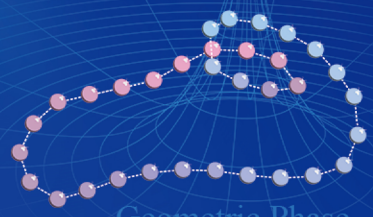
AIQMD2026



Geometric Phase

CECAM Flagship School
Frontiers in Ab Initio Quantum Molecular Dynamics

Conference Manual

Nonadiabatic Field

Organizers:

Jian Liu, Eberhard K. U. Gross, Daniel Escudero

Jul 25 – 29, 2026

College of Chemistry and Molecular Engineering, Peking University

Conference Website

Contents

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Conference overview

Time	Jul 24 (Fri)	Jul 25 (Sat)	Jul 26 (Sun)
08:20-08:30		Opening Remarks	
08:30-09:10		Nancy Makri	Matthias Scheffler
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11:40-13:30	lunch	lunch	lunch
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15:20-16:00	Seogjoo J. Jang	Garnet Chan	Basile Curchod
16:00-16:40	Akira Nakayama	Xiaosong Li	Eberhard K. U. Gross
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17:00-17:30	Bingbing Suo	Poster Session	Closing Remarks
17:30-18:00	Wei Hu	Poster Session	

Detailed Program

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H-1 17:00–18:00

SAI

Saturday, July 25, 2026

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L-2 09:10–09:50

Victor Batista (Yale University)
Quantum Machine Learning in Chemistry

S-3

Session Chair: **Jiushu Shao** (Beijing Normal University)

L-3 10:20–11:00

Jianshu Cao(MIT)
Polariton Chemistry: Quantum Control with Cavity Photons

L-4 11:00–11:40

Dmitry Shalashilin (University of Leeds)
Electrophore Model for Dissociation of Molecules After Electron Impact in Plasma

S-4

Session Chair: **Wenjian Liu** (Shandong University)

L-5 13:30–14:10

Weinan E (Peking University)
Large atomistic models: from DPA-1 to DPA-4

L-6 14:10–14:50

Mark Tuckerman (New York University)
From Quantum Statistics to Dynamics: Machine learning and other algorithms for quantum simulation via path integrals

S-5

Session Chair: **Xiaodong Wen** (Institute of Coal Chemistry, Chinese Academy of Sciences)

L-7 15:20–16:00

Xin Xu (Fudan University)
Efficient Pair-Density Functional Theory for Complex Molecular Systems

L-8 16:00–16:40

Andreas Savin (CNRS and Sorbonne University)
Correction of the Basis Set Error Due to the Absence of the Electron-Electron Cusp in the Wave Function by Using an Adiabatic Correction

S-6

Session Chair: **Basile Curchod** (University of Bristol)

H-2 17:00–17:30

hNaF

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DeepPotential

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Session Chair: **Hong Jiang** (Peking University)

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Matthias Scheffler (The NOMAD Laboratory at BIFOLD, TU Berlin)
Interpretable AI with Quantified Trust for the Discovery of Energy Materials

L-10 09:10–09:50

Reinhard Maurer (University of Goettingen & University of Vienna)
Ultrafast Dynamics at Surfaces with Machine Learning Surrogates

S-8

Session Chair: **Wei Hu** (University of Science and Technology of China)

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Shuhua Li (Nanjing University)
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Seiichiro Ten-no (Kobe University)
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Session Chair: **Haobin Wang** (University of Colorado Denver)

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Tucker Carrington (Queen's University)
Using a product contracted basis and optimised collocation points to solve the Schroedinger equation

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Rachel Crespo-Otero (University College of London)
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Session Chair: **Jiali Gao** (Shenzhen Bay Laboratory)

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S-11

Session Chair: **Reinhard Maurer** (University of Goettingen & University of Vienna)

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AIMC

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PySCF

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Session Chair: **Yajun Liu** (Beijing Normal University, Zhuhai)

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Session Chair: **Run Long** (Beijing Normal University)

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Leeor Kronik (Weizmann Institute of Science)

Advances in Optical Spectroscopy from Density Functional Theory

L-18 11:00–11:40

Zhenggang Lan (South China Normal University)

Ab Initio Simulation of Ultrafast Spectroscopy and Nonadiabatic Dynamics in Polyatomic Molecules

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Session Chair: **Andrey Vasenko** (HSE University)

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Piotr Piecuch (Michigan State University)

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L-20 14:10–14:50

Federica Agostini (Sorbonne University)

Theory and Simulations of Ultrafast Processes in Molecules

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Session Chair: **Xuefei Xu** (Tsinghua University)

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Seogjoo J. Jang (City University of New York - Queens College)

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Akira Nakayama (The University of Tokyo)

Molecular Insight into the Adsorption and Conversion at the Liquid/Solid-Oxide Interface

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Session Chair: **Daniel Escudero** (KU Leuven)

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BDF

H-9 17:30–18:00

PWDFT

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Francesco Paesani (University of California, San Diego)
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Zhigang Shuai (The Chinese University of Hong Kong - Shenzhen)
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Daniel Escudero (KU Leuven)
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Trond Saue (CNRS/Université de Toulouse)
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Christoph van Wüllen (TU Kaiserslautern)
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Session Chair: **Bingbing Suo** (Northwest University, China)

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Garnet Chan (California Institute of Technology)
Towards Reaction Mechanism Discovery in Biological Systems

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Xiaosong Li (University of Washington)
Breaking the Quadrillion Determinant Barrier in Numerically Exact Configuration Interaction

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Frank Neese (Max Planck Institut für Kohlenforschung)
New Developments in the Quantum Chemistry of Open Shell Systems

L-32 09:10–09:50

Wenjian Liu (Shandong University)
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S-22

Session Chair: **Hui Li** (Jilin University)

L-33 10:20–11:00

Eli Pollak (Weizmann Institute of Science)
The Semiclassical Route to Ab Initio Quantum Dynamics

L-34 11:00–11:40

Nandini Ananth (Cornell University)
Excited State Charge and Energy Transfer Mechanisms from Modern Semiclassical Theory

S-23

Session Chair: **William Glover** (NYU Shanghai)

L-35 13:30–14:10

Michele Ceotto (Università degli Studi di Milano)
Non-adiabatic Semiclassical Molecular Dynamics

L-36 14:10–14:50

Fabien Gatti (CNRS and Université Bourgogne Europe)
Quantum Dynamics with the Multi-Configuration Time-Dependent Hartree(MCTDH) Method

S-24

Session Chair: **Elise Dumont** (Université Côte d'Azur)

L-37 15:20–16:00

Basile Curchod (University of Bristol)
Describing Photoexcitation in Nonadiabatic Molecular Dynamics

L-38 16:00–16:40

Eberhard K. U. Gross (Hebrew University of Jerusalem & Tsientang Institute for Advanced Study, Hangzhou)
The Exact Factorization, A Universal Approach to Non-Adiabaticity

Numerically Exact Real-Time Path Integral Methods for Quantum Dynamics

Nancy Makri

Department of Chemistry, Department of Physics,
and Illinois Quantum Information Science and Technology Center
University of Illinois at Urbana-Champaign

The path integral formulation of time-dependent quantum mechanics offers an attractive alternative to the Schrödinger equation and the numerical obstacles associated with wavefunction storage. For Hamiltonians of the system-bath form, where a system is coupled to a large number of harmonic degrees of freedom, the path integral offers a unique advantage, allowing the analytical treatment of the bath and its replacement by a Gaussian influence functional. However, the path sum involves astronomical numbers of terms, and stochastic methods are unable to deal with the oscillatory quantum phase.

A series of developments have led to efficient real-time path integral methods for a variety of processes. Starting in the 1990s, the iterative, tensor-based *quasi-adiabatic propagator path integral* (QuAPI) methodology has enabled numerically exact, fully quantum mechanical simulations of system-bath dynamics at any temperature. Recent work showed that one can further disentangle the path integral variables through the rigorous *small matrix decomposition* (SMatPI), which leads to iterative propagation using matrices of size equal to that of the system's reduced density matrix (RDM). By eliminating tensor storage, the SMatPI algorithm enables the simulation of multistate systems and long-memory processes. Calculation of the SMatPI propagation matrices involves summing all paths within the entangled memory length, whose number increases rapidly with system size, although a drastic reduction is possible in some challenging regimes. Combination with *modular decompositions of the path integral* (MPI) applicable to systems with a (locally) one-dimensional topology enables *iteration in space and time*, leading to linear scaling with system size and propagation length. These (and several additional) methods are implemented in the quantum dynamics package PATHSUM, which is available on the Makri group website.

The methodology has been extended to systems coupled to some anharmonic environments. Recent work has shown that the quantum paths entering the path integral expression can be mapped on graphs, whose properties can be exploited to arrive at novel algorithms. Grouping the paths into *equivalence classes* allows the treatment of static disorder at the cost of a single SMatPI calculation.

