CECAM Flagship School: PIQM 2026

Path Integral Quantum Mechanics in the Era of Machine Learning

July 19–23, 2026
Fudan University
Shanghai, China

Poster Abstracts

Poster numbers follow the programme order.

July 16, 2026

Contents

POSTER P01

Nonadiabatic tunnelling using instanton theory beyond the stationary-action principle

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Abstract

Tunnelling has long been known to speed up and drive chemical reactions. While a large amount of work on tunnelling has been focussed on adiabatic reactions, recent studies have shown how tunnelling is even more important for nonadiabatic reactions due to their narrow and cusped reaction barriers [1]. Instanton theory provides a rigorous framework to calculate nonadiabatic rate constants and includes multidimensional tunnelling and zero-point energy contributions by locating the optimal tunnelling path, which corresponds to the stationary point of the action. However, the stationary-action principle can break down for certain reactions in the Marcus inverted regime, or for reactions that proceed via a third bridge electronic state. For the former, the optimal tunnelling path corresponds to a branchpoint singularity, which results in an infinite set of equally-likely tunnelling paths [2], while for the latter, it involves a below-bridge tunnelling mechanism with nonresonant hops to virtual bridge states [3, 4]. Using branch-point instanton theory with multireference electronic-structure PESs, we find that the nonradiative relaxation of singlet oxygen involves an enormous 27 orders of magnitude tunnelling factor at room temperature [2]. The instanton tunnelling mechanism correctly predicts the large experimentally-observed H_2O/D_2O kinetic isotope effect across a wide range of temperatures. Bridge instanton theory is used to study the high-spin $\rightarrow$ low-spin decay of a light-induced excited spin-state trapped iron(II) complex, where we find heavy-atom tunnelling of the entire ligand group and excellent agreement with experimental rate constants across a wide range of temperatures [5].

(a) (b)

Figure: The tunnelling mechanism of (a) the nonradiative decay of the singlet $O_2 \cdots H_2O$ complex to the triplet state and (b) the high-spin $\rightarrow$ low-spin decay of $[Fe(pic)_3]^{2+}$. The motion of atoms involved in tunnelling is depicted with a motion blur effect.

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POSTER P02

Molecular Spin Qubit Relaxation: Temperature Dependence and the Spin–Phonon Polaron Mechanism

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Abstract

Spin qubits are considered a highly promising platform for quantum information processing due to their long coherence times and high chemical tunability. Understanding spin–phonon dynamics is key to improving spin relaxation and decoherence, particularly how the relaxation time responds to temperature changes. The spin–lattice relaxation time T_1 has long been described by perturbation theories, but their ability to correctly predict T_1 -temperature relations is increasingly challenged by the emergence of new molecular systems.

To address these issues, we combine rigorous quantum dynamics methods with simple Fermi's golden rule calculations to demonstrate: (1) the breakdown of perturbation theory under strong spin–phonon coupling; and (2) the role of a "spin–phonon polaron" mechanism in modulating the temperature dependence of T_1. This polaron mechanism provides a new physical picture and interpretive framework for understanding the temperature-insensitive T_1 behavior observed in molecular spin qubits [Zn(HOTP)].

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POSTER P03

Vibrational Strong Coupling Enables Electronic Ground-State Reactivity

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Abstract

Electronic ground-state reactivity under vibrational strong coupling (VSC) is becoming a central topic in polariton chemistry. However, the underlying mechanisms and relations between vibrational energy transfer (VET) and chemical reactivity landscapes remain elusive. Here, we present an ab initio cavity quasi-classical trajectory (cav-QCT) framework to investigate vibrational pre-dissociation dynamics of dilute bend-excited ensembles of $(H_2O)_3$ coupled to a cavity. We demonstrate that collective VSC induces an otherwise energetically forbidden dissociation of $(H_2O)_3$ via cavity-mediated intermolecular VET. Dissociation accelerates with increasing size of ensembles of $(H_2O)_3$, even though single-molecule coupling strength decreases. Analyses of trajectories show collective VET as the microscopic mechanism and reveal largely consistent quantum-state distributions of dissociation products. This framework elucidates the microscopic relations between VET and chemical reactivity, suggesting collective VSC as an approach to control reactions while maintaining product-state selectivity.

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POSTER P04

Isotopic EPIGS: Learning Quantum Thermodynamics and Kinetic Energies Across Isotopologues

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Abstract

Entropic Path-Integral Coarse-Graining Simulations (EPIGS) enables rigorous quantum thermodynamics at near-classical cost by learning the centroid free energy and its temperature derivative, replacing expensive PIMD simulations with classical dynamics on a quantum effective potential. However, important energetic components such as quantum kinetic and potential energies remain inaccessible in the current centroid-only formulation, because their conventional estimators require bead-level ring-polymer configurations. Here, we extend EPIGS by incorporating quantum kinetic energy into the centroid-based framework. This further enables a consistent evaluation of quantum potential energy, allowing EPIGS to access not only free energies and enthalpies, but also the underlying kinetic and potential energy components.

