x_2; R)$ which was then used to solve the time-dependent Schrödinger equation with the full Hamiltonian, considering only two or three electronic surfaces. The comparison with the full dynamics simulation serves to identify the importance of the different degrees of freedom to the full ICEC process.

P09: Synthetic dimension-induced pseudo Jahn-Teller effect in one-dimensional confined fermions

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We demonstrate the failure of the adiabatic Born-Oppenheimer approximation to describe the ground state of a quantum impurity within an ultracold Fermi gas despite substantial mass differences between the bath and impurity species. Increasing repulsion leads to the appearance of non-adiabatic couplings between the fast bath and slow impurity degrees of freedom which reduce the parity symmetry of the latter according to the pseudo Jahn-Teller effect. The presence of this mechanism is associated to a conical intersection involving the impurity position and the inverse of the interaction strength which acts as a synthetic dimension. We elucidate the presence of these effects via a detailed ground state analysis involving the comparison of ab initio fully-correlated simulations with effective models. Our study suggests ultracold atomic ensembles as potent emulators of complex molecular phenomena.

P10: Theoretical description of X-ray absorption of laser-driven materials

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We developed an ab initio approach to describe a process, in which ultrafast X-ray absorption is applied to measure electron dynamics in a material during the action of a driving optical field.

We obtain laser-dressed electronic states within the Floquet-Bloch formalism combined with the Density Functional Theory [1] within the LAPW+lo method [2]. We describe the interaction of a laser-dressed electronic system with an X-ray pulse using the density matrix formalism and calculate the X-ray absorption probability. We show that the developed technique gives information about dynamical changes in the electronic population of valence and conduction bands in site- and orbital-resolved manner. We calculate the modification of partial density of states (PDOS) in the presence of external driving, analyze the connection between laser-induced electron dynamics and changes in X-ray absorption spectra by performing calculations for wurtzite ZnO.

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P11: Charge-Transfer Dynamics in Two-Dimensional Systems: Effect of Dynamic and Static disorder

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The development of high mobility organic semiconductors (OSC) is crucial for the advancement of most organic electronic devices. A significant theoretical effort is currently underway to provide effective numerical tools for the simulation of complex materials and to gain a detailed understanding of the fundamental mechanisms that can have a detrimental effect on this property.[1,2] Since early theories, the static and dynamic disorder of OSCs have been identified as two major physical properties controlling charge-transfer dynamics and delocalization.[3,4] An exact quantum dynamical analysis including both effects would be extremely helpful for disentangling their relative importance but, due to the inherent complexity of these systems, such analyses are very rare. Here we develop a model for charge transfer in two-dimensional systems including the effect of dynamic disorder and static disorder employing a novel method developed by Gelin and Borrelli.[5] The model considers the impact of low-frequency intermolecular vibrations of the OSC units on the transfer integrals and explicitly treats the high-frequency intramolecular modes that carry most of the reorganization energy of the process. The role of temperature is taken into account by using the Thermo-Field Dynamics methodology,[6] while static disorder is introduced via a set of auxiliary Gaussian variables. The high-dimensional quantum dynamical problem is then solved by employing a Tensor-Train representation of the full vibronic wave function.[7] The interplay of the two effects is discussed by computing the mean square particle deviation (MSD) as the inverse participation ratio (IPR). From these two parameters it is possible to infer a variety of properties related to charge mobility.

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P12: Inter-Chain Exciton Transport and Exciton Dissociation in P3HT:PCBM

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In a prototypical organic photovoltaic material composed of poly(3-hexylthiophene) (P3HT) and phenyl-C61 butyric acid methyl ester (PCBM), exciton migration in the P3HT domain is followed by ultrafast charge separation at the heterojunction interface to PCBM. Here, we present full quantum simulations of these processes, for an H-aggregated model system of regioregular P3HT (rrP3HT)[1] in conjunction with a coarse-grained PCBM acceptor domain.[2] A first principles parametrized electron-hole lattice Hamiltonian is employed featuring local high-frequency modes and anharmonic, site-correlated inter-chain modes. Temperature effects are included within a stochastic mean-field approach, using importance sampling from a thermal Wigner distribution of sets of bath modes. Quantum dynamical simulations are carried out with the multi-layer multi-configuration time dependent Hartree (ML-MCTDH) method for tens of electronic states and hundreds of vibrational modes. The observed exciton migration is driven by anharmonic low-frequency inter-chain modes and features transient localization effects. Upon reaching the interface, the exciton dissociates and population is transferred primarily to the interfacial charge transfer state. Depending on the effective Coulomb barrier to electron-hole separation, long-range charge separated states are generated on ultrafast time scales. Based on these simulations, the coherent nature of the elementary exciton migration and dissociation steps is analyzed.

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P13: Efficient time-dependent vibrational coupled cluster computations with time dependent basis sets at the two-mode coupling level

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Recently, theories have been developed for employing time-dependent modals with vibrational coupled cluster theory (TDMVCC) showing good accuracy illustrated in benchmark computations using pilot implementations.

Here we show work and results from an efficient implementation of TDMVCC at the two-mode level i.e. the cluster amplitudes and the hamiltonian contains couplings for up to two modes. In this implementation a careful regrouping of certain terms in some of the equations of motion results in propagation of the wave function with a computational scaling as a third order polynomial with respect to the number of modes in a given system.

Illustrative TDMVCC calculations showing the computational scaling are presented for polyaromatic hydrocarbons (PAHs) with up to 192 modes (66 atoms) as well as intramolecular vibrational energy redistribution (IVR) computations performed on benzoic acid are presented. These results will also contain data obtained in a limit of the modal basis giving a TDMVCC/TDH hybrid method presented as an alternative to freezing out modes of relatively low importance.

P14: Mixed quantum-classical dynamics for near term quantum computers

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Mixed quantum-classical dynamics is a set of methods often used to understand systems too complex to treat fully quantum mechanically. Many techniques exist for full quantum mechanical evolution on quantum computers, but mixed quantum-classical dynamics are less explored. We present a modular algorithm for general mixed quantum-classical dynamics where the quantum subsystem is coupled with the classical subsystem. We test it on a modified Shin-Metiu model in the first quantization through Ehrenfest propagation. We find that the Time-Dependent Variational Time Propagation algorithm performs well for short-time evolutions and retains qualitative results for longer-time evolutions. This lays the foundations for the use of near-term quantum computers to study high dimensional non-adiabatic quantum dynamics.

P15: Competition between proton transfer and resonant intermolecular Coulombic decay in water dimers

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Intermolecular Coulombic decay (ICD) is an ubiquitous, electron-correlation driven relaxation process in weakly bound systems, including liquid water. First proposed in 1997 by Cederbaum et al., ICD has been proven to often dominate over other relaxation channels. In ICD, an inner valence hole created upon ionization is refilled by an outer valence electron and the excess energy is released by ejection of a second electron from the neighbouring unit. When the process is triggered not by ionization but by a photoexcitation, it's defined as resonant ICD (RICD). Recent pump-probe experiments on RICD in water dimers [H. J. Wörner, private communication] showed that the process is substantially more efficient in deuterated water, hinting to the role of the proton transfer following excitation. We analysed the potential energy curves of the initial and final RICD states of a water dimer along the proton transfer coordinate. The results show that the excitation of the proton donor water molecule can trigger a nuclear dynamics which slows down the RICD channel. Using the multi-configurational time-dependent Hartree (MCTDH) approach, with non-Hermitian Hamiltonians containing the decay rates of RICD obtained by the Fano-Cl approach, we simulated the decay process initiated both by exciting the proton donor or the proton acceptor water molecule. The nuclear dynamics simulations shed light on the competition between RICD and the fast proton transfer, both occurring on a femtosecond timescale.

P16: Benchmarking a Partially Adiabatic Implementation of Centroid Molecular Dynamics with the High-Temperature Ansatz

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Imaginary-time path integral methods have attracted attention as effective tools for including nuclear quantum effects explicitly in the computation of both static and dynamic properties of complex chemical systems. Several different approximations targeting vibrational dynamics within this framework have been proposed. Recently, a formulation of centroid molecular dynamics (CMD) with a high-temperature ansatz has been shown to be free of the well-documented curvature problem while yielding very accurate vibrational properties for a wide range of molecular systems, liquids, and molecular solids[1].

The original implementation is based on a coarse-graining procedure, where a machine-learning potential for the centroid potential of mean force is trained at a chosen elevated temperature (and consistent phase of the system). Subsequently, classical molecular dynamics is run in this potential, constituting a fully-adiabatic procedure. Here we present an implementation of the partially-adiabatic version of this method, where we avoid the need for training an ML model for the centroid potential of mean force. This implementation is based on a two-temperature path-integral Langevin thermostat in the i-PI code [2].

We demonstrate benchmarks of this implementation by computing vibrational properties of water molecules and bulk water in different phases, a fluorinated carbonic-acid complex, and a hybrid organic-inorganic perovskite. We assess parameter ranges for the adiabatic separation and thermostat settings that yield the best agreement with the fully adiabatic case and discuss sources of inaccuracies of both procedures. Our results demonstrate overall good agreement with experimental data. The implementation of our approach not only showcases its versatility but also highlights its ability to accurately reproduce the vibrational spectra of diverse molecular and condensed matter systems.