In addition to state populations, path integral methods generate the entire RDM, which contains many off-diagonal elements that encode valuable information. *Coherence maps* offer a powerful visualization tool for understanding the creation and destruction of quantum superpositions and enable a state-to-state pathway analysis of dynamical processes.

Representative applications to exciton-vibration dynamics will be presented.

L-2

Quantum Machine Learning in Chemistry

Victor S. Batista

Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States

Email: victor.batista@yale.edu

The nexus of quantum computing and machine learning -quantum machine learning- offers the potential for significant advancements in chemistry. This talk specifically explores the potential of quantum neural networks on gate-based quantum computers within the context of drug discovery. We discuss the theoretical foundations of quantum machine learning, including data encoding, variational quantum circuits, and hybrid quantum-classical approaches. Applications to drug discovery are highlighted, including molecular property prediction and molecular generation. We provide a balanced perspective, emphasizing both the potential benefits and the challenges that must be addressed.

L-3

Polariton Chemistry: Quantum Control with Cavity Photons

Jianshu Cao[*]

Department of Chemistry, MIT, 77 Mass. Ave, Cambridge, MA 20139

*Email: Jianshu@mit.edu

'Polariton Chemistry' opens new possibilities of quantum control, but also presents new challenges. Inspired by recent experiments in optical cavities, we will present our work on (i) cavity-modified chemical reactions and (ii) cavity-enhanced exciton-polariton transport.

The first part of the talk, I will introduce the emerging topic of 'polariton chemistry' and discuss recent progress on cavity-catalyzed chemical reactions. Our transition state theory calculation [1] attributes the modification of reaction rates to the vibrational frequency shifts, thus explaining the thermodynamic origin of cavity-catalyzed reactions. Application of the generalized resonance energy transfer (gRET) theory [2] explains the resonant and cooperative effects in vibrational energy relaxation in cavities. Though the two theories reveal complementary perspectives of polariton dynamics, new mechanisms [3] are needed to explore the intriguing phenomena.

In the second part of the talk, I will discuss recent results on wave-packet dynamics of exciton-polaritons. In optical cavities, disordered molecules are coupled to cavity photons collectively, such that the cooperativity in the light-matter interaction can overcome the Anderson disorder and lead to a turnover in transport at an optimal level of static disorder.[4] Further, cavity photons can drastically enhance the coherent time-scale of wave-packet motion and lead to noise-enhanced wave-packet spreading in the ballistic regime. [5]

Key Words: polariton chemistry, cavity-catalyzed chemical reactions, cavity-enhanced exciton transport

(1) Yang and Cao, JPC Lett 11, 7204 (2021), Quantum effects in chemical reactions under Polaritonic vibrational strong coupling

(2) Cao, JPC Lett 13, 10963 (2022), Generalized resonance energy transfer theory: Applications to vibrational energy flow in optical cavities

(3) Cao and Pollak, JPC Lett. 16, 5466 (2025) Cavity-induced van-der-Waals interactions; Pollak and Cao, JCP 163, 234111 (2025) The effect of an optical cavity on diabatic tunneling in an ensemble of symmetric double-well systems.

(4) Engelhardt and Cao, Phys. Rev. Lett. 130, 213602 (2023), Polariton localization and dispersion properties of disordered quantum emitters in multi-mode microcavities; PRB 105(6), 064205 (2022), Unusual dynamical properties of disordered polaritons in microcavities

(5) Wu, Cerillo, and Cao, Nanophotonics, 13.14, 2575-2590 (2024). Extracting kinetic information from short-time trajectories: relaxation and disorder of lossy cavity polaritons; Tutunnikov, Qutubuddin, Sadeghpour, and Cao, arXiv:2410.11051 (2025), Noise-enhanced ballistic transport in an optical cavity

L-4

Electrophore model for dissociation of molecules after electron impact in plasma

Ryan Brook[1,2], Dmitry Makhov[1], Alfred Stonelake[1], Gregory Armstrong[2], Anna Nelson[2], Jonathan Tennyson[2,3] and Dmitrii V. Shalashilin[1*]

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[2]Quantemol Ltd., 320 City Road, The Angel, London EC1V 2NZ, United Kingdom
[3]Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
*Email: d.shalashilin@leeds.ac.uk

Chemical processes in low-temperature plasmas typically involve molecules excited by electron impact. Unlike photoexcitation, electron impact on closed shell species primarily produces molecules in triplet states, as triplet states are lower in energy. However, similar to excitation of singlet states by a photon, triplet excitation is localized in a small part of the molecule, which we called electrophore, by analogy with chromophore in photochemistry.

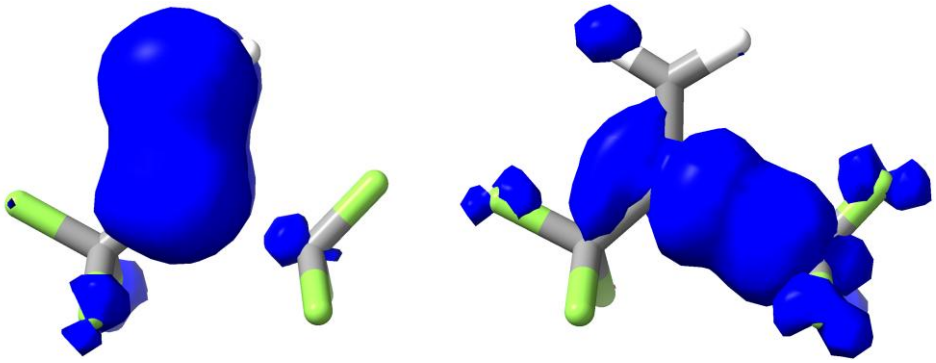

Fig.1 Spin density of the triplet state of the Iso $C_4F_6H_2$ (CH_2=$C(CF_3)_2$) molecule is initially localised at the double bond electrophore shown on the left for C–CF3 distance of 2.066 Å. Then it migrates to the dissociating C–CF3 bond shown on the right for C–CF3 distance of 2.316 Å. Only α spin is shown in these isosurfaces.

The electrophore model suggested by us [1,2] describes well the dynamics of dissociation in plasma. We have shown that nonadiabatic dynamics of energy transfer between different triplet states can be modeled using theories and codes developed previously for the dynamics of energy transfer between chromophores in photochemistry. We find that molecules in triplet states created by electron impact relax very quickly to the lowest triplet state and the dynamics of dissociation simplifies. Therefore, *Ab initio* molecular dynamics on the lowest triplet Potential Energy Surface is often sufficient for understanding the reaction. Plasma chemistry is crucial for plasma technologies in microelectronics manufacturing, and it has been a subject of many experimental studies. In particular, industry is looking for new environmentally friendly molecules to replace fluorocarbons currently used in plasma etching and plasma deposition. See for example [3,4].

Almost no theory of dissociation after electron impact has been reported previously. We hope that this work initiates a new direction of research for the nonadiabatic dynamics community and will help to find new molecules for the use in industry.

Key words: Plasma Chemistry, Dissociation after electron impact, Triplet state

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[2] Brook, R., Bramley, O., Makhov, D.V., Nelson, A., Armstrong, G., Yong, J., Saunders, E., de Viggiani, J., Tennyson, J., Shalashilin, D.V. *Journal of Vacuum Science and Technology* **2025 A43**, 043003.
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L-5

Large atomistic models: from DPA-1 to DPA-4

Weinan E[1,*]

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Large atomistic models (LAMs) are emerging as foundation models for molecular and materials simulation, aiming to learn universal representations of atomistic forces from large-scale quantum-mechanical data. In this talk, we present the development of the DPA model family, from DPA-1 to the latest DPA-4, highlighting how attention-based pretraining, multi-task learning, line-graph neural networks, and new efficient architectures enable improved accuracy, transferability, and scalability. We further discuss DPA-3.1-3M as a representative LAM (large atomic model) trained on multi-disciplinary first-principles datasets, demonstrating strong zero-shot generalization and efficient fine-tuning across molecular and materials tasks. Finally, we demonstrate how LAMs can accelerate scientific discovery.

L-6

From Quantum Statistics to Dynamics: Machine learning and other algorithms for quantum simulation via path integrals

Mark Tuckerman[1,2,3,4,5*]

[1] Department of Chemistry, New York University

[2] Department of Physics, New York University

[3] Courant Institute of Mathematical Sciences, New York University

[4] NYU-ECNU Center for Computational Chemistry at NYU Shanghai

[5] Simons Center for Computational Physical Chemistry at New York University

*Email: mark.tuckerman@nyu.edu

Large-scale simulation of quantum equilibrium and quantum dynamical processes in complex chemical systems requires a combination of technical innovations. In this talk, I will discuss the training of transformer network based energy/force models for use in path integral simulations of structure and charge transport processes in complex chemical environments [1-3], specifically organic electrolyte solutions, I will introduce new algorithms for improving the accuracy of quantum time correlation functions using imaginary time approaches [4], and finally, I will discuss preliminary work on the development of quantum algorithms for direct calculation of quantum time correlation functions [5].