POSTER P05

Nuclear quantum effects at the ZnO-water interface

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Abstract

Zinc oxide is a widely studied material for sustainable hydrogen production via photocatalytic and photoelectrochemical water splitting. At the ZnO-water interface, the interfacial hydrogen-bond network gives rise to complex dynamical behavior, including water dissociation and recombination, as well as long-range proton transport. The mechanisms underlying these processes have previously been investigated in detail using classical molecular dynamics simulations based on highdimensional neural network potentials (HDNNPs), which enable near-first-principles accuracy at the system sizes and timescales required for statistically converged interfacial properties [1]. However, the extent to which nuclear quantum effects influence the interfacial dynamics of this system, in particular proton transfer reactions, remains unclear. In this work, we employ a newly developed efficient parallel implementation of path-integral molecular dynamics [2] combined with HDNNPs to investigate the role of nuclear quantum effects at the ZnO-water interface. We find that nuclear quantum effects substantially lower free energy barriers for proton transfer and thereby significantly influence the interfacial reaction dynamics.

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POSTER P06

Path Integral Molecular Dynamics Simulation Accelerated by Artificial Intelligence Framework

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Abstract

Nuclear quantum effects (NQEs) are vital in light-atom chemical reactions and condensed matter systems. Path integral molecular dynamics (PIMD) rigorously captures NQEs but faces severe computational bottlenecks from high bead-scaling costs, expensive ab initio calculations, and cross-platform communication latencies.

This work presents an efficient PIMD scheme implemented within an artificial intelligence-enhanced molecular simulation (AIMS) framework, where MD engines are directly built upon an existing AI architecture. Combining the machine learning force field (MLFF) and PIMD evolution within a unified Python environment eliminates cross-platform communication overheads, while leveraging the native auto-parallelism of the AI framework drastically accelerates simulations with massive bead counts. Furthermore, we employ a novel Graph Field Network (GFN) model to directly predict forces as edge attributes, bypassing the heavy backpropagation costs of energy-derivative models. The performance of this AI-accelerated PIMD approach is demonstrated across three multiscale applications: successfully capturing NQEs in formic acid dimer proton transfer and water-ice phase transitions; enabling 1000-bead simulations to precisely reproduce experimental hyperfine interactions; well interpreting the exceptional kinetic isotope effect in a Pd-based catalysis.

This study demonstrates that fusing AI frameworks with path integral formalisms provides a powerful, low-cost computational platform for exploring NQEs in largescale quantum materials and complex chemical systems.

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POSTER P07

Physics-informed neural networks for solving saddle-point equations in strong-field physics with tailored fields

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Abstract

We develop an unsupervised physics-informed neural network (PINN) to solve the saddle-point equations (SPEs) governing direct above-threshold ionization (ATI) within the strong-field approximation [1]. This setting provides a well-understood testbed in which the saddle-point structure is known for tailored driving fields, enabling systematic validation of the proposed solver. The network is trained by minimizing the residual of the SPEs and requires only the definition of the drivingfield shape and its parameters. We introduce a window parametrization strategy that maps unconstrained network outputs to prescribed regions of the complex-time plane, guiding the optimization toward physically relevant solutions and improving convergence stability. We benchmark the PINN against a traditional local gradientbased solver for a range of tailored fields. The network naturally tracks changes in ionization event dominance as laser parameters are varied, rendering it much less sensitive to initial guesses than conventional solvers. We compute coherent ATI photoelectron momentum distributions and show that the symmetries of the driving fields are reflected in both the saddle-point structure and the resulting spectra. These results establish PINNs as a promising computational framework for semiclassical strong-field calculations and provide a foundation for extending machine-learning solvers to Coulomb-corrected models or to more complex strong-field processes, such as rescattered ATI for which the SPEs are highly nonlinear and the presence of multiple closely-spaced solutions makes conventional Newton-type root-finding highly sensitive to initial guesses, which hinders systematic investigations across laser-parameter spaces, particularly for tailored fields [2]. The present method is transferrable to other research areas in which similar saddle-point equations are solved.

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POSTER P09

Quantum-classical datasets for vibrational energy transfer and transport properties

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Abstract

Accurate kinetic and fluid modeling of non-equilibrium molecular gases and plasmas requires extensive state-resolved collisional data for vibrational energy transfer and transport properties. Mixed quantum-classical (MQC) methods [1,2] provide an efficient and physically sound route to generate such datasets by treating vibrations quantum mechanically (preserving state-to-state transitions) while describing translation and rotation classically. The recent improved MQC approach [2] enables efficient calculation of state-to-state vibrational cross sections, rate coefficients, and transport properties for collisions involving highly excited vibrational states, providing a unified framework for microscopic energy transfer and macroscopic transport observables. Applications to $N_2 + N_2$ [2], $N_2 + O$ [3,4], $N_2 + H_2$ [5], and other collision systems demonstrate the methodology. Gaussian-process regression is further used to assist in interpolating and extending the computed observables across all relevant vibrational states and temperatures [6]. The resulting datasets are openly available in the GassData database (http://stsdata.vlcc.cn), providing physically grounded input for state-to-state and reduced-order kinetic models.