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P17: Overall rotation and large amplitude motions couplings in tetratomic molecules with MCTDH

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The multiconfiguration time-dependent Hartree (MCTDH) method[1] has been applied to the computation of the rotational energies of polyatomic molecules in a very limited number of investigations. These include the study of Sadri *et al.*[2] where an Eckart frame was used to compute rotational energies for the water and HONO molecules; and the work of Sala *et al.*[3] where the effect of the overall rotation on the *cis-trans* isomerization of HONO were studied.

Skew-chain ABCD tetratomic molecules with a non-linear geometry, like HONO, HNCO, and HSOH, will be dealt with taking into account their rotational degrees of freedom. These molecules are usually non-rigid and display at least one large amplitude motion corresponding to a torsional motion about their BC bond. Some of them display additional large amplitude motions. In HNCO, the \angle HNC bending angle also is a large amplitude motion⁴ as the barrier to linearity[5] is only 1899cm^{-1} .

In this poster, the rovibrational energy levels of HNCO will be computed with the help of the MCTDH method. A preliminary test calculation where only the overall rotation and the torsional motion are considered will be carried out. Two degrees of freedom will be considered corresponding to the torsional motion and to the overall rotation. Non-diagonal effects due to the asymmetry and to the rotation-torsion coupling will be included in the residual Hamiltonian. The challenge is to model correctly the Coriolis rotation-torsion coupling which gives rise to a contribution to the rotational energy which does not vary in k^2 , where k is the usual rotational quantum number. The results obtained with MCTDH will be numerically verified using an already available model.[6]

In the final calculation, using an already available 6-D potential energy surface,[7] we will attempt to add the five remaining degrees of freedom so as to be able to compute rotational energies for any vibrational state. The vibrational energies and B values thus calculated will be compared to those reported in numerous experimental investigations, like, for instance, that of Niedenhoff *et al.*[8]

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P18: A deep variational Monte Carlo approach to efficiently learn multiple potential energy surfaces

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Ultra-fast excited state dynamics are a core component of many fundamental processes occurring in nature, ranging from photosynthesis in plants to photo-protection mechanisms in human bodies. Addressing these phenomena from a theoretical perspective requires an accurate description of multiple potential energy surfaces (PESs), posing a significant challenge for contemporary quantum chemistry methods.

Here, we leverage on deep quantum Monte Carlo (QMC) techniques to tackle this issue. Quantum Monte Carlo methods are rapidly establishing as highly accurate tools for solving the Schrödinger equation. However, despite their favourable scaling with the number of electrons (N^3), they are currently limited by their computational cost.

In this work, we show how by creating a neural network model of the wave function which is transferable across multiple geometries we can amortise the computational cost while maintaining the aforementioned accuracy. We demonstrate this focusing on a prototypical molecule, where we accurately and efficiently learn the multiple PESs relevant for its photo-dynamics.

We elucidate the steps necessary to achieve such a description, emphasising how the accuracy of QMC can lead to valuable contributions in the field of photo-dynamics.

P19: Low-rank representations of smooth models of the Coulomb potential

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Inter-particle Coulombic electron capture (ICEC) is an environment-assisted process, where a free electron can efficiently attach to an acceptor system (e.g. ion, atom, molecule, quantum dot), while the excess attachment energy is transferred to a neighboring electron-donor system [1]. The latter can then be ionized or simply electronically excited as is the case in van der Waals or hydrogen bonded systems. Based on previous studies on the related inter-particle Coulombic decay (ICD) process [2], nuclear motion should have an effect on the efficiency of the process as well as a major role in determining the final state of the participating systems. In our simple two-active-electron approximation, the (first-quantisation) Multiconfiguration Time-Dependent Hartree (MCTDH) algorithm provides a direct means of simulating the coupled dynamics of electrons and nuclei in a strictly non-Born-Oppenheimer manner. The accuracy of these simulations will strongly depend on the quality of the (sum-of-products, SOP) representations of the different Coulomb interactions. This scenario becomes even worse due to the fact that the physics of the process prescribes the use of dense grids providing a reasonable description of the continuum. Furthermore, extended boundaries are necessary to describe simultaneously the long-range interaction, for the incoming electron, as well as the electron capture or release processes for which the short-range interaction plays the main role. These requirements lead to bottlenecks in terms of storage and computational resources. Tensor decomposition (compression) methods become hence demanding. Additionally, obtaining such compact, yet accurate, SOP expressions for the Coulomb (or Coulomb-like) operators is a significantly burdensome task, due to the presence of a (possibly regularized) singularity together with a slowly vanishing asymptotic tail. In this contribution, we present a systematic comparison of different grid-based [3,5] and grid-free (analytical) [6] approaches to SOP representations of smooth models of Coulomb operators.

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P20: Vibro-Polaritonic Chemistry with Perturbative Electron-Photon Correlation: Dressed Hessians and Sum-of-Products Ensemble Potentials

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Resonant vibrational strong coupling (VSC) between infrared-active molecular vibrations and low-frequency modes of optical cavities underlies the emergent field of vibro-polaritonic chemistry[1], which is motivated by the experimentally observed peculiar impact of resonant VSC on both infrared spectroscopy[2] and ground state chemistry[3]. From a conceptual perspective, VSC is accompanied by non-resonant interactions between low-frequency cavity modes and the electronic subsystem, whose potential role in vibro-polaritonic chemistry is not yet explored.

In this contribution, we discuss the cavity Born-Oppenheimer perturbation theory (CBO-PT) approach[4], which approximately accounts for non-resonant electron-photon interactions in VSC scenarios. Specifically, CBO-PT approximates the extended electronic ground state problem in the CBO approximation[5] by treating the cavity as perturbation of the electronic subsystem. We consider electron-photon correlation corrections for intramolecular potential energy surfaces, which are in sum-of-products form with respect to light and matter degrees of freedom, as well as related second-order dressed Hessians and ground state dipole moments.[4,6,7] Application to correlation-corrected vibro-polaritonic IR spectroscopy is discussed.[6] Further, we show that second-order CBO-PT leads for dipole-coupled molecular ensembles under VSC to a many-body expansion of the intermolecular interaction potential, which contains up to three-body terms in addition to a cavity-altered van-der-Waals interaction with enhanced long-range character.[7]

In perspective, the sum-of-products form of the CBO-PT many-body potential in combination with the multilayer MCTDH method might provide a methodological framework to gain further insight into the interplay of collective effects and local chemical transformations in molecular ensembles under VSC.

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P21: Compensation States Approach in the Hybrid Diabatization Scheme: Extension to Multidimensional Data and Properties

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

Recently, we addressed this problem by the compensation states approach developed in the context of our hybrid diabatization scheme. This scheme utilizes wave function as well as energy data in combination with a diabatic potential model.

In regions where the initial diabatic state basis becomes insufficient for an appropriate representation of the adiabatic states, new model states are generated. The new model states compensate for the state space not spanned by the initial diabatic basis. Such a compensation state is obtained by projecting the initial diabatic state space out of the adiabatic wave function. This yields a very efficient basis representation of the electronic Hamiltonian.

The present work presents two new aspects. First, it is shown how other operators like the spin-orbit operator in the framework of the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) can be evaluated in this compact model state space without losing the correct wave function information and accuracy. Second, the extension of the approach to multidimensional potential energy surface models is presented for methyl iodide including the C-I dissociation coordinate and the angular H3C-I bending coordinates.

P22: Energy Transport In Quantum Fermi-Pasta-Ulam Model

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Fermi-Pasta-Ulam (FPU) model, which describes energy transport in chains of nonlinear oscillators, occupies a special place in science: It was the first model investigated by numerical computer simulations. Nowadays, there exists a huge literature on the classical FPU simulations. On the other hand, due to the complexity and large dimensionality of the problem, there are literally few studies of the FPU dynamics in the quantum regime. We present the first numerically accurate tensor-train simulations of the energy transfer in the fully quantum anharmonic FPU chain of 10, 20, 30 and 60 sites. We demonstrate that anharmonicities open up a new channel for the energy transfer, accelerate initial (ballistic) transport, and profoundly affects the subsequent population recurrences.

P23: Photodynamics study of Retinal Chromophores Beyond the Standard Counterion Model of Bacteriorhodopsin

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Discovered over 50 years ago, bacteriorhodopsin (BR) is the first recognized microbial retinal protein (MRP). It is a light-activated proton pump contained in the purple membrane of *Halobacterium salinarium* and serves as an archetypal ion-pumping protein. Upon photoexcitation, the all-trans, 15-anti retinal chromophore (AT) bound to LYS216 via a protonated Schiff base (PSB) linkage, isomerizes in ~ 0.5 ps to the first metastable intermediate 13-cis, 15-anti configuration. In this contribution, we used CASPT2/MM computations to complement the experimental findings and to shed light on the electrostatic modulation associated with the different protonation states of the protein, in retinal photoisomerization. The calculations show that: i) models incorporating a deprotonated counter ion poorly reproduce vertical energy gaps to the reactive S1 excited state (Figure 1) and are unable to explain ultrafast decay in bacteriorhodopsin and the peculiar multi-phased slow photochemistry in "K"; and ii) assuming single protonation of ASP212 corrects the disagreement of the calculated gaps with experimental values, and remarkably predicts triple ground state structural heterogeneity involving the site of protonation and orientation of the Schiff base. Minimum energy paths calculated for these configurations exhibit significantly different barriers, predicting triply inhomogeneous photoisomerization kinetics as observed in experiments. These results prompting a reconsideration of counter ion protonation of the Schiff base in bacteriorhodopsin. While our experimental and computational data primarily focus on BR, the insights can be extended well beyond it, eventually delivering a generalized energetic tuning mechanism (see Figure 1) that accounts for the effect of the electrostatic embedding on both the spectral and photoisomerization properties of retinal chromophores in whatever environment (proteins, solvents or isolated condition)

P24: A bivariational, stable, and convergent hierarchy for time-dependent coupled cluster with adaptive basis sets

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Adaptive or moving basis functions are highly useful for describing large-amplitude motion such as dissociation (nuclear dynamics) or ionization (electron dynamics) in a computationally attractive way. Of particular importance is the division of the one-particle basis into an *active* and a *secondary* part. This division allows a compact and highly flexible active basis, something that has been used to great effect within the MCTDH and similar frameworks.