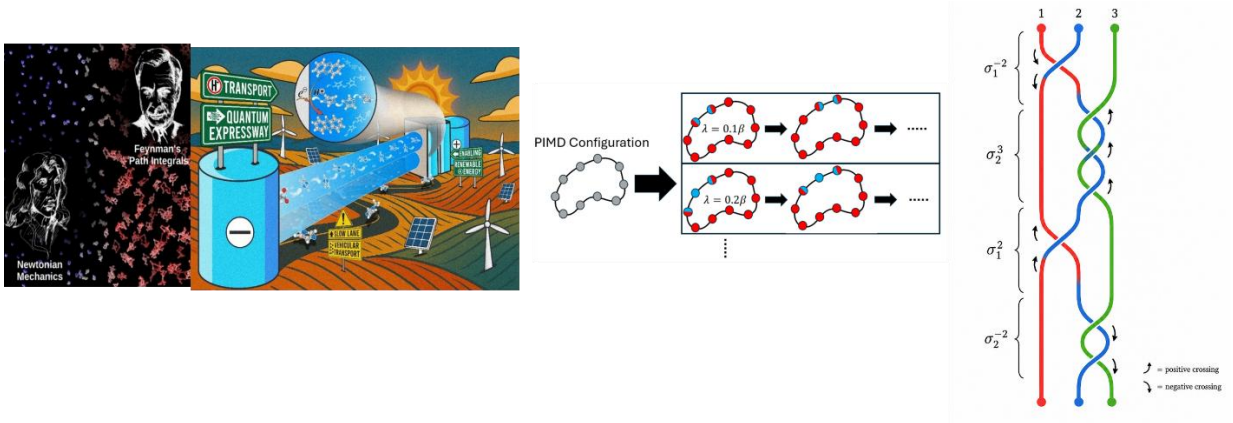

Fig. 1: Illustration of different aspects of path integral quantum dynamics: (Left) Quantum effects influence charge transport in complex electrolyte systems. (Middle) New imaginary time approaches to more accurate quantum time correlation functions for use in condensed-phase simulations. (Right) Quantum algorithms for computation of quantum time correlation functions.

Keywords: Charge transport, path integrals, imaginary time, quantum algorithms

Reference

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[4] H. Kwon, H. Hu, M. E. Tuckerman (in preparation).

[5] K. Polley, M. E. Tuckerman (in preparation).

L-7

Efficient Pair-Density Functional Theory for Complex Molecular Systems

Xin Xu (Research Center for Chemical Theory, Fudan University, P. R. China)

Accurately describing systems with simultaneous static and dynamic electron correlation remains a central challenge in quantum chemistry. Multireference (MR) perturbation and configuration-interaction methods are accurate but costly, while conventional density functional theory (DFT) methods often fail for describing bond-breaking processes and near-degenerate electronic states. In this contribution, we present a systematic development of pair-density functional theory (PDFT) for complex molecular systems. First, we introduce a cross-entropy approximation to tune the complete active space self-consistent field (CASSCF) correlation. Benchmark calculations on the thus-developed on-top exchange-correlation functional, tB4LYP, translated from the successful B3LYP functional, show improved accuracy for main-group and transition-metal bond dissociation energies, spin-flip excitation energies, Cr2 spectroscopy, ethylene torsion, and ethyne dissociation (Nat Commun 2025, 16, 235). Second, we reduce the reference-wavefunction cost by replacing CASSCF densities and on-top pair densities with those from spin-projected unrestricted (SU) Hartree–Fock, leading to SU-PDFT and its hybrid variants. This approach retains the essential static-correlation physics of spin projection while avoiding the exponential active-space scaling of multiconfigurational references (JCTC 2025, 21, 5965). Finally, we develop density-corrected (DC) SU-PDFT, in which a range-separated (rs) SU-rsDFT self-consistent step improves the pseudo-spin density before PDFT energy evaluation. Across spin splittings, diatomic bond dissociation energies, and m-benzyne isomerization, DC-SU-PDFT substantially improves over SU-PDFT and approaches MR-PDFT-level accuracy at a favorable computational cost (DOI: 10.1002/jcc.70398). Together, these developments establish PDFT as a practical, systematically improvable framework for complex molecular systems.

L-8

Correction of the basis set error due to the absence of the electron-electron cusp in the wave function by using an adiabatic correction

Anthony SCEMAMA[1], Andreas SAVIN [2]

[1]Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France

[2]Laboratoire de Chimie Théorique, CNRS and Sorbonne University

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An analytical method addresses the slow convergence of electronic structure calculations caused by the inability of finite one-particle basis sets to describe the electron-electron cusp. An equivalence is made between a calculation using a finite basis set with the physical Coulomb interaction and a calculation using a complete basis set with a model interaction (specifically, the error-function screened Coulomb potential characterized by a range-separation parameter μ). By leveraging the adiabatic connection formalism, a simple, parameter-free correction formula is derived. It depends only on the on-top pair density and a locally defined range-separation parameter (μ) derived from the basis set itself. This 'adiabatic connection based basis set error correction' (ABC) is derived from the asymptotic expansion of the wave function at large μ for small inter-electronic distances. Therefore it is applicable to both ground and excited states without the restriction imposed by the Hohenberg-Kohn theorem. Numerical tests illustrate that the method achieves chemical accuracy using smaller basis sets than typically required.

Keywords: adiabatic connection, basis set error correction, short-range behavior of the wave function

L-9

Interpretable AI with Quantified Trust for the Discovery of Energy Materials

Akhil S. Nair[1, 2], Lucas Foppa[1, 3], Sreejani Karmarkar[1, 2], and Matthias Scheffler[1]

https://nomad-laboratory.de/

1) The NOMAD Laboratory at the Berlin Institute for the Foundations of Learning and Data (BIFOLD) at Technische Universität Berlin, Berlin, Germany
2) Institute of Chemistry and Biochemistry, Freie University Berlin, Germany / DFG Walter Benjamin program
3) Molecular Simulations from First Principles e. V., Berlin, Germany

Machine-learning models promise to accelerate the discovery of new or improved materials, but two obstacles limit their impact in practice: the models are typically black boxes, and they are trained on data that rarely represent the full materials space relevant to a given application. Predictions may therefore be unreliable exactly where discovery matters most, in the unexplored regions.

We address both challenges with the sure-independence screening and sparsifying operator (SISSO) [1], a symbolic-regression approach that identifies explicit, interpretable descriptors of materials properties. We present recently developed uncertainty-quantification schemes tailored to SISSO that indicate, for each candidate material, how far its prediction can be trusted [2, 3]. Embedding these uncertainty estimates into active-learning workflows turns them from a caveat into a search strategy: the workflow deliberately targets the promising yet uncertain regions of the materials space, improving both the reliability and the efficiency of materials discovery. The approach is illustrated with applications to energy-relevant materials.

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L-10

Ultrafast Dynamics at Surfaces with Machine Learning Surrogates

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Ultrafast dynamics at surfaces (driven by light, electrons, or hyperthermal scattering) involve the concerted motion of electrons and atoms at comparable energy and time scales, giving rise to nonadiabatic effects. Excited electrons drive chemical conversions, induce phase transitions, and mediate energy transfer between adsorbates and surfaces. To reliably predict such effects with scalable, state-of-the-art nonadiabatic dynamics simulations requires the use of accurate and data-efficient high-dimensional machine learning (ML) surrogate models. This includes data-efficient representations of energy landscapes, but also nonadiabatic couplings or excited-state properties that are required for nonadiabatic simulations. I will present recent strategies to construct high-dimensional ML surrogate models of electronic structure, including active learning and fine-tuning of foundation models that allow us to reduce the required electronic structure data to a few hundred data points per gas-surface dynamics model. [1] Electronic properties such as electron-phonon coupling tensors [2] or electronic Hamiltonians can be efficiently represented by encoding physical equivariance properties in the model. [3] I will showcase the utility of the introduced models with recent applications of nonadiabatic chemical dynamics at metallic surfaces using the molecular dynamics with electronic friction approach [4] and trajectory surface hopping [5]. Applications include reactive molecular scattering and light-driven surface dynamics. [6]

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L-11

Equation-of-motion Block-correlated Coupled Cluster Methods as Electronic Structure Drivers for Nonadiabatic Dynamics Simulations

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We present recent advances in electronic structure methods for nonadiabatic dynamics simulations. Block-correlated coupled cluster methods based on the generalized valence bond (GVB) reference (GVB-BCCC in short)[1] serves as a practical multi-reference coupled cluster approach for systems requiring large active spaces, in which conventional multi-reference methods are not available. GVB-BCCC with both static and dynamic correlation offers a practical and accurate descrption for the ground state of various systems with multireference character. They can deliver accurate results for systems with large active spaces, including potential energy sufaces, singlet-triplet gaps, and reaction barriers.[2-4] For excited states, we developed an equation-of-motion extension (EOM-GVB-BCCC). EOM-GVB-BCCC with up to four-block correlation has been implemented.[5-6] Pilot calculations demonstrate that EOM-GVB-BCCC4 can provide satisfactory excited-state potential energy surfaces for a number of systems with large active spaces, which are beyond the capability of traditional excited-state methods like CASSCF, EOM-CCSD or time-dependent density function theory.