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POSTER P11

Combining harmonic sampling with the worm algorithm to improve the efficiency of path integral Monte Carlo

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Abstract

We propose an improved Path Integral Monte Carlo (PIMC) algorithm called harmonic PIMC (H-PIMC) and its generalization, mixed PIMC (M-PIMC). PIMC is a powerful tool for studying quantum condensed phases. However, it often suffers from a low acceptance ratio for solids and dense confined liquids. We develop two sampling schemes especially suited for such problems by dividing the potential into its harmonic and anharmonic contributions. In H-PIMC we generate the imaginary time paths for the harmonic part of the potential exactly and accept or reject it based on the anharmonic part. In M-PIMC we restrict the harmonic sampling to the vicinity of local minimum and use standard PIMC otherwise, in order to optimize efficiency. We benchmark H-PIMC on systems with increasing anharmonicity, improving the acceptance ratio and lowering the autocorrelation time. For weakly to moderately anharmonic systems, at $\beta\hbar\omega = 16$, H-PIMC improves the acceptance ratio by a factor of 6–16 and reduces the autocorrelation time by a factor of 7–30. We also find that the method requires a smaller number of imaginary time slices for convergence, which leads to another two- to threefold acceleration. For strongly anharmonic systems, M-PIMC converges with a similar number of imaginary time slices as standard PIMC but allows the optimization of the autocorrelation time. We extend M-PIMC to periodic systems and apply it to a sinusoidal potential. Finally, we combine H- and M-PIMC with the worm algorithm, allowing us to obtain similar efficiency gains for systems of indistinguishable particles.

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POSTER P12

Primitive and Virial Estimators for High-Order Derivatives of Quantum Time Correlation Function

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Abstract

Quantum time correlation functions (QTCFs) are central to the description of quantum dynamics but are difficult to compute directly in real time. In this work, we develop a path integral molecular dynamics [1] (PIMD) framework to evaluate highorder derivatives of complex-time quantum correlation functions. These data provide a quantitative benchmark for assessing the accuracy of the ring polymer molecular dynamics [2] (RPMD) Kubo correlation function and can further serve as fitting data for its systematic reconstruction.

We derived both primitive and virial estimators for high-order derivatives of QTCFs and introduced efficient formulations that significantly reduce computational cost by expressing high-order quantities in terms of a small set of building blocks. This allows practical evaluation of high-order derivatives within standard PIMD simulations. The method is applied to one-dimensional quartic and double-well potentials. In both cases, the reconstructed correlation functions show systematic improvement over RPMD, demonstrating enhanced accuracy in capturing quantum dynamical behavior from equilibrium path integral data.

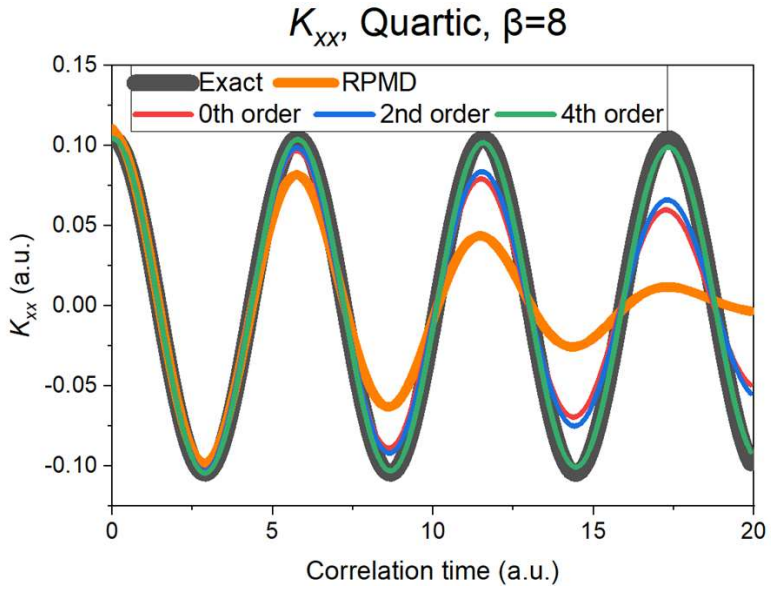

Figure: Comparison of Kubo quantum time correlation functions (QTCFs). The n-th order reconstruction is obtained by fitting RPMD data using derivatives up to order n.