Combining the idea of an evolving active basis with the attractive features of the coupled cluster (CC) *Ansatz* is, however, a non-trivial problem. It is known [1–5] that a biorthogonal basis is needed for reproducing the exact solution correctly, which is certainly an important property. However, the choice of a biorthogonal basis comes with a subtle caveat: There is no guarantee that the active bra and ket functions span the same space if a biorthogonal basis is divided into active and secondary parts. We have previously described how the two spaces tend to drift apart during propagation, eventually leading to numerical breakdown [6].

In a recent paper [7], we introduced a new parameterization of the evolving basis that avoids this problem completely. The idea is to split the basis set transformation into an interspace (active–secondary) and an intraspace (active–active) part. Choosing a unitary interspace transformation and a non-unitary intraspace transformation guarantees that the active bra and ket functions are biorthogonal while spanning the same space. The former ensures convergence to the correct limit, while the latter ensures numerical stability. While the formalism applies equally well to electron and vibrational dynamics, we have specialized the theory to the vibrational case under the name *split time-dependent modals vibrational coupled cluster* (sTDMVCC).

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P25: Quasi-direct Quantum Molecular Dynamics

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A new quasi-direct quantum molecular dynamics (QMD) method is presented which offers a compromise between quantum dynamics using a pre-computed potential energy surface (PES) and fully direct quantum dynamics. The method is termed the time-dependent adaptive density-guided approach (TD-ADGA) and is a method for constructing a PES on the fly during a dynamics simulation. This is achieved by acquisition of new single point (SP) calculations and refitting of the PES depending on the need of the dynamics.

The TD-ADGA is a further development of the adaptive density-guided approach (ADGA) for PES construction where the placement of SPs is guided by the density of the nuclear wave function. In the TD-ADGA, the reduced one-mode density of the time-dependent nuclear wave function is used to guide the placement of SPs such that the PES is extended or updated if the nuclear wave function moves into new areas or if a certain area becomes more important.

Carrying out wave function dynamics with the TD-ADGA is essentially a black-box procedure, where only the initialization of the system and how to compute SPs must be provided by the user. The TD-ADGA can be used in conjunction with any time-dependent wave function method as long as a wave function density is available. Further developments of the method will be presented together with QMD simulations showcasing the method and its accuracy. Using the TD-ADGA it thus becomes much easier to carry out QMD simulations and the quasi-direct framework opens up the possibility to compute quantum dynamics accurately for larger molecular systems.

P26: Vibronic Spectra of *cis*- and *trans*-Stilbene: A Quantum Dynamics Study

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cis- and *trans*-Stilbene have a long-studied photochemistry arising from their photo-initiated isomerization process, in which the large-amplitude relative motion of the phenyl rings has led to the molecule being identified as a molecular switch. A quantitative description of the corresponding absorption spectrum would therefore be essential for a complete account of the ensuing dynamics. However, previous assignments of the absorption spectra for these molecules, which neglected the vibronic coupling effects, fail to properly characterize the spectra. We present here detailed analyses of the vibronic spectra of *cis*- and *trans*-stilbenes simulated from wavepacket propagation calculations using the multi-configuration time-dependent Hartree (MCTDH) method. To do so, vibronic coupling Hamiltonian models are constructed by direct fitting to diabatic potential matrices computed using the novel QD-DFT/MRCI(2) approach. Our simulated spectra reproduce the main features of the experimental spectra in solution. The role of intensity borrowing from transitions to $\pi\pi^*$ states, and the excited state dynamics of each molecules, are also examined in our study.

P27: Development of a Potential Energy Surface(PES) of the H₂O on TiO₂ System for Quantum Dynamics Simulations

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Photocatalytic water splitting has been envisaged as a new potential way of green hydrogen production. While the phenomenon has been extensively studied from the electronic structure point of view, dynamics simulations have been given less attention. A few research work pieces making use of molecular dynamics [1] and quantum molecular dynamics simulations [2] have been attempted in the recent past. On one hand, the changes in the water molecule structure as a result of being at the substrate interface including adsorption and dissociation of the molecule at specific substrate surface sites have been established. On the other hand, favorable dissociation pathways have been examined by calculating photo-dissociation probabilities. We are following the later work with the goal to shade more light on the photocatalytic water splitting from exact quantum dynamics simulations with the MultiConfiguration Time Dependent Hartree (MCTDH) approach. We are adopting a simple-to-complex approach consisting in progressively complexifying the description of the system, starting from a rigid water 4-D description to a full dimensional 9-D characterization of water over a rigid TiO₂ substrate surface. We will present in our talk, the electronic structure calculation methodology and preliminary results of the fitting of the potential energy surface along with some quantum dynamics simulations.

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P28: Hagedorn Wave packets and Time-Dependent Schrodinger Equation on Ground and Excited States.

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The simulation of molecular quantum dynamics is done by numerically solving the time-dependent Schrodinger equation. There are several ways to represent the solution of this equation. The traditional way is to project it on a time-independent basis. Another way is to represent it on a time-dependent basis. In this last category, there are several techniques such as semi-classical method proposed by Heller [1], MCTDH [2], Hagedorn wavepackets tehnics [3], DD-vMCG[4] etc... We are developing a simulation code based on the Hagedorn wavepackets technics for which, the basis set and the grid move over timefollowing the evolution of the wavepackets. We make applications on models potential (HenonHeiles 6D) and on non-adiabatic models. We show that this way of carrying out propagation makes it possible to optimally reduce the number of primitive basis functions and delay exponential growth. Therefore, it is possible to save time.

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P29: Runtime for Vibrational Structure on Quantum Computers

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One of the primary challenges prohibiting demonstrations of practical quantum advantages for near-term devices is excessive measurement overheads for estimation of physical quantities such as ground state energies. The electronic structure problem on quantum computers has been investigated significantly in recent years while the vibrational structure problem remains relatively unexplored. Importantly, research suggests that classically intractable vibrational structure problems may be solved on quantum computers prior to their electronic equivalents [1].

Bosonic commutation relations, distinguishable Hilbert spaces and vibrational coordinates allow manipulations of the vibrational system in order to optimize the use of computational resources.

These avenues of resource reduction, unique to the vibrational problem, remain relatively unexplored compared to their electronic counterparts.

The new program package Midas Quantum bridges the gap from MidasCpp [2] to quantum hardware. Midas Quantum can also estimate quantities of near-term interest, like runtime through variance computations. With MidasCpp and Midas Quantum the dependency of runtime on both the molecular Hamiltonian and quantum computing preprocessing can be explored.

This work [3] investigates the impact of different coordinate systems and measurement schemes on the runtime of estimating anharmonic vibrational states for a variety of three-mode (six-mode) molecules. We demonstrate an average of 3-fold (1.5-fold), with up to 7-fold (2.5-fold), runtime reductions using appropriate coordinate transformations. Despite such reductions, crude estimates of runtimes with realistic potential energy surfaces are considerable. Further improvements are thus necessary to demonstrate practical quantum advantages.

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P30: Ultrafast Hydrogen Migration in a Photoionized Glycine by a Mixed Quantum-Classical Dynamics

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We have theoretically investigated the intra-molecular hydrogen migration in the glycine molecule ionized by XUV attosecond pulse train of duration 1.5 fs to explain previous experiments by R. Cireasa et al [*The journal of physical chemistry letters* **9** (2018) 6012-6016]. The interaction of the glycine molecule with the XUV pulse leads to a superposition of electronic states which dynamics is coupled to the nuclear one. We have combined the Correlated Single Channel Approach to evaluate the ionization amplitudes with the trajectory surface hopping to describe the coupled electron-nuclear dynamics. A statistical analysis is then performed to evaluate the theoretical hydrogen migration time in order to compare with the experimental one which is approximately 48 fs. We do observe a hydrogen migration often occurring from the electronic ground state of the ionized ground state.