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L-12

Recent advances of projective transcorrelation theory

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There has recently been a resurgence of interest in the transcorrelated (TC) method, driven primarily by two objectives. The first is to combine the TC method with approximate full configuration interaction (aFCI) solvers, and the second is to reduce the number of qubits required for quantum simulations by downfolding high-energy contributions into the Hamiltonian. Inspired by F12 electronic structure theory [1], the recently developed projective transcorrelated (pTC) method [2] addresses a key limitation of the original transcorrelated (TC) method with Jastrow correlators: its inability to satisfy the distinct electron-electron cusp conditions for singlet and triplet pairs. In this lecture, I will first present the fundamentals of the pTC method and its assessments in conjunction with CCSD(T), MRCI, FCI, and selected CC. I will then introduce recent implementations of quantum algorithms based on the pTC Hamiltonian within the quantum extension of our GELLAN quantum chemistry program.

Keywords: Effective Hamiltonian, Correlation Factor, Cusp Conditions, Direct Downfolding

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L-13

Using a product contracted basis and optimised collocation points to solve the Schroedinger equation

Abstract

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Product contracted (PC) bases are efficient for computing (ro-)vibrational spectra of molecules. However, to account for coupling between subsystems, all previous PC methods require computing integrals by quadrature. The cost of the quadrature is significant and increases with the dimensionality of the molecule. In this talk, I outline a weighted and chopped rectangular collocation method that obviates quadrature. The key ingredients are Christoffel weights, Fekete collocation points, and matrix chopping. We are able to achieve sub-0.1 cm-1 accuracy for both 9-D CH2NH and 6-D HF dimer using a point set whose size is about 10% of the quadrature with which similar accuracy is obtained.

Keywords: vibrational spectroscopy, collocation, contracted basis sets

L-14

Understanding excited state processes in molecular crystals

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Modelling excited states in molecular crystals is particularly challenging, owing to the complexity of the underlying processes and the interplay between radiative and nonradiative pathways. Gaining insight into how these competing mechanisms balance, and how inter- and intramolecular contributions differ, is essential for understanding the emissive behaviour of molecular materials and for guiding the design of more efficient fluorophores. In recent years, my group has developed a suite of methods and tools within the open source code fromage[1,2] to study excited state processes in molecular crystals. In this talk, I will present a selection of these approaches and their applications, encompassing both static and nonadiabatic dynamics treatments in the solid state. I will also highlight the use of machine learning to accelerate simulations and discuss systems spanning weakly bound molecular crystals to covalently connected frameworks such as MOFs.

Keywords: Effective Hamiltonian, Correlation Factor, Cusp Conditions, Direct Downfolding

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L-15

From Functional Approximations to Excited State Theory and Computation in DFT

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This talk will feature our work starting from understanding and correcting systematic delocalzation error in density functional approximations (DFAs) to establishing the theoretical foundation for excited state ΔSCF approach and developing novel, accurate, and efficient methods for excited state calculations. While powerful, conventional DFAs suffer from significant delocalization errors, leading to underestimating energy gaps in molecules and materials, incorrectly predicting the dissociation limits of chemical bonds, overdelocalizing charge distributions, and misaligning energy levels at interfaces. These inaccuracies arise because most DFAs violate the exact quantum mechanical conditions that govern systems with fractional electron charges and spins. To address these fundamental limitations, our group has developed the Localized Orbital Scaling Correction (LOSC). This approach corrects the delocalization errors inherent in standard DFAs, elevating DFT to a new level of robustness and accuracy, with major improvement in total energy, density and energy levels for finite and periodic systems.

Furthermore, the orbital energies derived from LOSC-DFT calculations provide valuable information about a system's excited states directly from the ground-state calculations, paving the way for a more complete theory of electronic excitations. Parallelly in terms of total energies, ΔSCF has been used since the 1970s to achieve impressive accuracy for excited states, but it has lacked formal justification. We have now established the theoretical foundation, demonstrating that a valid functional for excited states requires going beyond electron density alone and using the first-order density matrix of the non-interacting reference system. The minimum of this functional corresponds to the ground state energy, consistent with ground state DFT, while the stationary solutions yield excited-state energies and electron densities, validating the ΔSCF approach. Our further work establishes linear conditions for fractional charges in excited states and introduces the concept of excited state chemical potentials, which clarifies the physical meaning of occupied and virtual orbital energies. Building on this robust ΔSCF foundation, we have formulated novel, highly accurate, and efficient methods for excited state calculations, based on occupancy extrapolation to reach many excited states from ground state calculations, and quasiparticle Hamiltonian to describe multiconfigurational states. These developments should have board applications for excited states and nonadiabatic dynamics.

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AIQMD2026

The One-Determines-All (ODA) Principle of MSDFT and the Design of Approximate Matrix Functionals

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How can one construct a matrix functional for interacting electronic states without introducing an entirely new class of density functionals? The answer, I will argue, is a One-Determines-All (ODA) principle. The principle shows that a matrix functional contains no more fundamental information than a single scalar functional; the remaining matrix structure is determined by the matrix density **D**(r) itself.

This observation transforms the design of matrix functionals from a many-function problem into a one-function problem and establishes a direct bridge between conventional Kohn–Sham density functional theory and the multistate theory. It also provides a systematic route for converting existing exchange-correlation approximations into matrix functionals.

I will discuss the mathematical foundation of the ODA principle and illustrate its practical consequences through the development of a local matrix density approximation (LMDA), implemented within a multistate SCF (MSSCF) framework. Applications to excited states, bond dissociation, and strongly correlated systems demonstrate the promise of matrix functionals for describing state interactions and strong-correlation effects beyond the scope of conventional Kohn-Sham theory.

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L-17

Advances in optical spectroscopy from density functional theory

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I will review recent work that shows progress towards true predictive power for optical spectroscopy within density functional theory (DFT). I will focus on solid-state optimal-tuning within time-dependent DFT [1] and on including density-driven correlation within ensemble DFT [2].

Keywords: optical spectroscopy, time-dependent DFT, ensemble DFT

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L-18

Ab Initio Simulation of Ultrafast Spectroscopy and Nonadiabatic Dynamics in Polyatomic Molecules

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Abstract:

We present a comprehensive theoretical framework for simulating nonadiabatic dynamics and time-resolved spectroscopic signals in polyatomic molecular systems. Our approach accommodates arbitrary nuclear motions by combining on-the-fly surface-hopping simulations of nonadiabatic dynamics with the doorway–window approximation for the nonlinear response functions describing light–matter interactions. This scheme enables the first-principles simulation of ultrafast spectra for realistic molecular systems, including time-resolved transient-absorption, time-resolved fluorescence, and two-dimensional electronic spectroscopy.

The resulting simulations reveal rich dynamical details, such as the identification of key nuclear motions in the excited-state processes. Furthermore, we extend this methodological framework to simulate ultrafast electron diffraction (UED), allowing direct comparison with experimental measurements. In close collaboration with experimental groups, we apply these tools to investigate the intricate nuclear motions underlying nonadiabatic events, providing atomistic insights into conical intersection passage, excited-state decay pathways and reaction product formations.

L-19

H_3^+ Formation from Methyl Halogens and Pseudohalogens: Experiment, Theory, and Governing Factors

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The formation of H_3^+ following the double ionization of small organic compounds via a roaming mechanism that involves the generation of a neutral H_2 molecule and a subsequent proton abstraction has recently gained significant attention. In our recent study [1], which is the subject of this talk, we developed a cohesive microscopic model explaining these important reactions. To do this, we performed yield and femtosecond time-resolved measurements following the strong-field double ionization of several CH_3X molecules, where X = OD, Cl, NCS, CN, SCN, and I, which were accompanied by double-ionization-potential equation-of-motion coupled-cluster and *ab initio* molecular dynamics computations. The combination of the state-of-the-art experiment and theory allowed us to obtain detailed understanding of the key factors that govern the formation of H_3^+ by some doubly ionized CH_3X species and its absence in the others and develop useful guidelines for examining alternative sources of H_3^+ in the universe.

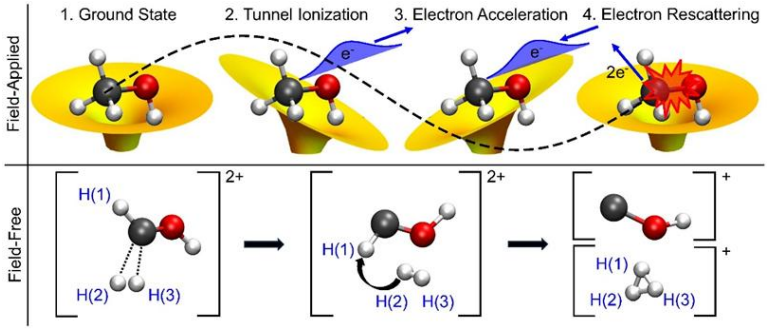

Fig. 1 The formation of H_3^+ following the strong-field double ionization of methanol. Image taken from [1].