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POSTER P13

A Fragmented Monomeric Machine Learning Potential For General Covalent Molecules

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Abstract

Machine-learning potentials (MLPs) have become important tools for modern molecular simulations. However, developing models that simultaneously achieve high accuracy and high computational efficiency remains a significant challenge. In this work, we extend the recently proposed MB-PIPNet framework to general covalently bonded molecular systems by combining monomer-based energy decomposition, permutationally invariant polynomial (PIP) descriptors, and neural networks within a fragmentation-based strategy. Within this framework, the total potential energy is represented as a sum of effective monomeric contributions, where PIPs provide compact and chemically motivated descriptions of both monomer internal structures and their local chemical environments. As a proof-of-concept application, we apply the MB-PIPNet framework to linear alkanes, using $C_{14}H_{30}$ as a representative system, and benchmark its performance against established atomistic machine-learning models. The resulting MB-PIPNet potential accurately reproduces reference ab initio electronic energies and reliably captures key molecular properties, including torsional potential energy profiles, harmonic vibrational frequencies, and vibrational power spectra obtained from molecular dynamics simulations. Importantly, MB-PIPNet demonstrates a substantial advantage in computational efficiency over other MLP models for combined energy and force evaluations. These results establish MB-PIPNet as a scalable and efficient framework for constructing MLPs, providing an additional route for large-scale quantum and classical simulations of complex molecular systems.

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POSTER P15

Field-selective criticality in 2D melting revealed by multi-field Lee–Yang zeros

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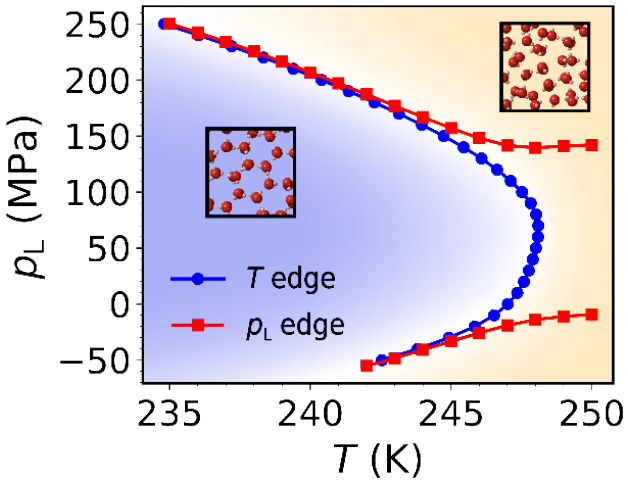
Abstract

The nature of 2D melting remains controversial after six decades of study because different observables can suggest conflicting transition orders. Here we combine multi-field Lee–Yang zero (LYZ) analysis with enhanced sampling to map the phase diagram of bilayer nanoconfined water, disentangling its responses to temperature (T) and lateral pressure (p_{L}). We found that the Lee-Yang edges of T and p_{L} separate near the maximum of the hexagonal ice–liquid coexistence line and along the solid–hexatic transition. This separation exposes a field-selective criticality absent in conventional transitions: T- and p_{L}-response can differ either in continuity itself or sensitivity to size effect, explaining why different probes can yield conflicting classifications of 2D melting. Guided by the LYZ structure, finite-size scaling in the two-step melting regime further reveals that the hexatic–liquid transition—previously regarded as continuous—is first-order: a 1024-molecule supercell yields a bimodal enthalpy distribution, reconciling earlier molecular simulations with hard-disk results and a recent experiment on AgI. These results establish multi-field LYZ combined with finite-size scaling as a rigorous diagnose for complex phase transitions.



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POSTER P17

Quantum Vibrational Coupling Manipulates the Structure of Water

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Abstract

Water is the most ubiquitous liquid in nature, playing a central role in fundamental chemical and biological processes. Its anomalous macroscopic properties, such as density anomalies and complex phase behavior, have been extensively studied. However, their microscopic origin lies in the highly dynamic and fluxional hydrogenbond (H-bond) network. Accurately describing the structural evolution of liquid water remains a challenge due to strong molecular anharmonicity and pronounced nuclear quantum effects (NQEs). In this work, we perform path-integral molecular dynamics (PIMD) simulations and full-quantum vibrational self-consistent field/configuration interaction (VSCF/VCI) calculations based on the CCSD(T)-level q-AQUA-pol potential. We obtain, for the first time, linear infrared (IR) spectra in quantitative agreement with experiment and successfully reproduce 2D-IR features. By analyzing the VCI wavefunctions, we elucidate the regulation mechanisms of intra- and intermolecular vibrational couplings on water structure. The calculations demonstrate that intramolecular coupling induces a transition from anti-correlation to positive correlation in the OH-stretch 2D-IR cross-peaks, originating from a symmetrization effect on the OH bonds.