P31: Development of a machine-learning method to solve the time-dependent Schrödinger equation

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Machine-learning (ML) methods such as neural networks (NNs) are becoming alternatives to conventional algorithms in many domains because of their efficiency and accuracy of prediction. However, there are only a few attempts to employ ML to obtain time-dependent properties in quantum systems by solving the time-dependent Schrödinger equation (TDSE) which is a partial differential equation (PDE). New ML architectures based on the universal operator approximation theorem have shown the ability to solve PDEs accurately. In this work [1], two of these ML architectures, the deep operator network [2], and the Fourier neural operator [3] are used to model wavepacket propagation with different Hamiltonians via density. In the poster, I will discuss the potential of these ML methods to replace traditional TDSE solvers with better efficiency and acceptable accuracy.

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P32: Gaussian Progress Regression for Quasi-Direct Quantum Molecular Dynamics

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Quantum Molecular Dynamics (QMD) simulations offer unparalleled insights into chemical reactions, making them an enticing prospect for studying systems of interest. However, the main challenge with these simulations is the computational cost, which rapidly becomes prohibitive as the size of the system increases. Both evaluating the time evolution of the nuclear wave function and constructing the Potential Energy Surface (PES) it propagates on are computationally expensive tasks. This computational cost prevents simulations for many larger systems of interest, so the development of efficient methods for both remains an important and exciting field of ongoing research.

Methods typically fall into two categories: running dynamics simulations on a precomputed PES or performing fully direct QMD. The recently developed Time Dependent Adaptive Density Guided Approach (TD-ADGA) presented a new approach to QMD, compromising between the two. This quasi-direct method constructs an initial PES from the vibrational density and then adds points on the fly as required by the vibrational density when it evolves through time. In this way the PES construction remains flexible and is guided by the dynamics, only constructing the regions of the PES needed while still allowing for the exploration of new regions of the PES. By utilizing a fitted PES, TD-ADGA circumvents the computational overhead of fully direct QMD methods. While it was shown that the method produced accurate results for dynamics simulations while only calculating the needed regions of a PES, the method still requires a large number of single point calculations.

Here, we present an improvement to TD-ADGA, utilizing Gaussian Process Regression (GPR) to minimize the number of single points required. In this new method, named TD-GPR-ADGA, a simulation is run using the TD-ADGA framework but the single points are replaced with predictions from a GPR model trained on an evolving set of single points. The training set is iteratively improved whenever predicted points have too high an uncertainty, ensuring that the smallest possible set of points is used and drastically reducing the number of single point calculations required. The TD-GPR-ADGA follows the principles of the previously published GPR-ADGA method for PES construction and can be seen as a combination of the GPR-ADGA and TD-ADGA methods.

Illustrative simulations demonstrate the efficiency of TD-GPR-ADGA, showing up to a 90% reduction in single point requirements while maintaining accuracy. Furthermore, significant computational savings are observed in simulations with costly single points. Notably, application to a larger 21-mode system showcases the method's potential for studying complex systems, opening the possibility of performing QMD simulations on larger molecules.

P33: Combined computational and dynamical study of disorder effects in one- and two-dimensional models of hole transfer materials.

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In recent times, a multitude of organic semiconductors (OSCs) have been proposed across various domains, such as electronics, flexible displays, and cost-effective solar cells. [1] Since the early investigation into their charge mobility, it has become evident that the measurement of chemico-physical properties of real molecular systems is invariably influenced by thermal motion and the inherent static disorder of the microscopic degrees of freedom (DoFs) of matter. [2] Thermal motion gives rise to dynamic disorder both in energies and in electronic couplings, while static disorder arises from uncorrelated fluctuations of microscopic structural parameters whose values exhibit significant dispersion but remain relatively stable during the observation time. The combination of these two effects can greatly impact the overall mobility especially in systems with preferential direction for the charge transport.

Building upon this understanding, we compare the quantum dynamics of charge transfer in uni- and two-dimensional model systems of hole-transport materials (HTM). To address both thermal and static disorders, we utilize the thermo-field-dynamics (TFD) [3] theory augmented with artificial DoFs representing static disorder, which allows us to assess the expectation value of any physical variables, averaged over static disorder through a single time-dependent simulation. The solution of the TFD Schrodinger equation requires efficient numerical methods, in our approach a tensor-trains (TT) decomposition has been adopted. [4]

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P34: Electron dynamics of the inter Coulombic decay in higher excited states

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Quantum dots (QDs) are semiconducting nanoparticles important due to their size-tunable excitation energy and optical properties: in their self-assembled form they can host electronic or spin qubit states with a decent lifetime. To model electronic processes like the interatomic Coulombic decay (ICD), in QDs, we apply the multiconfiguration time-dependent Hartree (MCTDH) algorithm in an antisymmetrized version.

ICD is described as a decay process between two or more atomic species facilitated by the long-range Coulomb interaction between electrons at different spatial locations: on the one hand, an electron in a high energy state relaxes to a lower energy state while the energy is transferred to an neighbour quantum dot, which is simultaneously ionised.

The system studied in this work consists of a one-dimensional double-well GaAs potential. It is modeled to accommodate different electronic levels (s to d energy levels) and allows ICD to occur among higher excited states. The regular ICD process is studied along three different pathways.

P35: Ab initio Open Quantum Dynamics of Slowly Relaxing Molecular Spins

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Single-molecule magnets (SMMs) hold the potential for realising affordable high-density data storage and quantum information processing at the molecular scale, thanks to the possibility of chemically tuning their electronic and vibrational properties. Their spin dynamics are determined by the interplay between few electronic states and a large number ($> 10^3$) of vibrational degrees of freedom, which can couple coherently and eventually lead to spin thermalisation on much slower timescales than typical vibronic dynamics [1,2]. In particular, describing slow magnetic relaxation of SMMs in realistic condensed phase environments forces us to account for higher-order phonon scattering events, which cannot be reproduced by standard weak-coupling Redfield theory [3]. Building on an *ab initio* description of the spin-phonon coupling, we present a quantum master equation able to capture both one- and two-phonon processes, which are essential to accurately describe long-time magnetic relaxation. We combine a complex pole expansion of the phonon correlation functions together with tensor compression techniques, in order to obtain an efficient representation of the long-time dynamics. This allows us to overcome the limitations imposed by both classical master equations based on Fermi's golden rule and Redfield theory.

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P36: Photodissociation dynamics of NOCl molecules under electronic strong coupling

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Strong coupling between confined light and molecular degrees of freedom inside optical cavities opens the way to create hybrid light-matter states called polaritons, which were found to modify several chemical properties, such as reaction rates, energy transfer mechanisms, charge transfer, and singlet-fission. Despite drawing a lot of attention among physicists and chemists, there has so far been a lack of experimental studies on simple (unimolecular) chemical reactions in the gas-phase, which are more easily accessible for fully quantum mechanically and *ab initio* theoretical descriptions. Nevertheless, a few successful experiments have recently reported achievement of vibrational strong coupling in gas-phase cavities [1], providing a first step into the investigation of isolated systems.

In this work, we present a full-dimensional, fully quantum dynamical study on the photodissociation process of nitrosyl chloride (NOCl) molecules under electronic strong coupling in the presence of orientational static disorder. The photodissociation of this molecule, extensively studied both experimentally and theoretically [2], is initiated by an excitation onto the S1 state, leading to the detachment of the chlorine atom. When this transition is coupled to a photon mode, distortions of the potentials around the Frank-Condon region are introduced. To quantify the impact of these modifications on the dynamics, we inspected both population dynamics of the excited states and the quantum flux along each dissociative degree of freedom.

To tackle the challenging dimensionality of the system (up to 32 molecules), we employ the Multi-Layer Multiconfigurational Time-Dependent Hartree (ML-MCTDH) algorithm [3], enabling an investigation of quantum dynamics on full-dimensional multi-reference potential energy surfaces [4].

Our results provide a solid theoretical comparison for interpreting future experiments on gas-phase molecules in the electronic strong coupling regime.

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P37: Optimal mode combination in vibronic coupling Hamiltonians

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We propose an approach based on the protocol given by Mendive-Tapia et. al. [1] for the selection of multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) wavefunctions [2] in vibronic coupling Hamiltonians. The approach is based on the computation of correlation matrices between degrees of freedom and subsequent derivation into the corresponding multi-layer tensor tree employing data mining algorithms, i.e. hierarchical clustering, factor analysis and principal component analysis. [3] The method is applied to the excited state decay of pyrazine, benzene, naphthalene and anthracene cations employing different dimensionalities and model descriptions (i.e. linear, bi-linear and quadratic). In the smallest cases, we are able to benchmark the method by computing all the possible tree permutations, showing that the algorithm is able to find a good and even the most efficient tensor network decomposition. For larger cases, we are able to uncover much better mode combinations than the ones employed in the bibliography. A remarkable finding is the fact that deep ladder architectures of the wavefunction, which are reminiscent of density matrix renormalization group (DMRG) approaches, [4] are particularly efficient. Finally, from the observed recurrent emerging patterns, we infer a set of heuristic rules for the construction of multi-layer trees that rely on the parameters available in the Hamiltonian at the outset.

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P38: Towards the quantum reactive scattering of CH₄ on Ni(111) in 13D with MCTDH using a compact Canonic Polyadic representation of the potential

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Dissociative chemisorption of methane on the metal surface, in which breakage of the C-H bond is the rate-limiting step, is the main route for producing molecular hydrogen at the industrial scale. Given its high activation energy of about 1 eV, understanding the dynamical effects that influence and possibly reduce this barrier at the molecular level is of great economic importance. In addition, as a relatively small polyatomic molecule with a variety of vibrational modes that exhibit different reactivity, methane is a suitable candidate for benchmarking and studying heterogeneous catalysis in general.