Keywords: trihydrogen cation, methyl halogens and pseudohalogens, femtosecond time-resolved measurements, equation-of-motion coupled-cluster theory, *ab initio* molecular dynamics

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L-20

Theory and simulations of ultrafast processes in molecules

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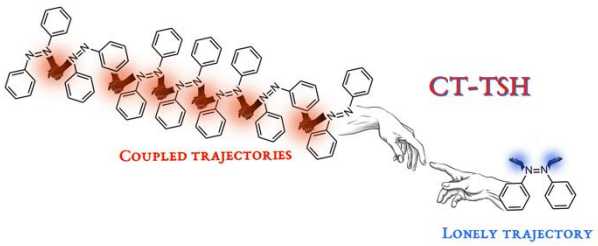
The interaction of light and matter is responsible for a variety of photophysical and photochemical phenomena occurring in nature, like photosynthesis, in the human body, like vision, and in technological devices, like photovoltaics. Theoretical modeling of these phenomena requires to be able to describe the complex interplay of electronic and nuclear motion beyond the Born-Oppenheimer approximation [1], ie including nonadiabatic effects, over ultrafast time scales ranging from femtoseconds to picoseconds.

The exact factorization of the electron-nuclear wavefunction is a formalism introduced in 2010 by Gross and coworkers to analyze and to simulate nonadiabatic processes [2]. Its original electron-nuclear formulation has been used to derive various flavors of trajectory-based algorithms [3, 4] to simulate ultrafast relaxation processes initiated by photoexcitation, like photoisomerizations (see Fig. 1) or photodissociations. However, extensions of the original formalism to treat electron-only systems (exact electron factorization) and photon-electron-nuclear systems (exact photon-electron-nuclear factorization) have been proposed to develop density functional theory or to study photodynamics in the strong light-matter coupling regime [5].

In this talk, I will present an introduction to the theory of nonadiabatic ultrafast dynamics with the exact factorization and I will give an overview of its recent applications.



[Carlotta Pieroni, Eduarda Sangiogo Gil, Lea Maria Ibele,, Maurizio Persico, Giovanni Granucci, Federica Agostini, *J. Chem. Theory Comput.*. **20**(2), 580596 (2024)]

Fig. 1 Schematic representation of the idea of coupled trajectories applied to the photoisomerization process of *trans*-Azobenzene.

Keywords: nonadiabatic dynamics, photodynamics, exact factorization

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L-21

New theoretical advances towards first principles calculation of Fermi's golden rule rates for nonadiabatic transitions

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Great advances have been made over many decades in characterizing electronic excited states and their quantum transitions in complex molecular environments. Depending on the nature of the system and its environments, these quantum transitions can be described either by rates or through more complete quantum dynamical calculations. Although all the dynamics can ultimately be described if a satisfactory first-principles level dynamics calculation method exists, for which significant advances have been made during the past decade, many important physical changes can be or need to be described only as rate processes. For calculating the corresponding rates, Fermi's golden rule (FGR) has been widely and successfully used. However, when applied to complex molecular systems in nontrivial environments, current methods for calculating FGR rates faces some ambiguities and limitations that call for further development. In this talk, I will present our recently developed quantum rate theories for the nonradiative decay of electronic excited states due to nonadiabatic couplings, along with some applications. These include a generalization [1] of the energy gap law that accounts for the effects of low frequency environmental modes, quantitative modeling of the nonradiative decay of near infrared dye molecules [2], a new FGR rate expression [3] for nonadiabatic transition that includes non-Condon effects due to nuclear momentum and the application of this theory to elucidate the anti-Kasha behavior of azulene [4]. Finally, further theoretical and computational advances necessary for satisfactory and efficient evaluation of first-principles level calculation of FGR rates will be discussed.

Keywords: Fermi's golden rule, Energy gap law, nonadiabatic transition

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L-22

Molecular Insight into the Adsorption and Conversion at the Liquid/Solid-Oxide Interface

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Neural network potentials (NNPs) provide a powerful route to extend first-principles molecular simulations to complex catalytic surfaces and solid/liquid interfaces, where bond rearrangements, molecular transport, adsorbate interactions, and surface restructuring occur under finite-temperature and finite-pressure conditions. In this talk, I will present recent developments in our group in NNP-based reactive and statistical molecular simulations for catalytic interfaces.

First, I will discuss NNP-based molecular dynamics simulations of water and alcohol interfaces with metal oxides such as CeO_2 and ZrO_2[1-3]. Nanosecond-scale simulations reveal surface hydroxylation equilibria, proton hopping, hydroxide/proton transport, and facet-dependent adsorption and dissociation dynamics that are difficult to capture by conventional DFT-based molecular dynamics. These applications demonstrate how surface coordination, hydrogen-bond networks, and collective interfacial fluctuations govern reactivity at oxide/liquid interfaces. Second, I will introduce NNP-coupled grand canonical Monte Carlo simulations for hydrogen adsorption on metal surfaces. The combination with modified cavity-bias insertion/deletion enables efficient sampling of hydrogen configurations under prescribed thermodynamic conditions. Applications to Pt, Pd, Ir, and stepped Pt surfaces reveal coverage-dependent site preferences, hydrogen-hydrogen interactions, and adsorbate-induced restructuring[4-6]. Finally, I will present an on-the-fly kinetic Monte Carlo framework in which adsorption and activation energies are evaluated using NNPs during the simulation, enabling explicit treatment of coverage-dependent lateral interactions in surface diffusion and reactions.[7]

These examples illustrate a NNP-based framework for connecting atomistic reaction dynamics, statistical thermodynamics, and mesoscopic kinetics in realistic catalytic environments.

Keywords: NNP, CeO_2, ZrO_2, GCMC, KMC

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L-23

Water clusters and bulk simulations with an accurate universal potential

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In this talk, I will first present a new universal potential for water, constructed solely by fitting many-body interaction energies from high-level electronic structure calculations using fundamental-invariant neural networks. With this potential, we calculate vibrational energies for $(H_2O)_n$ (n = 2, 4) using a neural-network method recently developed by our group, and compute thermodynamic and dynamical properties of bulk water. All the results consistently show excellent agreement with experimental observations, indicating that the long-sought "universal water model" is now within reach.

L-24

From Water to Biomolecules: Data-Driven Many-Body Potentials for Predictive Molecular Simulations

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Achieving chemical accuracy in molecular simulations of aqueous systems has remained a central challenge for decades due to the interplay of many-body interactions and nuclear quantum effects. In this contribution, I will introduce a unified, data-driven many-body (MB) formalism that has enabled realistic simulations from small gas-phase clusters to bulk solutions and interfaces [1]. Our data-driven many-body energy (MB-nrg) potentials, such as MB-pol and its extensions, systematically integrate physics-based representations with machine-learned components trained on coupled-cluster reference data. The MB-nrg approach not only reproduces structural, thermodynamic, and spectroscopic properties across all phases, but also accurately predicts emergent phenomena such as the location of the liquid–liquid critical point in supercooled water. Building on this foundation, I will present recent applications that extend this framework from water and aqueous solutions to generic covalently bonded molecules, enabling predictive biomolecular simulations with chemical accuracy.

Keywords: many-body interactions, data-driven methods, chemical accuracy

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L-25

Time-dependent DMRG for quantum dynamics

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DMRG in the matrix product state (MPS) formulation is of great application not only for electronic structure theory but also for its time-dependent simulation for quantum dynamics of complex system due to the efficient reduction of Hilbert space dimensionality from exponential to polynomial. For quantum dynamics, the MPS is constructed as a direct product state of electron/exciton state and vibrational states. We have developed an algorithm which allow automatically efficient construction of matrix product operator based on bipartite graph theory. Our time evolution algorithm has been built on time-dependent variational principle with projector splitting scheme on the tangent space, which can keep both wavefunction norm and energy conservation. Thermal field dynamics has been carried out through Bogoliubov transformation to take finite temperature into account. We further developed hierarchical equation of motion in the MPS form for system-bath quantum dissipation problem. We applied our TD-DMRG for the carrier transport, thermal electric conversion, light-emitting, molecular junction, and chirality induced spin selectivity phenomenon.

Keywords: time-dependent density matrix renormalization group, bipartite graph theory, hierarchical equation of motion, organic electronic materials.