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POSTER P18

Radical Localization and Hole Transfer in CcP:Cc Protein Complex

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Abstract

Redox reactions are responsible for biological functions ranging from respiration and photosynthesis1. Establishing a fundamental, atomistic level picture of these pathways key step towards energy devices, therapeutic drugs. Current theoretical efforts to characterize redox processes in biological systems typically employ multiscale QM/MM approaches[2], that provide static thermodynamic and structural information, with classical molecular dynamics to account for nuclear motion. However, charge transfer reactions are inherently quantum dynamical processes requiring that we go beyond static methods to accurately capture reaction pathways and compute reaction rates. Ring Polymer Molecular Dynamics (RPMD)[3] has emerged as an approximate method for realtime quantum dynamic simulations that. capture nuclear quantum effects including zero-point energy and tunneling accurately. We aim to couple our

path integral dynamic studies with static QM/MM approaches to map out reactivity and rate. The complex formed between yeast cytochrome c peroxidase (CcP) and cytochrome c (Cc) (Fig 1A) has long stood as a model system for understanding interprotein ET[4]. The radical exchange between $ZnP^{\bullet+}/Trp^{\bullet+}$ (Fig 1B) in the protein is a key step determining the rate of overall electron transfer reaction4. We aim to apply MixPI[5] for constrained RPMD simulation to generate free energy profile and rate calculation on structures drawn from QM/MM static and dynamic calculation.

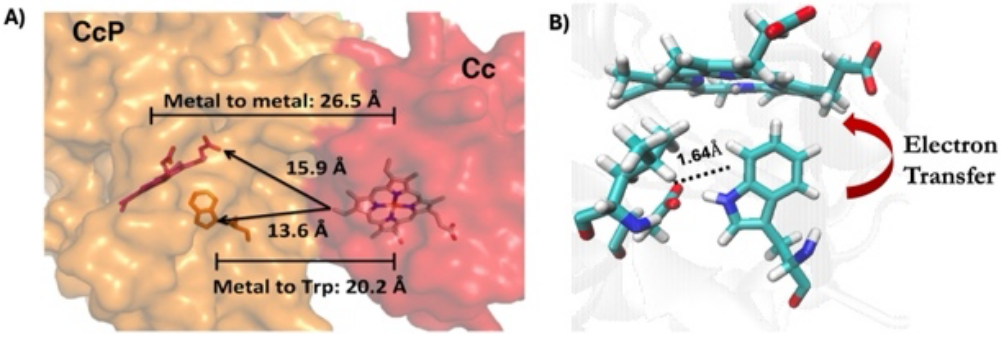

Figure: A) CcP:Cc protein complex where long range electron transfer occurs between two active sitesmediated by Tryptophan (Trp) radical. B) The active site containing Trp, Glutamate (Glu), and Zn-porphyrin where the elctron transfer occurs from Trp to metal center.

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POSTER P19

Semiclassical Spin Exchange via Temperature-Dependent Transition States

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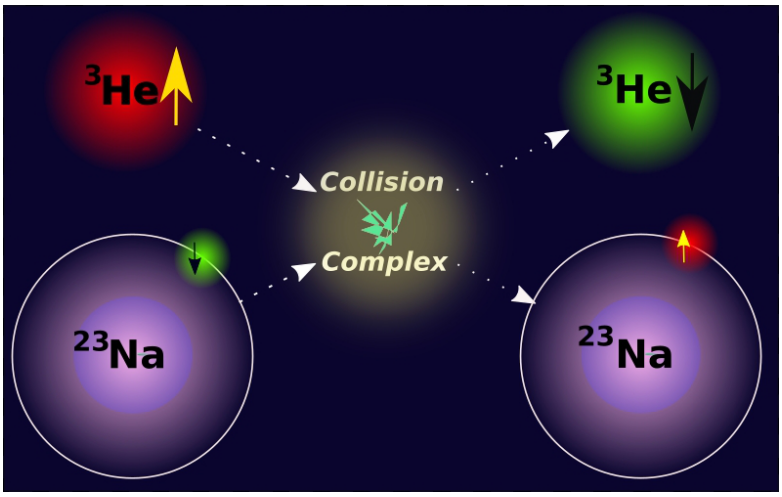
Abstract

Spin-exchange collisions have been widely studied in recent years, and various quantum-mechanical scattering approaches have been developed to calculate the rates. However, these methods based on global knowledge of wave functions can be computationally demanding, are limited to small systems, and do not offer a mechanistic interpretation. Here, we present a semiclassical transition-state theory (SCTST) derived from first principles to describe the nonadiabatic transition between two states that differ only in their spins, where classical TST and Landau-Zener theory fail. We apply our theory to describe the spin-exchange collision between the nuclear spin of ^{3}He and the electronic spin of ^{23}Na. SCTST reveals that the reaction proceeds via temperature-dependent transition states, determined by an intricate compromise between minimizing the activation energy and maximizing the hyperfine coupling. It further demonstrates the importance of quantum delocalization effects prevalent in spin exchange even when tunneling is suppressed and successfully explains the observed weak temperature dependence of the rate. Finally, we showcase the power of SCTST by making predictions for the ^{3}He + CH_3 spin-exchange collision in full dimensionality, where we find that the internal degrees of freedom induce symmetry-broken transition states.