Our approach to studying this system relies on quantum dynamical calculations using the powerful Multiconfiguration Time-Dependent Hartree (MCTDH) method [1]. To fulfill the well-known requirement needed in order to make use of its computational efficiency, we express the available potential energy surface [2] in a form suitable for the MCTDH. Given the dimensionality of the system (13/15D) and the grid size necessary for this system ($\approx 10^{19}$ grid-points), the compact Canonical Polyadic (CP) representation of the potential is ideally suited. In this respect, we use the recently proposed Monte Carlo Canonical Polyadic Decomposition (MCCPD) [3] that has emerged as a particularly promising approach for refitting high-dimensional surfaces. Taking into account that it performs the decomposition on a subset of the primitive grid and the nature of the given potential (unbound one with significantly different relevant regions: asymptotic, physisorption, transition states, chemisorption), by using a judiciously chosen subset, one can ensure the global and accurate representation of all the regions of interest for the dynamics. [4]

In this contribution, we present our results for the above mentioned system in 13D, that is, including all the vibrations and rotations of the molecule, but constraining the impact site to the top on Ni atom. [4]

P39: Representing non- A_1 Operators: C_{nv} Diabatic Dipole Transition Surfaces

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Besides the electronic Hamiltonian, accurately simulating dynamics and rovibrational spectra requires representing other operators. Unlike the Hamiltonian, neither orbital angular momentum nor dipole operator are totally symmetric (A_1). We derived a symmetry-adapted arbitrary-order expansion of non- A_1 operators in a diabatic representation. The aim is to extend the scheme presented by Weike et al. [1], developed for A_1 operators of C_{nv} and D_{nh} symmetry, to this more general case.

$E \otimes e$ Jahn-Teller systems form a prototypical class of molecules where the Born-Oppenheimer approximation breaks down near a symmetry induced conical intersection, necessitating the treatment of geometric phase effects. In the case of sufficiently strong vibronic coupling, the multi-well character of these systems radically departs from simple harmonic pictures. We constructed low-order 2×2 vibronic coupling Hamiltonians and dipoles for the $n = 3$ and $n = 4$ case. In search of physical pictures to help assign experimental spectra, we numerically investigated these models for possible Franck-Condon-like (multi-well adapted) "selection rules".

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P40: Resolving the Experimental Photoelectron Spectra of CAI_3Si^-

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The experimental photoelectron spectra concerning the six electronic states of $CAI_3 Si^-$ are resolved through electronic structure calculations and quantum nuclear dynamics in this study. It incorporates a model diabatic Hamiltonian to evaluate the coupling parameters and fit the potential energy curves (PECs). The analysis of these PECs showed us that there are sufficient non-adiabatic effects in the photoelectron spectra through the presence of various conical intersections. Poisson intensity distributions (PIDs) and the wave packet density plots are utilized for assigning the fundamental and first overtone excitations. The nuclear dynamics study is accomplished employing time-dependent (TD) and time-independent (TI) quantum chemistry methods. Ultimately, our theoretical results concurred well with the experimental findings exhibiting vibronic coupling amidst the nearly positioned electronic states.

P41: Developing a method to simulate chemicurrents.

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We are developing a method to model non-adiabatic dynamics for the Anderson-Holstein Hamiltonian. We are developing this method to simulate the currents generated when gas atoms are scattered over metal surfaces. We are benchmarking this method against the results of the simulations performed using the rate constants obtained from the Marcus theory.

42: Analytical Hierarchical Tucker Binary Trees

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Tensor decomposition methods have become widely popular (and even essential) in fields ranging from Deep Learning [1] to engineering and scientific problems. Among the latter, this is particularly true in fields such as electronic structure or quantum dynamics (QD) [3]. One can distinguish different tensor-decomposed ansätze differing on their algorithmic properties, their compression capabilities as well as their ability to split a multi-dimensional data-structure into a series of low-dimensional ones. From a formal perspective, commonly used sum-of-products ansätze are Tucker [4,6], Tensor-Train [7] or the powerful Canonical Polyadic (CP) [8] forms. In addition to these, one has the Hierarchical Singular Value Decomposition or Hierarchical Tucker Decomposition (HTD) [9] which, in its so-called Algorithm 2 flavour, was later introduced in the QD community as the Multilayer POTFIT [10].

In this work, we make use of the so-called algorithm 1 of HTD [9]. Our implementation yields a binary tree data-structure comprising d factor matrices (leaves) and $d - 1$ transfer tensors (parent nodes) where d is the dimensionality of the original reference tensor. We show [11] that it is possible to interpolate these factors using a set of interpolating basis functions (FBR) as it has been previously shown for the Tucker and CP formats. [12,13]. As a result, we obtain an analytical binary tree (HT-FBR) which is much more compact than the original reference tensor and that enables interpolation to finer grids of any density, provided that the underlying scalar field is smooth. Our analytical HT-FBR tree can be optimised from a set of sample data-points arbitrarily chosen from a given domain thanks to the use of single-entry evaluation of the intermediate transfer tensors. The elements of the latter are optimised by mini-batch stochastic gradient descent and the Adam optimizer. To illustrate our methodology we have performed the training of grid-free HT-FBR in both 6D and 12D tensors.

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P43: Theoretical description of attosecond momentum-resolved resonant inelastic x-ray scattering of photo-excited molecules

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We explore the capabilities of attosecond momentum-resolved resonant inelastic x-ray scattering (RIXS) [1,2] for imaging charge migration. We theoretically describe an experiment in which an optical pump pulse induces electron dynamics in sexithiophene through photo-excitation, and an attosecond x-ray probe pulse resonant to the Sulfur K-edge is employed to probe the dynamics. We analyze the probability of scattering of a photon with a certain momentum and connect it to the properties of electron dynamics being probed.

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P44: Efficiently targeting interior excited eigenstates using tensor network states

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Interior excited states are responsible for many important processes like core ionization, chemical dynamics through conical intersections, and high-energy vibrational excitations. Hence, an accurate simulation of these states is very important.[1] However, compared to the many efficient eigensolvers for ground and low-lying excited states, there are much fewer effective algorithms available for interior states. Here, we develop new approaches to solve interior states using a combination of [1] tensor network states (TNSs)[2] and (2) both inexact Lanczos and Green's function-based methods.[3] We extend these two methods from standard matrix-vector algebra to TNSs. By computing vibrational eigenstates of large molecules (12 to 30 vibrational degrees of freedom), we demonstrate excellent performance of our approach and a significant improvement, compared to existing methods for targeting vibrational states. This will not only be relevant for simulating vibrational systems of large and fluxional molecules, but also for computing electronic excited states and other challenging quantum applications.

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P45: Unraveling Quantum Effects in the Scattering of Hydrogen Atoms on W(110) Surface

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An understanding of the dynamics of hydrogen atom scattering on metal surfaces is of great importance for a number of applications, including catalysis and material science. Of particular interest is the case of tungsten surfaces, as it will be the material of plasma facing components in future fusion reactors. In this study, we investigate the scattering of hydrogen atoms on the W(110) surface, employing both classical and quantum dynamics approaches to elucidate the importance of quantum effects in this system.

The stochastic multi-configurational time-dependent Hartree method is employed, which permits to incorporate energy dissipation to electronic degrees of freedom in the description of the system. This enables the quantification of energy dissipation and direct comparison with ab initio molecular dynamics results, where the dissipation of energy to electrons is routinely accounted for by means of a friction coefficient.

The focus of this study is on several key observables, including the sticking probability and diffraction channels, which are used to characterise the scattering process. Furthermore, the vibrational excitation spectra of H atom adsorbed on the tungsten surface is studied at both the semiclassical and quantum levels.

P46: Unravelling the Non-Ergodic Behavior of IR Photo-Initiated Dissociation of Mix-Ligand Ion Complexes; A Quantum-dynamics Simulation.

[ROBERTSON, Christopher](#) (Heriot-Watt University)

Mackenzie et al [1,2] performed experiments of IR photo initiated, vibrationally induced dissociation experiments of mass selected mixed ligand ion-molecule complexes. A group of complexes with trigonal CO ligands (like diagram), exhibited an unusual dissociation distribution. The N₂O ligands have a “weak” barrier of approx. 0.2 eV, while the CO dissociation in contrast has a higher barrier of 0.3 eV. Upon IR excitation of either CO/N₂O Stretches to an energy of 0.45 eV, one would expect the rate of dissociation depend exponentially with the barrier height (Ergodic outcome). Instead, they measured a 6:1 ratio of CO preference of dissociation. This non-ergodic behavior is not the expected outcome of such experiments. We have fitted a high-dimensional potential energy surface model describing all competing dissociation channels and simulated the outgoing flux of the ligands. The dissection of the model offers some insight into the mechanism and non-ergodic behavior of this system, which may serve as a reference on when to expect such behavior in analogous systems.