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Quantum chemical and dynamical simulations to unravel complex photophysics

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In this contribution I present computational protocols to model complex photophysics in molecular systems. Our protocols merge state-of-the-art quantum chemical calculations, excited state decay rate theories (i.e., Fermi-golden rule based)[1] along with semi-classical nonadiabatic excited state dynamics (NAMD) to enable the quantitative determination of lifetimes and quantum yields. In particular, I present an extensive analysis of the parameters influencing the excited state decay rate calculations.[2] Further, I present benchmark studies for the excited-state decay rate constants calculations of Multi-resonance (MR) and inverted singlet-triplet gap (INVEST) thermally activated delayed fluorescence (TADF) emitters, using our state-of-the-art techniques. Specifically, the fluorescence, direct and reverse intersystem crossing (RISC) rate constants were calculated. Our studies highlight the importance of including Herzberg-Teller effects in the ISC and RISC rate constant calculations.[4,5] In order to accelerate the molecular discovery, we also developed wavefunction-based descriptors enabling to discern between INVEST and MR-TADF systems, importantly without the need of expensive highly correlated electronic structure calculations. In addition, to assess the role of higher-lying excited states in the excited state dynamics of TADF dyes, we have developed multistate (four-states and five-states) kinetic models and we have implemented them in our code KinLuv.[6] Finally, complex excited state reactivity scenarios involving higher-lying excited states are studied with NAMD simulations.[7]

Keywords: NAMD, excited state decay rate constants, photophysics, photochemistry, excited states

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L-27

Quantum electrodynamics for chemistry

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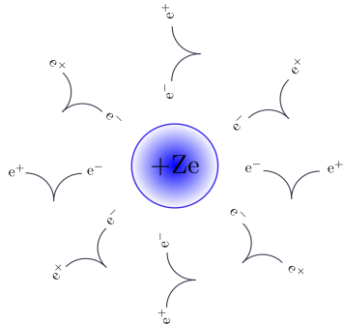
An ideal situation for accurate calculations is a molecule alone in space at 0K. However, is the vacuum really empty ? It has been shown that placing a molecule in an otherwise empty cavity will change its reactivity [1]. This is explained by the coupling of the molecule to the zero-point vibrations of the quantized electromagnetic field.

In the HAMP-vQED we are particularly interested in the effects leading to the Lamb shift, a splitting between the $2S_{1/2}$ and $2P_{1/2}$-levels of one-electron atoms, not predicted by the Dirac equation, but observed for the first time in 1947 by Lamb and Retherford.



- **Vacuum polarization**: A charge in space is surrounded by virtual electron-positron pairs. This will contribute to the observed charge.
- **Electron self-energy**: A charge drags along its electromagnetic field. This will contribute to the observed mass.

The splitting is a mere 4 μeV, but for hydrogen-like uranium the splitting has grown to an impressive 76 eV. It is therefore legitimate to ask if QED-effects could play a role in the chemistry of heavy elements [2]

Keywords:

relativistic molecular calculations, quantum electrodynamics

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L-28

Quasi-Relativistic (Two-Component) Hamiltonians

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Keywords: quasi-relativistic, spin-orbit, picture change, Dirac equation

Relativistic four-component quantum chemical calculations based on the Dirac equation can be substantially more demanding than two-component calculations in the integral evaluation and integral transformation steps, therefore the quest for a two-component Hamiltonian that provides the same results as a Dirac calculation at lower cost has kept us busy for decades. Twenty years ago, it turned out that the solution is surprisingly simple if the transformation is not done at operator level but in a finite basis set representation, basically because the spectral representation of an operator in impossible in general, but trivial for a matrix with finite dimension. In this lecture I shall first review the development leading to the so-called *exact two-component* (X2C) formalism, and then ask what we have gained, since this is exact for a one-electron system only. It turns out that a simple but adequate treatment of electron interaction is of utmost importance to cover the shielding of the nuclear potential in the spin-orbit operator. It is also important to be aware of how to reduce the formal scaling of the method below cubic, and of some technical problems that may arise for contracted basis sets.

The Dirac operator is linear in an external magnetic as well as an external electric field. A main complication that is usually referred to as the picture change problem is that the first-order terms in the quasi-relativistic Hamiltonian do not match their Dirac counterparts, and that the quasi-relativistic operator contains all higher-order terms as well. To calculate a first-order property like the electron density or the electric field gradient at the nucleus, a rather simple picture change correction procedure is possible if certain conditions are met, but for second-order properties and beyond one needs the full response (up to the target order) of the quasi-relativistic Hamiltonian with respect to the perturbation(s) in question, although this response may be linear for both the Dirac and the Schrödinger equations.

The present status is that unless one needs the negative-energy Dirac states to include quantum field effects, one can reproduce any four-component result in a two-component calculation, within the limits of the simplified treatment of electron interaction. Whether or not the higher complexity of quasi-relativistic methods (especially if it comes to higher-order properties), together with the necessary approximations on electron interaction, outweighs the computational savings compared to a full four-component treatment is a technical question where the answer may change in the foreseeable future.

L-29

Towards reaction mechanism discovery in biological systems

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I will describe our current efforts to understand electronic structure and reaction mechanisms in metalloenzymes, focusing in particular on recent work on hierarchical machine learning of *ab initio* quantum molecular dynamics.

Breaking the Quadrillion Determinant Barrier in Numerically Exact Configuration Interaction

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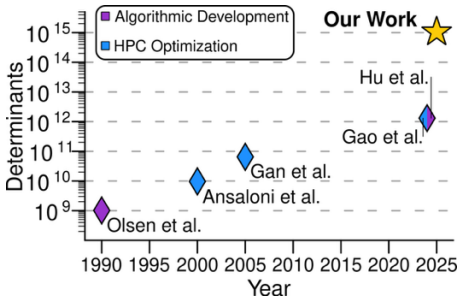
The combinatorial growth of configuration interaction (CI) has long limited this formally exact quantum chemistry method to only the smallest molecules. Here, we report a numerically exact CI calculation exceeding one quadrillion (10^{15}) determinants, made possible by a lossless categorical compression strategy within the small-tensor-product distributed active space (STP-DAS) framework. This approach overcomes the traditional memory bottlenecks of CI by a numerically exact compression of the wavefunction representation and reformulating the most computationally demanding matrix–vector operations. Using this method, we performed a fully relativistic CI calculation of the ground state of HBrTe with over 10^{15} complex-valued determinants in just 34.5 h on 1000 computing nodes—the largest CI calculation ever reported. We further achieved fast computation for systems with hundreds of billions of determinants on only a few compute nodes. Extensive benchmarks confirm that the method retains full numerical exactness while cutting memory and computational cost by orders of magnitude. Compared to previous state-of-the-art CI calculations, this work achieves a 1000 times increase in CI space, a 10^6-fold increase in floating-point operations performed, and a 10^6-fold improvement in computational speed.



[Agam Shayit, Can Liao, Shiv Upadhyay, Hang Hu, Tianyuan Zhang, A. Eugene DePrince III, Chao Yang, Xiaosong Li, Nature Communications, 2025, 16, 11016)]

Fig. 1 The evolution of the state-of-the-art for CI calculations over time. Each historical point is colored according to the nature of the key development of the respective work, which we classify as either intrinsic algorithmic developments or optimizations on the HPC hardware of the time.

Keywords: full CI, X2C, Electronic Structure Theory

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L-31

New Developments in the Quantum Chemistry of Open Shell Systems

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Open shell systems are a fascinating branch of research in quantum chemistry. The challenges posed by the coupling of unpaired electrons are plentiful and intellectually inspiring. In striving for quantum chemical methods that do as little as possible and as much as necessary work, we have recently engaged in the further development of general restricted open shell Hartree-Fock (g-ROHF) theory. I will provide an introduction to the methodology and provide examples of use.

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L-32

Size-Extensive General-Model-Space Many-Body Theories

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In the parlance of second-quantized formalism, a strongly correlated systems of electrons features both static correlation (or strong coupling) between nearly degenerate electron configurations (which span collectively a model space M_0) and dynamic correlation (or weak coupling) between the electron configurations of M_0 and those of $M_0^{\perp}$. The two components of the overall correlation are entangled and interchangeable, so that they must be treated self-adaptively. This means essentially that a suitable model space M_0 should first be constructed without making use of a priori information of the considered system (at any geometry). This can certainly and readily be achieved via a selection of important configurations over the full Hilbert space [1-3]. The remaining dynamic correlation can then be treated via a lowest-order perturbation theory. However, the so-constructed model space M_0 is in general incomplete, which renders the formulation of a size-extensive perturbation theory extremely difficult. In this lecture, we will discuss necessary and sufficient conditions for the size-extensivity of multireference methods that work with a general model space (or partial active space) and present a cost-effective state-universal MRPT2 (dubbed PASPT2[4]) that fulfills all criteria but one for a good wavefunction. Time permitting, we will also discuss how to achieve unified implementation and parallelization of all relativistic and nonrelativistic Hamiltonians and wavefunctions[5-8].