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POSTER P20

Program Synthesis for Quantum Dynamics

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Abstract

Incorporating nuclear quantum effects (NQEs) remains a key challenge in computational modelling of chemical dynamics. There are a variety of existing methods that can include NQEs, using the path integral molecular dynamics (PIMD) framework. One particularly popular method is ring polymer MD (RPMD), which can describe dynamical properties by calculating approximate quantum time correlation functions - but can introduce artificial frequencies when calculating vibrational spectra due to internal polymer modes [1].

New computational / theoretical methods require significant development time and often require domain-specific scientific knowledge. An alternative framework that has gone largely untapped within the chemical sciences is that of program synthesis (PS), or 'self-writing code'. Previously, we have used PS to identify algorithms that can solve the time dependent Schrödinger equation (TDSE) faster than DVR methods [2] and eliminate the use of self-consistent field (SCF) cycles in electronic structure problems [3].

Here, we explore the use of PS in deriving approximate symbolic force expressions that seek to reproduce quantum time correlation functions using classical MD.

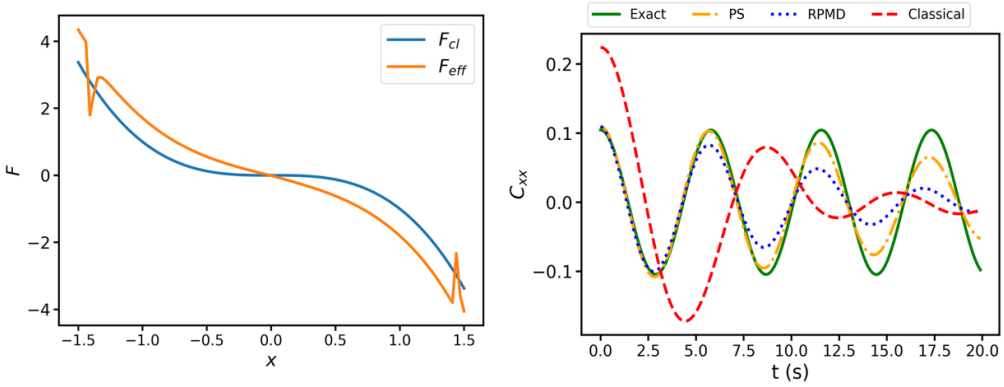

Figure: (a) Classical and PS-derived effective force for the 1D quartic oscillator. (b) 1D position-autocorrelation functions for the 1D quartic problem, calculated with: exact solutions to the TDSE (green), RPMD (blue), classical MD (red), and classical MD using the PS-derived effective force in (a) (yellow).

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POSTER P21

Inverse Isotope Effect in Furan-Water Complex Unraveled by Microwave Spectroscopy and Instanton Theory

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Abstract

Quantum tunneling, a phenomenon central to various physical and chemical processes, is intricately tied to the mass of the tunneling particle. Here, microwave spectroscopy reveals coupled tunneling and inverse H/D isotope effect in a hydrogen-bonded furan-water double-well system. Despite the greater mass of the furan moiety compared to water, deuteration of furan significantly decreases the tunneling splittings, suggesting substantial tunneling involvement. More remarkably, the tunneling splitting doubled upon deuteration of the hydrogen-bonded hydrogen, contrary to typical mass effects on tunneling. Ab initio instanton theory calculations reproduced the tunneling splitting and the anomalous isotope effects, revealing a coupled rotation of both H_2O and furan in opposite directions during tunneling. The inverse H/D isotope effect arises from the variation of the hydrogen bond bending vibrational mode orthogonal to the tunneling pathway, which stems from changes in the hydrogen bond strength during tunneling.

POSTER P22

The Spin-MInt Algorithm: An Accurate and Symplectic Propagator for the Spin-Mapping Representation in Nonadiabatic Dynamics

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Abstract

Mapping methods reformulate discrete quantum dynamical quantities as continuous variable representations amenable to classical-like trajectory approximations. Therefore, the accuracy of propagation techniques for such representations is of great importance, especially in path integral-based approaches. Numerical integration methods for semiclassical trajectories are well studied and symplecticity is one of the most desirable criteria for such a method to have. Recent work1 has shown that the only symplectic propagator for the Meyer–Miller–Stock–Thoss (MMST) mapping representation is a numerical method called the Momentum Integral (MInt)[2] algorithm. The benefits of the spin-mapping representation[3] over that of the MMST representation therefore motivate the study of a symplectic algorithm for the propagation of spin mapping variables. Here, we present the Spin-MInt algorithm which propagates spinmapping variables directly. It is shown to be a symplectic, symmetrical, second-order, time-reversible, angle-invariant and geometric-structure-preserving algorithm[4]. We focus on a two-level system whose dynamics are described by a spin-vector restricted to the surface of a sphere. However, this algorithm may be fully generalized to consider an arbitrary number of electronic states using the SU(N) Lie group[5], retaining all the desirable properties from the two-level case. The predicted properties are observed in numerical tests on standard and system-bath spin boson models, as well as on a threestate Morse potential[4]. The Spin-MInt is faster than the MInt algorithm for all tested models, with the most noticeable improvement occurring for large numbers of nuclear degrees of freedom[4]. To our knowledge, this is the first and only known symplectic algorithm for propagating the nonadiabatic spin-mapping Hamiltonian.