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P47: Vibronic coupling Hamiltonian within the ab initio MCTDH-SQR formalism

[SASMAL, Sudip](#) (Heidelberg University), [VENDRELL, Oriol](#) (Heidelberg University)

A first-principles quantum formalism to describe the non-adiabatic dynamics of electrons and nuclei based on a second quantization representation (SQR) of the electronic motion combined with the usual representation of the nuclear coordinates is introduced. This procedure circumvents the introduction of potential energy surfaces and non-adiabatic couplings, providing an alternative to the Born–Oppenheimer approximation. Application of this method to the photodissociation of the HeH^+ molecule effectively captures all the non-adiabatic effects through the time evolution of the nuclear-electronic wavepacket, facilitated by the introduction of diabatic orbitals and associated matrix elements.

A significant challenge of the approach is the fact that the matrix elements of the second-quantized electronic Hamiltonian, the one- and two-body integrals become nuclear-space potential operators, in general, of dimensionality $3N - 6$ ($3N - 5$ for linear systems), where N is the number of atoms in the system. However, these integrals exhibit simpler dependency on nuclear coordinates compared to potential energy surfaces. Therefore, expanding the electronic integrals around a reference geometry up to, e.g., second order, thus yielding the equivalent of a vibronic coupling Hamiltonian in an N-SQR representation is possible. By employing a hole particle formalism, the electronic Hamiltonian is reformulated into separable terms exhibiting distinct variations with respect to nuclear coordinates.

First, we analyze the model to determine the requisite polynomial orders for various terms of the Hamiltonian, ensuring numerical accuracy in describing electronic energy. Subsequently, we employ this methodology to describe the non-adiabatic dynamics in triatomic systems.

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P48: Learning Basis Sets of L2 and Applications to Quantum Molecular Physics

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Standard methods for solving molecular Schrödinger equations such as, e.g., spectral methods, suffer from the curse of dimensionality. Moreover, these methods suffer from suboptimal convergence rates for approximating highly-oscillatory functions. This results in limited calculability of various important phenomena, such as modelling dissociation dynamics and spectra of hot exoplanets. Recently, neural networks have been under intensive investigations for modelling diverse quantum dynamical and mechanical properties. Interestingly, they were shown to mitigate the curse of dimensionality while still providing highly accurate approximations. However, the use of neural networks for quantum mechanical and dynamical simulations faces convergence issues and still requires a lot of engineering. Black-box solvers via neural networks seem to be unrealistic in many relevant applications.

We present a new computational paradigm to solve differential equations of quantum physics. Our approach is based on approximating wavefunctions in the linear span of basis functions that are augmented and optimized via composition with normalizing flows. We provide necessary and sufficient conditions on the flow to conserve the completeness of the underlying basis. Moreover, we analyse the convergence rate of the approximations. Our calculations of various vibrational time-independent Schrödinger equations show orders of magnitude improved accuracy over standard spectral methods. Due to its well-posedness, our framework enjoys convergence guarantees and promises to serve as a black box for simulations of various quantum phenomena.

P49: Time evolution as an optimization problem - solving the time-dependent Schrödinger equation with Explicitly Correlated Gaussian wave packets

[SCHRADER, Simon Elias \(University of Oslo\)](#), [KRISTIANSEN, Håkon Emil \(University of Oslo\)](#), [KVAAL, Simen \(University of Oslo\)](#), [BONDO PEDERSEN, Thomas \(University of Oslo\)](#)

A linear combination of Explicitly Correlated Gaussians (ECGs) is a very flexible and compact parameterization of multidimensional wave functions and has been extensively used for very accurate calculations of atomic and molecular properties. While uncorrelated, frozen Gaussian wave packets can be effectively propagated variationally, giving rise to the variational multi-configurational Gaussian (vMCG) method, propagating ECGs using a time-dependent variational principle is extremely challenging due to ill-conditioning of the Gramian matrix that needs to be inverted at every time step. This problem can be evaded by using Rothe's method, where time evolution is rephrased as an optimization problem. We show that Rothe's method can be used to propagate linear combinations of ECGs, illustrated by calculating the spectrum of the multidimensional Henon-Heiles potential using only 10-20 Gaussians; and electronic wave functions in strong fields, illustrated by calculating the High-Harmonic Generation (HHG) spectrum of the Hydrogen atom in a strong electric field, using only 50-180 Gaussians. This paves the way for the inclusion of continuum contributions into real-time, time-dependent electronic-structure theory with ECGs for strong fields, and eventually accurate simulations of the time evolution of molecules without the Born-Oppenheimer approximation.

P50: Full quantum dynamic study for the H atom scattering from graphene surface

SHI, Lei (Université Paris-Saclay), GATTI, Fabien (Université Paris-Saclay)

The adsorption of hydrogen atoms onto a graphene surface has garnered significant attention due to its wide-ranging applications in fields such as astrophysics, hydrogen storage, and semiconductor manufacturing [1]. Recently, a comprehensive potential energy surface (PES) for a periodic graphene surface, comprising 24 carbon atoms and one free hydrogen atom, was reported [2],[3]. Employing this PES, classical molecular dynamics (MD) simulations were conducted to study hydrogen atom scattering on the graphene surface [2],[3]. The PES demonstrated accurate predictions of the hydrogen atom sticking probability and successfully replicated energy loss spectra when compared with experimental results. However, in certain collision conditions, for example, when hydrogen atoms are incident perpendicularly to the surface, revealed disparities between experimental and modeling outcomes.

In our earlier quantum dynamics (QD) investigations [7] employing a reduced 15-dimensional model of this system, a benchmark was established for comparing classical MD simulations with quantum dynamics simulations, revealing notable quantum effects in the scattering process. However, direct comparisons between simulation outcomes and experimental data remained elusive. Through persistent endeavor, we have now achieved full-dimensional (75D) QD simulations for this system, surpassing prior limitations.

The realization of full-dimensional QD simulations entailed employing the Monte-Carlo Canonical Polyadic Decomposition (MCCPD) method [6] to refit the original neural network PES, transforming it into a sum-of-products form. Although challenging, the MCCPD method effectively addressed the high-dimensional nature of the system, with hydrogen atom periodicity confined to the graphene element cell, as shown in Fig. 1, to concentrate sampling and reduce refitting errors to 223 cm^{-1} . Subsequently, the Multilayer Multi-configuration time-dependent Hartree (ML-MCTDH) method [3],[4],[5] facilitated the evaluation of the system's wave function using a multilayer tree optimized via hierarchical clustering [8]. Flux and operated flux calculations were then employed to derive sticking probabilities and scattering distributions.

Comparisons between QD and MD simulations for this full-dimensional system revealed striking similarities. Besides, these results enabled discernment that disparities between experimental and MD simulation outcomes stem from PES accuracy and quantum effects, such as zero-point energy. Notably, an examination of graphene phonons during collisions underscored the pivotal role of longitudinal phonons in the collision process.

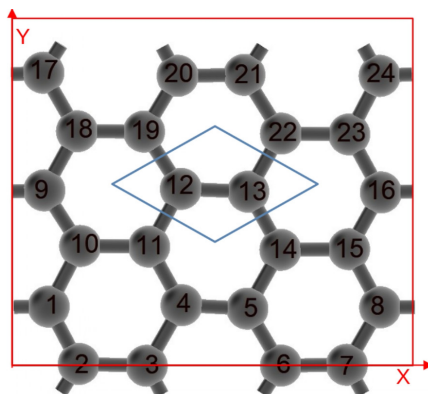


Figure 1: The PES Graphene cell which contains 24 C atoms. The H atom is periodic in the element cell indicated by the blue rhombus.

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P51: A quantum rate model to investigate an orientational isomerization reaction in CO/NaCl (100)

[SINHA, Shreya \(Universität Potsdam\)](#), [SAALFRANK, Peter \(Universität Potsdam\)](#)

This poster presents a theoretical study of a rotational isomerization reaction [1] in a condensed phase system, CO on NaCl (100), showcasing signatures of heavy-atom thermally-activated tunneling at temperatures 19-24 K experimentally, flipping from an “O-bound” to a “C-bound” isomer on the substrate [2]. A reduced dimensional Fermi’s golden rule model is utilized which treats tunneling as a system-bath problem; transitions occur between bound states of an asymmetric double-well potential (obtained ab-initio from DFT [3]) under weak perturbations from the surface phonon bath. Our model is able to qualitatively explain an erratic mass dependence of the kinetic isotope ratios via “tunneling gateways”, which are essentially pairs of system states bound on either well, closely spaced in energy, contributing and yielding a non-intuitive mass-dependence to the isomerization rates, in a phonon-assisted mechanism. We also present a comparison with classical Eyring’s transition rate theory, without and with quantum mechanical correction factors, as well as a semi-classical WKB theory. In addition, a quantum dynamical study of vibrational relaxation of librational modes associated with the isomerization process is presented.

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P52: Effective Modeling of Open Quantum Systems by Low-rank Discretization of Structured Environments

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The interaction between a quantum system and its environment leads to various physical phenomena, which are crucial for multiple scientific domains, including quantum phase transitions, and the dynamics of exciton and charge transport in organic electronics. In practical scenarios, the environment is often modelled as a continuous boson or fermion field linearly coupled to the system. The effect of the environment on a system is characterized by the spectral density through the fluctuation-dissipation theorem. Some methods for calculating the dynamics of a system, such as the thermos field dynamics (TFD) [1,2], require converting the continuous environment into a discrete set of bosons or fermions. Previous studies have typically used simple equispaced sets of frequencies [3,4], lacking an optimal method for selecting sample frequencies and coupling coefficients based on spectral density.