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L-33

The semiclassical route to ab initio quantum dynamics

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Quantum tunneling was discovered by Friedrich Hund in 1927[i]. The semiclassical theory of tunneling was developed by Wigner in 1932[ii] and Kemble in 1935[iii]. Yet, even after almost a century, quantum tunneling is an enigma. Modern practical algorithms for computing tunneling rates are incorrect even at high temperatures. The semiclassical low temperature theory of deep tunneling, initiated by Miller[iv] in terms of instanton trajectories – periodic orbits moving on the inverted potential, suffered from a divergence at the so called crossover temperature between tunneling and thermal activation. Kemble's uniform semiclassical theory predicts wrongly that the transmission probability through a barrier will always be ½ when the energy equals the barrier energy.

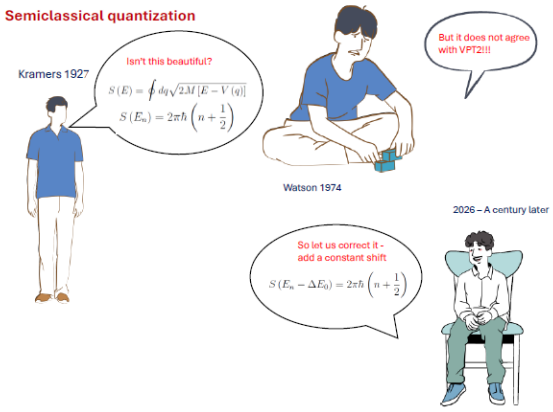
A related topic is the semiclassical quantization of bound state systems. Its origin is in 1927 with the seminal papers of Brillouin, Wentzel and Kramers (BWK theory, also known as WKB theory). Interestingly, it does not agree with second order quantum perturbation theory.

From a practical point of view, the central advantage of semiclassics is its use of classical trajectories which depend only on local information from the force field and are thus amenable to ab-initio on-the-fly computations. Another strong point is that semiclassics do not suffer from the difficulty involved in accounting for the quantization of energy levels.

In this talk I will describe our recent solutions to some of the challenges which still faced semiclassical theories. The divergence inherent to instanton theory will be removed[v], with the conclusion that the crossover temperature between tunneling and thermal activation is twice as high as the one considered by Affleck[vi]. The half point puzzle will be solved.[vii]

Some recent applications and implications of the resulting modern theory of tunneling will be discussed, not the least of which is a critique of present-day numerical algorithms for the computation of tunneling rates[viii]. A simple modification of the BWK theory will be presented and discussed.[ix] Examples will show that it too can be very accurate even in systems with many degrees of freedom.

All this indicates that semiclassics will continue to be an important tool in predicting and analyzing molecular reaction rates and molecular spectra[x].



Keywords: semiclassics, tunneling, WKB theory, spectroscopy, reaction rates

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Excited State Charge and Energy Transfer Mechanisms from Modern Semiclassical Theory

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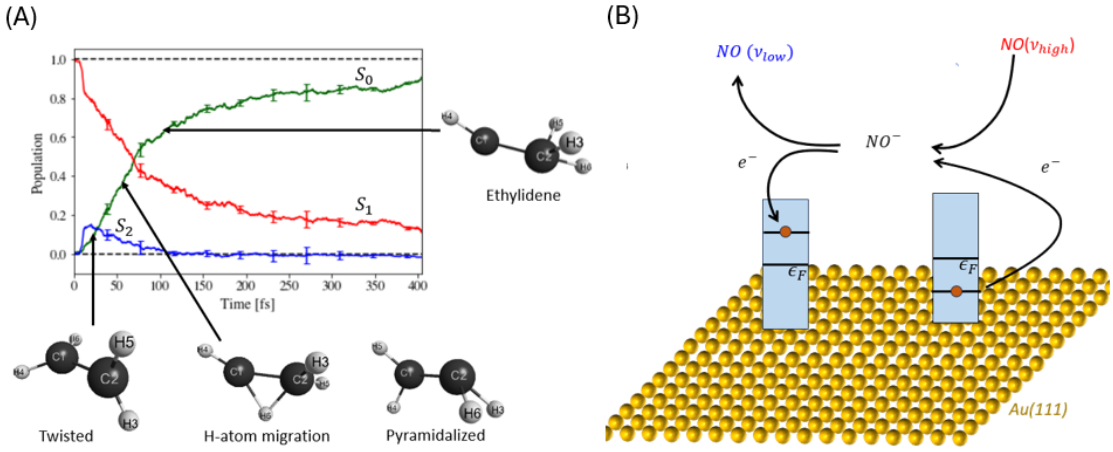

Figure 1: (A) Ethylene photo-isomerization mechanism from on-the-fly semiclassical dynamics (B) Nonadiabatic mechanism for vibrational relaxation at a metal surface

Charge and energy transfer reactions play a key in role in many complex chemical and biological systems. The inherently quantum mechanical nature of these processes is a significant challenge, motivating the development of new simulation methods that can incorporate quantum effects including zero-point energy, nuclear tunneling, and nonadiabatic effects at a computational cost comparable to classical molecular dynamics. This talk will introduce modern semiclassical (SC) theory as a versatile, efficient, and accurate quantum dynamics tool to discover nonadiabatic reaction mechanisms in high-dimensional systems.

We will discuss two key applications of classical-limit SC theory. The first is an atomistic investigation of the photo-isomerization and photo-fragmentation of ethylene with on-the-fly GPU-accelerated ab-initio forces. Uniquely, these methods identify multiple reaction pathways, uncover conical intersection structures, and predict fragmentation pathways without any *apriori* assumptions. The second study focuses on the mechanism of vibrational de-excitation at a metal surface where nonadiabatic effects play a surprising role. We show that while classical-limit SC theory captures some state-to-state dynamics and energy transfer mechanisms, it fails in regimes where experiments report near-resonant energy transfer. The talk concludes with an overview of the mixed quantum-classical SC theory, Hybrid Wigner Dynamics, its applications to adiabatic and nonadiabatic processes and a discussion of future directions.

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Non-adiabatic Semiclassical Molecular Dynamics

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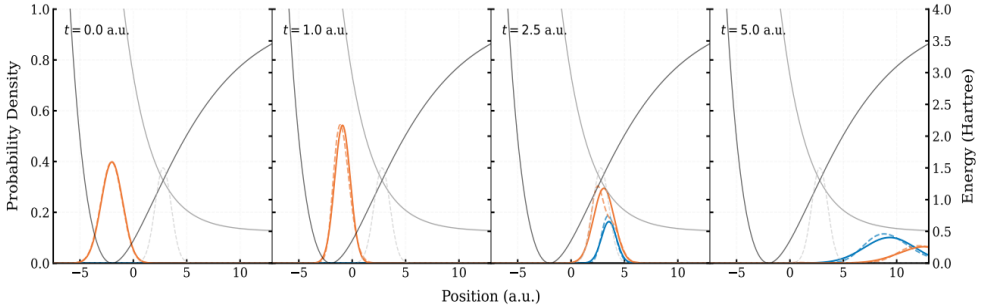
I will introduce the Semiclassical Initial Value Representation (SCIVR) approximation to the quantum propagator and show how we have developed over the years several implementations for complex system spectroscopic calculations.[1] Specifically, these implementations allowed us to extend the applicability of SCIVR to on-the-fly ab initio MD not only for gas phase cluster systems but also for gas-surface and liquid solvated molecules.[2,3] After this introduction, I will focus on our more recent SCIVR developments in non-adiabatic molecular dynamics. Two different methods will be presented. The first one is derived from the Path Integral and applied to the vibronic spectrum calculation of a model of the pyrazine molecule.[4] The second one is derived from the thawed Gaussian approach and applied to electron-trasfer and photodissociation type of reactions.[5] I will show how both tools are promising for including nuclear quantum effects in non-adiabatic molecular dynamics.



[Lorenzo Bocchi, Jia-Xi Zeng, and Michele Ceotto, *J. Chem. Phys.* (submitted)]

Fig. 1 Diabatic wavepackets time-evolution.

Keywords: Thawed Gaussian Wavepacket, Semiclassical Initial Value Representation, Spectroscopy, Rate Constants, Non-adiabatic Molecular Dynamics.

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Quantum dynamics with the Multi-Configuration Time-Dependent Hartree (MCTDH) method

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ABSTRACT

The impact of nuclear quantum effects—including tunneling, zero-point energy, and non-adiabatic transitions—is now recognized across chemistry and physics, from heterogeneous catalysis to attosecond spectroscopy. Interpreting modern experiments in these diverse fields demands a theoretical approach that moves beyond the classical treatment of nuclei. Molecular Quantum Dynamics [1,2] provides this essential framework, allowing for a fully quantum-mechanical description of nuclear motion.

A major challenge, however, lies in extending these quantum simulations to larger molecular systems. To address this, we have developed and applied the Multi-Configuration Time-Dependent Hartree (MCTDH) method [3,4,5]. This powerful algorithm, akin to a time-dependent MCSCF for nuclei, propagates wavepackets across one or multiple potential energy surfaces. With its multi-layer extension [6], the method can handle systems with thousands of degrees of freedom. Here, we will illustrate the capabilities of MCTDH by presenting our recent full-dimensional studies on protonated water clusters, which include up to 18 atoms [7].