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POSTER P23

Rigorous Quantum Thermodynamics from Entropic Path Integral Coarse-Graining

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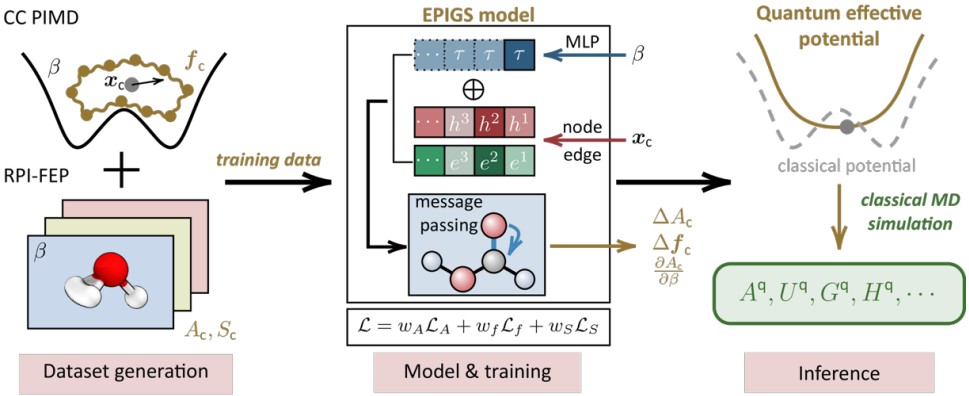
Abstract

Nuclear quantum effects are usually treated with multi-replica path-integral simulations, whose cost limits large-scale applications. We introduce entropic path-integral coarse-graining (EPIGS), in which quantum free energies, entropies, and enthalpies are encoded in the temperature-dependent absolute centroid free-energy surface $A_c(x_c;\beta)$. An instanton-based free-energy perturbation scheme evaluates this surface at lower cost than a centroid-force calculation, while a temperature-conditioned equivariant network learns a representation transferable across system size and temperature. Molecular dynamics on the learned surface reproduces path-integral free energies and enthalpies to sub-meV per atom across hydrogen-bonded clusters and bulk liquid water at near-classical cost.



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POSTER P24

The Phase-Coupled Caldeira–Leggett Model: Non-Markovian Open System Dynamics beyond Linear Dissipation

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Abstract

We introduce the *Phase-Coupled Caldeira–Leggett* (PCL) model of quantum dissipation and develop an exact framework for its dynamics. Unlike the conventional Caldeira–Leggett model with linear system-bath coupling $H_{\rm SB} \propto \hat{F}$, the PCL model features an exponential interaction $H_{\rm SB} \propto {\rm e}^{{\rm i}\lambda\hat{F}}$, where $\hat{F}$ denotes the collective bath coordinate. The PCL coupling arises naturally when an elementary system transition (tunneling or hopping) is accompanied by a unitary phase/displacement action on the environment, as in charge transfer through ultrasmall junctions in quantum circuits, impurity scattering in Tomonaga-Luttinger liquid, dissipative motion in periodic potentials, etc. Despite the nonlinear coupling, the Gaussianity of the bath allows an in-principle exact, nonperturbative, and non-Markovian treatment. Using the dissipaton formalism, we derive a closed hierarchical equation of motion for the reduced density operator, enabled by a generalized normal ordering and a Hermitepolynomial construction for the exponential coupling. Numerical simulations for a two-level system are presented to reveal departures from the linear Caldeira–Leggett limit.

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POSTER P25

Investigating Nuclear Quantum Effects in Water at Nuclear Reactor Operating Temperatures

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Abstract

Nuclear quantum effects (NQEs) in water have been extensively studied for ambient liquid water and various ice phases. In this context, we have investigated the autoionization constant of water [1] and the structure of hydrogen isotopologues using path integral molecular dynamics (PIMD) [2]. However, the computational cost of ab initio PIMD remains prohibitive for large-scale studies of complex systems and slow dynamical processes. To address this challenge, we developed the self-learning path integral hybrid Monte Carlo with mixed ab initio and machine-learned potentials (SL-PIHMC-MIX) method [3], which enables efficient phase space sampling while simultaneously training accurate machine learned potentials (MLPs). These MLPs can subsequently be used for PIMD simulations and have been applied, for example, to the calculation of the heat capacity of water [4], a property requiring both large bead numbers and extensive sampling. These methods have been implemented in the locally developed PIMD software package [5]. In this presentation, we focus on NQEs in subcritical water [6]. Water under these conditions serves as both coolant and neutron moderator in light-water reactors, making an accurate description of its structure and dynamics important for reactor applications. Using SL-PIHMC-MIX, we evaluate the performance of different DFT functionals for modeling water under subcritical conditions. The data generated during the self-learning process are further used to train dedicated MLPs, enabling calculations of infrared and neutron-scattering spectra through path integral Brownian chain molecular dynamics (BCMD) [7].