In this study, we propose a novel method that exploits a low-rank approximation to compress the time, frequency and temperature information in the fluctuation-dissipation relation [5].

The approach was tested on a model system of the Fenna-Mathews-Olsen (FMO) complex [6] at different temperatures. The results demonstrate that our method achieves accurate dynamics simulations while reducing the degrees of freedom (DoFs) by more than five times compared to existing approaches, thereby yielding significant computational savings.

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P53: On the vibronic level structure of cubic point groups

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This project is a theoretical study of the $T_\alpha \otimes t_\beta$ Jahn-Teller and Berry phase effects in general cubic groups T_d and O_h . Its aim is to extend previous efforts carried out by Weike *et al.* for systems of C_{nv} symmetry [1]. Vibronic coupling effects play a crucial role in molecular systems where a symmetry-induced conical intersections (CIs) are dynamically relevant. Most works focus on the $E \otimes e$ Jahn-Teller case for C_{3v} systems and linear vibronic coupling. However, insights derived from this restricted case do not trivially generalize to Jahn-Teller systems of different symmetry.

Here, a simple, parametrized $T_2 \otimes t_2$ model using symmetry adapted coordinates was studied. Such an expression helps us investigate the potential's topography, in particular the location of CI seams and dependence on higher order terms. In the linear vibronic coupling case, the system is already characterized by 4 conical intersection seams meeting at the origin, each locally resembling a Jahn-Teller system of lowered symmetry. Diagonalizing the Hamiltonian allows us to study the Berry phase around the CIs in an adiabatic picture.

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P54: Developing a full dimensional 2 state diabatic PES for CH_3F^+ using artificial neural networks

[VOSSSEL, Maik](#) (Universität Bielefeld), [EISFELD, Wolfgang](#) (Universität Bielefeld)

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

P55: Manipulating spin populations through ring currents

[WALLNER, Lisamaria](#) (Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg), [VENDRELL, Oriol](#)

Ring currents, circular flows of π -electrons in aromatic molecules, are responsible for intriguing effects, for instance modifying light absorption properties of phthalocyanine molecules [1]. These currents can either be initiated by applying a magnetic field perpendicular to the π -system or by applying circularly polarized light. The ability to generate and manipulate electronic currents within ring-shaped molecules and materials with polarized light fields has recently attracted considerable interest, in view of the potential applications of these processes in optoelectronics [1,2], including the development of ultrafast switching qubits [3].

The possibility to manipulate a central spin through the use of a magnetic field induced by the ring current is therefore highly desirable. For this purpose, we have developed a simple model that describes electronic states of a quasi-planar molecule coupled to a free spin located at its center via spin-orbit coupling.

We investigate various laser excitation schemes including continuously pumping the system with circularly and linearly polarized light.

The quantum dynamics of the laser-driven model system is simulated with the Heidelberg Multiconfigurational Time-Dependent Hartree program [4] for our simulations.

Our results shed light on the ensuing electronic and spin population dynamics and the impact of the optical excitation scheme.

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P56: Diabatic Potential Energy Surfaces for Renner-Teller Systems using Artificial Neural Networks

[WILLIAMS, David](#) (Institute of Physics of Rennes, University of Rennes), [VIEL, Alexandra](#) (Institute of Physics of Rennes, CNRS & University of Rennes)

As the list of detected molecular species in the interstellar medium keeps expanding, so must our theoretical arsenal to understand the chemical processes at play. Linear carbon chain molecules have been discovered, including (cyano-)polyynyl radicals and their anions. Several open questions remain about their formation. A proposed key mechanism is radiative electron attachment [1], $A + e^- \rightarrow [A^-]^* \rightarrow A^- + h\nu$, together with its reverse process, photodetachment. The theoretical treatment of such systems hence hinges on the availability of accurate potential energy surfaces (PESs). Together with quantum dynamics simulations, appropriate models provide direct access to spectroscopic quantities and cross sections. Unfortunately, modeling is severely complicated in the case where the Born-Oppenheimer approximation breaks down, as is the case for linear molecules with pronounced pseudo Renner-Teller coupling.

Butadiynyl (C_4H) is a pertinent example where this problem arises, as neglecting its low-lying 2II excited state underestimates the system's effective dipole to the point of quantitatively disagreeing with experimental observation [2]. Expressing the electronic Hamiltonian in a so-called diabatic representation yields each as a fully occupied matrix of smoothly varying functions at the cost of various technical challenges. In this work we develop techniques for the construction of accurate diabatic PESs beyond the Franck-Condon approximation using novel machine learning techniques, extending previous approaches [3].

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P57: Computing excited states of molecules using normalising flows

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The calculation of excited molecular states, including electronic and nuclear rotational-vibrational states, presents significant challenges. The complexity of excited-state calculations using variational approach tends to increase almost exponentially as the number of required states grows. The variational method relies on expanding the states' wavefunctions within the span of a selected basis set. Consequently, the effectiveness of this method, particularly its fast convergence with the number of basis functions, depends on the appropriateness of basis functions selected for the problem at hand and the coordinates used to describe the system.

Despite ongoing efforts to develop stable methods that optimise basis sets, relatively little progress has been made in devising approaches for identifying optimal coordinates. In our approach, we introduce and develop a new framework designed to optimise the coordinates representing the system. The framework utilises normalising flows, a machine learning method for constructing highly expressive parametrisable invertible functions. The parameters of the normalising flow are optimised based on the variational principle. We will present results demonstrating enhanced convergence of basis sets, hence enhanced overall efficiency, through the use of normalising flows. Additionally, we will analyse the results for optimised coordinates for molecular systems such as H_2S , HCN and H_2CO .

P57: Computing Non-Adiabatic X-ray Absorption Spectra of Ethylenic Molecules Using a Vibronic Coupling Hamiltonian

[YAGHOUBI JOUYBARI, Martha \(University of Ottawa\)](#), [NEVILLE, Simon \(National Research Council Canada, Ottawa, Ontario, Canada\)](#), [S. SCHUURMAN, Michael \(University of Ottawa\)](#)

Advancements in ultra-fast X-ray sources now offer unprecedented capabilities in X-ray spectroscopy, providing high-quality data that demands increasingly sophisticated computational methods for analyzing and interpreting experimental results. One key challenge lies in understanding the interplay between electronic transitions and vibrational motion, known as vibronic coupling. This interaction influences X-ray absorption spectra (XAS) by broadening and shifting absorption peaks, leading to the observed fine structures.

Simulating XAS poses a significant challenge due to the requirement to consider a large number of excited states. As energy increases, the excited state manifold becomes denser, ensuring the existence of strong vibronic coupling between excited states. In the realm of XAS, vibronic coupling significantly influences spectral features.

Our study aims to investigate the impact of vibronic coupling on the XAS of Ethylenic Molecules. To achieve this, we employed Quantum Dynamics (QD) simulations based on a vibronic coupling Hamiltonian. For the quantum dynamics calculation, we employed the Multi-Configuration Time-Dependent Hartree (MCTDH) method using the MCTDH package. The simulation results underscore the crucial role of incorporating vibronic coupling to accurately reproduce the experimental XAS spectrum.

P59: Simulating Quantum Chemistry Hamiltonians with Relativistic Effects on Fault-Tolerant Quantum Computers

[ZAK, Emil \(BEIT TECH\)](#)

We present a quantum computing algorithm for calculating the spectra of electronic Hamiltonians, including relativistic effects. Fault-tolerant quantum computer resources are estimated by counting the number of qubits and T-gates. These resources are reduced through efficient implementations of quantum data-access oracles and tensor factorization techniques. Our method addresses, among other challenges, the modeling of mechanisms for intersystem crossing in molecules.

P60: Implementing Discrete Variable Representations on a Fault-Tolerant Quantum Computer

[ZAK, Emil](#) (BEIT sp. z o. o.), [PLIŚ, Szymon](#) (BEIT sp. z o. o.), [JARNICKI, Witold](#) (BEIT sp. z o. o.)

We present a quantum computing algorithm implementing the discrete variable representation (DVR) transformation. This technique can be used to calculate the energy levels of rotational-vibrational Hamiltonians. We thus estimate the fault-tolerant quantum computing resources required for such simulations involving non-sum-of-product potential energy surfaces.

P61: The CH₃ umbrella reporter mode in the D+CH₄ reaction

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First-principles based studies of quantum state-to-state reaction dynamics aims to provide insights into the most detailed dynamical processes of chemical reactions and has achieved great success in predicting and explaining fascinating quantum effects in various tri-atomic systems. This field has now advanced to polyatomic reaction systems, and reactions of CH₄ with various atoms are the most studied systems.

Recently, we performed a theoretical study of the D+CH₄→HD+CH₃ reaction with the time-dependent wave packet method using a seven-dimensional model Hamiltonian developed by Palma and Clary. The velocity and angle-resolved state-specific differential cross sections (DCSs) at three collision energies are investigated in detail. An interesting angular distribution of the CH₃(v'=1) product umbrella bending vibrational state is observed to be more in the sideways direction than the CH₃(v'=0) one. By monitoring the transient wave function evolution along the reaction coordinate, the CH₃ umbrella bending mode, existing in both the CH₄ reactant and the CH₃ product, is established as a unique reporter mode that continuously reveals how the reactant D atom dynamically approaches the CH₄ co-reactant and how the HD and CH₃ products recoil from each other.