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L-37

Describing photoexcitation in nonadiabatic molecular dynamics

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A significant number of computational strategies have been developed over the past decades to simulate the excited-state dynamics of molecules beyond the Born-Oppenheimer approximation. When combined with advanced electronic-structure methods, these techniques – often based on coupled or uncoupled trajectories – have the potential to unravel the mechanistic details of photochemical reactions of direct interest to physical, atmospheric, and material chemists. Despite all these extensive developments, the very first step of any photochemical reaction – photoexcitation – is dramatically approximated in most applications of nonadiabatic dynamics.[1] In an ideal world, the initial ground-state nuclear wavefunction, representing the molecule of interest, should be coupled, for example, to the time-dependent electromagnetic field of a laser pulse, leading to a transfer of nuclear amplitude to an excited electronic state depending on the precise characteristics of the field. In practice, two strong approximations are made to simplify the photoexcitation process:[2] (1) A harmonic Wigner distribution is often used to represent the ground-state distribution of the molecule, from which initial nuclear positions and momenta can be sampled; (2) These pairs of nuclear positions-momenta are then promoted to a given excited electronic state and used to initiate the nonadiabatic molecular dynamics – a so-called sudden excitation approximation.

In this talk, I will discuss the limitations of these two approximations, supported by numerical simulations of realistic molecular systems. I will then present more rigorous strategies to describe the photoexcitation process: ab initio molecular dynamics with a quantum thermostat to sample pairs of nuclear positions-momenta in the ground electronic state[3] and the promoted nuclear density approach to incorporate the effect of a laser pulse at the level of the initial conditions at no cost.[4]

Keywords: Nonadiabatic molecular dynamics, photoexcitation, laser pulse

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L-38

The exact factorization, a universal approach to non-adiabaticity

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The adiabatic approximation, describing the full wave function of a molecule or solid as a single product of a Born-Oppenheimer state and a nuclear wave packet, is a corner stone of modern quantum chemistry and solid-state physics. It not only makes computations feasible, it also provides an intuitive picture of many chemical processes. Yet, many fascinating phenomena appear outside the adiabatic regime. Prime examples are phonon-driven superconductivity as well as the phenomenon of electronic decoherence, i.e. the loss of quantumness well-known for its capacity of preventing genuine scalable quantum computing to this day. In this lecture a unified approach to non-adiabaticity, known as the *exact factorization*, will be presented. The approach starts from a formally exact representation [1] of the full electron-nuclear wave function as a product of a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for the two factors provide an ideal starting point to develop efficient algorithms for the study of non-adiabatic phenomena. The successful prediction of laser-induced isomerization processes [2], the ab-initio description of decoherence [2,3,4], calculations of the molecular Berry phase [5] as well as vibrational circular dichroism will demonstrate the power of the approach. We shall develop the concept of exact forces on the nuclei which involve a time-dependent potential-energy surface and a time-dependent Berry-connection-type vector potential [6]. Consequences of the latter will be discussed for systems exposed to external electromagnetic fields [7] and for current-carrying molecular junctions [8,9].

Keywords: nonadiabaticity, exact factorization, Berry connection, current-induced force, atomic waterwheel

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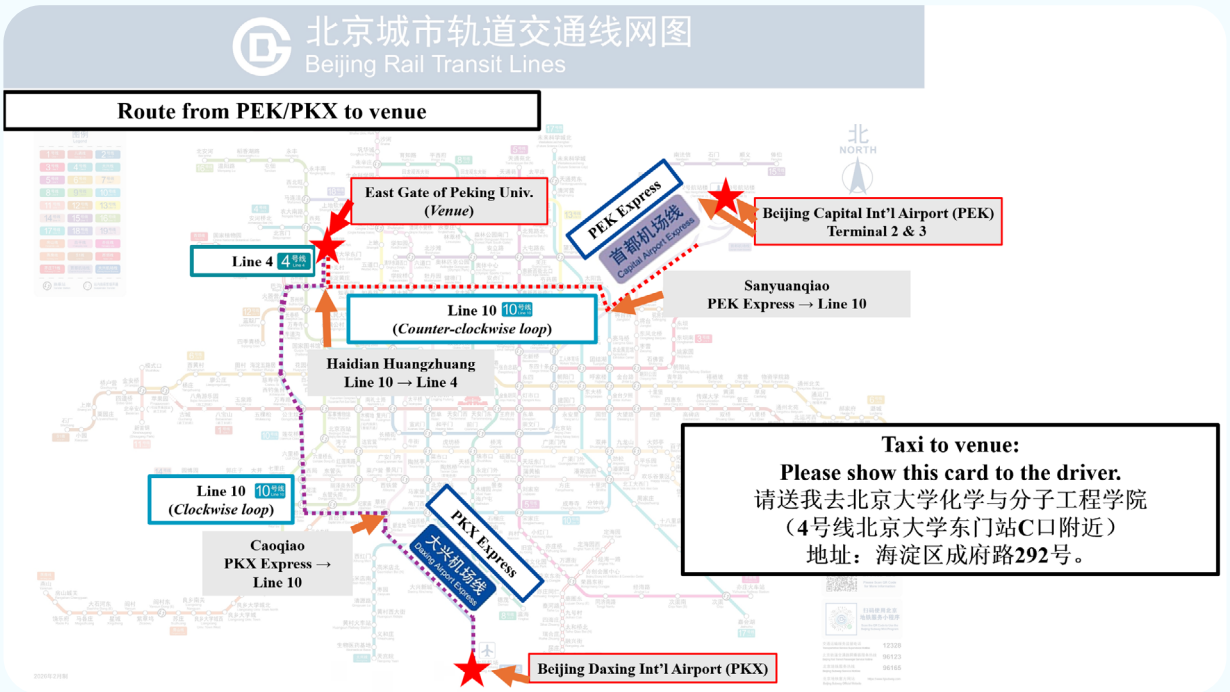
Maps

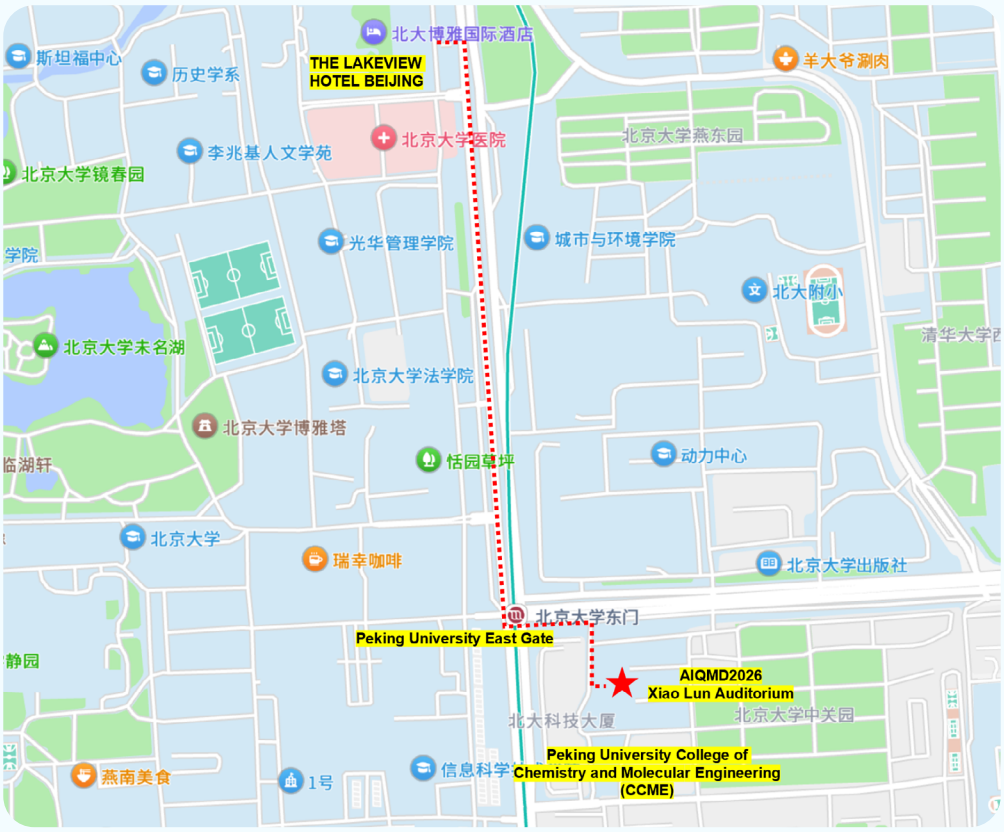
Subway Route

Route from subway station to venue (< 100M)



Route from airport to subway station / venue

Route to hotels



The Lakeview Hotel (~900M)

Zhongguanyuan Global Village (~350M)