General organisational information

All *talks, welcome and the concluding remarks* take place at the DESY lecture hall (**building 5**, Room Auditorium)

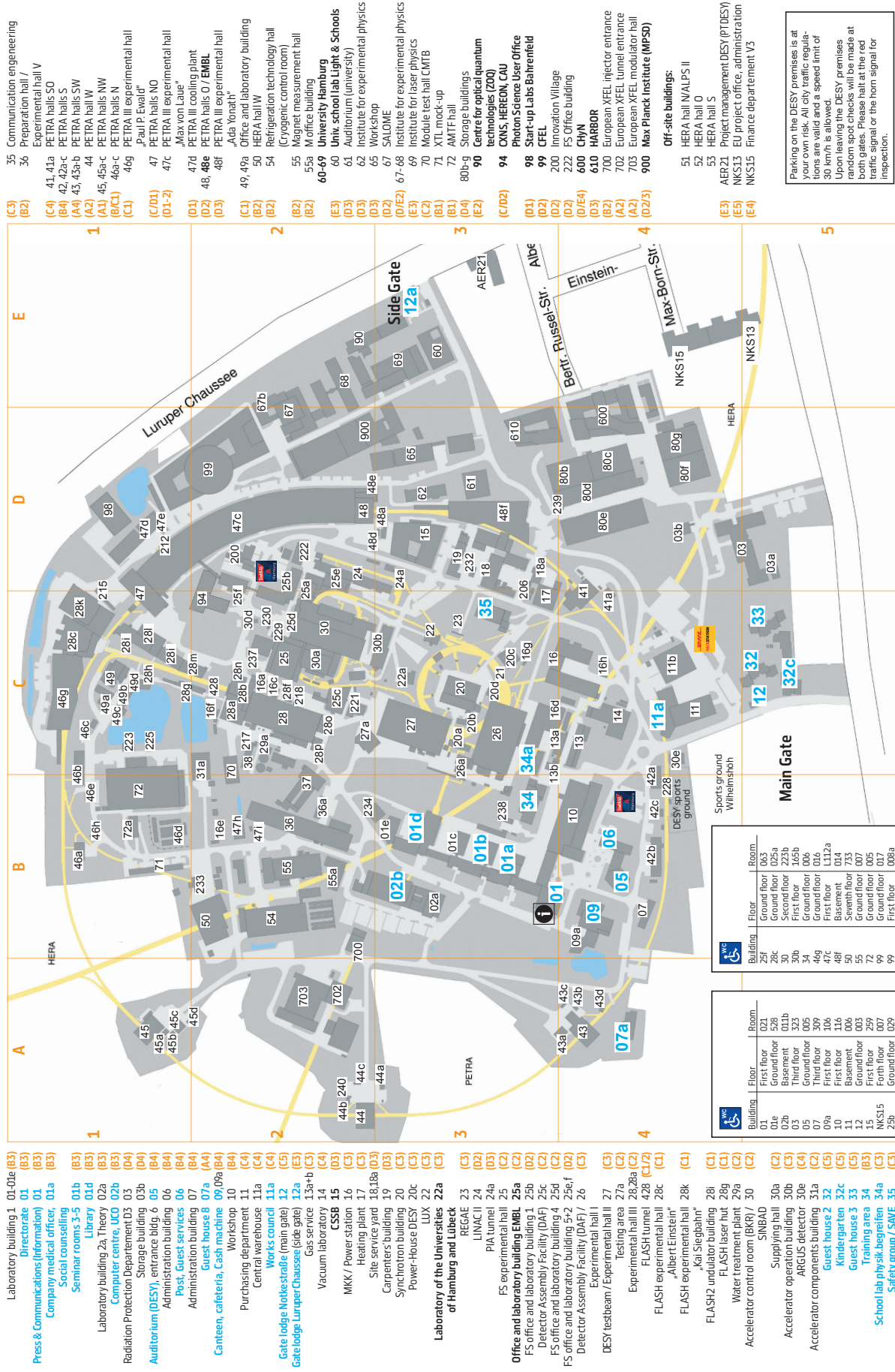
If you do not have an Eduroam account, please contact us and we will provide you with an appropriate account to access the Wi-Fi. In the DESY lecture hall, only a few seats have a power connection. At the lectern in particular, only a USB-C power connection is available.

The *welcome reception and coffee breaks* are in the foyer of the DESY lecture hall (**building 5**).

On Tuesday, the group photo is taken immediately at the start of the lunch break in front of building 5

Lunch is served in the DESY Kantine (**building 9**, next to the lecture hall). Payment can only be made in cash.

The *poster session* is in the basement of the CFEL (center for free electron laser science, building 99 on the DESY campus.)



- Laboratory building 1 01-01e (B3)
- Directorate 01 (B3)
- Press & Communications (Information) 01 (B3)
- Company medical officer, 01a (B3)
- Social counselling (B3)
- Seminar rooms 3-5 01b (B3)
- Library 01d (B3)
- Laboratory building 2a, Theory 02a (B3)
- Computer centre, UCO 02b (B3)
- Radiation Protection Department 03 (B4)
- Storage building 03b (B4)
- Auditorium (DESY), entrance bldg 6 05 (B4)
- Administration building 06 (B4)
- Post, guest services 06 (B4)
- Administration building 07 (B4)
- Canteen, cafeteria, Cash machine 07a (A4)
- 07b (A4)
- Workshop 10 (B4)
- Purchasing department 11 (C4)
- Central warehouse 11a (C4)
- Works council 11a (C4)
- Gate lodge Notkestraße (main gate) 12 (C5)
- Gate lodge Luruper Chaussee (side gate) 12a (E5)
- Gas service 13a-b (E5)
- Vacuum laboratory 14 (C4)
- CS58 15 (D3)
- MKK / Power station 16 (C3)
- Heating plant 17 (C3)
- Site service yard 18,18a (D3)
- Carpenters' building 19 (D3)
- Synchrotron building 20 (C3)
- Power-House DESY 20c (C3)
- LUX 22 (C3)
- Laboratory of the Universities 22a (C3)
- REGAE 23 (C3)
- LINAC II 24 (C3)
- PIA tunnel 24a (D3)
- FS experimental hall 25 (C2)
- Office and laboratory building EMBL 25a (C2)
- FS office and laboratory building 1 25b (C2)
- Detector Assembly Facility (DAF) 25c (C2)
- FS office and laboratory building 4 25d (C2)
- FS office and laboratory building 5-2 25e,f (C2)
- Detector Assembly Facility (DAF) 26 (C3)
- DESY (testbeam) / Experimental hall 27 (C3)
- Testing area 27a (C2)
- Experimental hall III 28,28a (C2)
- FLASH tunnel 428 (C1/2)
- FLASH experimental hall 28c (C1)
- "Albert Einstein" FLASH experimental hall 28k (C1)
- "Kai Siegbahn" FLASH2 undulator building 28i (C1)
- FLASH laser hut 28g (C2)
- Water treatment plant 29a (C2)
- Accelerator control room (BKRY) / 30 (C2)
- SINBAD
- Supplying hall 30a (C2)
- Accelerator operation building 30b (C2)
- ARGUS detector 30c (C4)
- Accelerator components building 31a (C4)
- Guest house 2 32 (C5)
- Kindergarten 32c (C5)
- Guest house 3 33 (C5)
- Guest house 3 33 (C5)
- Training area 34 (B3)
- School lab physik, begeffen 34a (C3)
- Safety group / SWE 35 (C3)

Parking on the DESY premises is at your own risk. All city traffic regulations are valid and a speed limit of 30 km/h is allowed. Upon leaving the DESY premises random spot checks will be made at both gates. Please halt at the red traffic signal or the horn signal for inspection.

October 2021

Conference dinner

Welcome to Hamburg. . .



... and welcome aboard the Klein Fritzen

This is where you'll get to know Hamburg from its best side and discover Europe's second largest port city from the sea side with all its beauty, charm and flair.

During the three hours boat trip on the Elbe a nice dinner will be served.

The trip will start at Landungsbrücken at 6 pm on Thursday, July 18, 2024.

Meeting point: Überseebrücke, 20459 Hamburg at 5:30 pm

Public transport: Get of at *Baumwall U3* or *Landungsbrücken S1/S3*



QR Code to access the meeting point on Google Maps

Sponsors

We are grateful for financial support generously provided by the

EXZELLENZCLUSTER **CUI: ADVANCED** **IMAGING OF MATTER**

The cluster of Excellence has been awarded to the University of Hamburg in the framework of the Federal Excellence Initiative of Germany.

Functionalities are at the heart of the cluster of excellence CUI: "Advanced Imaging of Matter". Atoms bind together and form solids, molecules interact and react - new functionalities emerge with increasing complexity and growing system size. 185 scientists from different disciplines such as physics, chemistry, and structural biology have joined forces to observe, understand, and control these processes. Thereby teams of Universität Hamburg cooperate with scientists of the Deutsche Elektronen-Synchrotron (DESY), the Max Planck Institute for the Structure and Dynamics of Matter (MPSD), and the European XFEL GmbH (XFEL).

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