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POSTER P26

Herman–Kluk–like semi-classical initial-value representation for Boltzmann operator

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Abstract

The coherent-state initial-value representation (IVR) for the semi-classical real-time propagator of a quantum system, developed by Herman and Kluk (HK), is widely used in computational studies of chemical dynamics. On the other hand, the Boltzmann operator $e^{-\hat{H}/k_B T}$, with $\hat{H}$, k_B, and T representing the Hamiltonian, Boltzmann constant, and temperature, respectively, plays a crucial role in chemical physics and other branches of quantum physics. One might naturally assume that a semi-classical IVR for the matrix element of this operator in the coordinate representation (i.e., $\langle \widetilde{x}|e^{-\hat{H}/k_B T}|x\rangle$, or the imaginary-time propagator) could be derived via a straightforward "real-time $\rightarrow$ imaginary-time transformation" from the HK IVR of the real-time propagator. However, this is not the case, as such a transformation results in a divergence in the high-temperature limit ($T \rightarrow \infty$). In this work, we solve this problem and develop a reasonable HK-like semi-classical IVR for $\langle \widetilde{x}|e^{-\hat{H}/k_B T}|x\rangle$, specifically for systems where either the gradient of the potential energy (i.e., the force intensity) has a finite upper bound or the potential becomes harmonic in the long-range limit. The integrand in this IVR is a real Gaussian function of the positions x and $\tilde{x}$, which facilitates its application to realistic problems. Our HK-like IVR is exact for free particles and harmonic oscillators, and its effectiveness for other systems is demonstrated through numerical examples.

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POSTER P27

Lee–Yang Zeros and Path Integral Molecular Dynamics of Indistinguishable Particles

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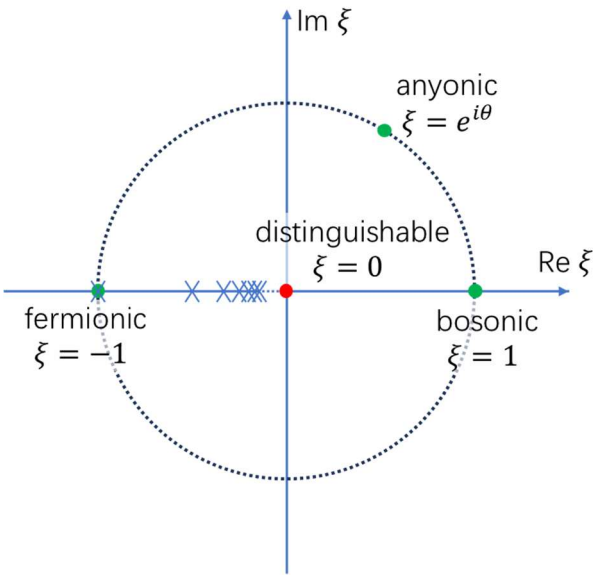
Abstract

Path integral molecular dynamics (PIMD) enables the calculation of properties of indistinguishable identical particles, including bosons and fermions, by exploiting a recurrence relation that circumvents the explicit enumeration of all permutations in the partition function. Recently, we investigated the fermion sign problem (FSP) from the perspective of Lee–Yang (LY) zeros in the complex ξ plane and analyzed the distribution of these zeros for general systems at zero temperature. In this work, we examine the evolution of the LY zeros with increasing temperature, thereby rationalizing the success and failure of current methods such as the ξ -extrapolation method. By implementing re-weighted estimators in PIMD, we obtain the properties of indistinguishable particle systems across different ξ values. The region in the complex ξ plane where results become unattainable is found to coincide with the locations of the Lee–Yang zeros.



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POSTER P28

Nuclear Quantum Effects on High-Harmonic Generation in an Isolated Water Molecule and Water Clusters

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Abstract

Nuclear quantum effects are significant in hydrogen-containing systems such as water and may influence high-harmonic generation under intense laser fields. This work aims to study the effects of nuclear quantum motion on high-harmonic generation (HHG) from a single water molecule and water clusters. By combining ring-polymer molecular dynamics with real-time electronic dynamics, we will describe how O-H vibrations, proton delocalization, and quantum fluctuations of hydrogen-bond networks modulate electron motion and harmonic responses. We will focus on how nuclear quantum effects change charge-density distribution, electronic coherence, harmonic intensity, and other HHG spectral features.

In a single water molecule, nuclear wave-packet motion is expected to modulate ionization and recombination processes and may lead to pronounced isotope dependence. In water clusters, quantum fluctuations of the hydrogen-bond network may affect electronic coherence, intermolecular charge transfer, and HHG spectral features. This study will help clarify the relationship between nuclear quantum effects and strong-field ultrafast electron dynamics in water systems, and provide theoretical guidance for probing quantum dynamics in water molecules and hydrogen-bond networks using HHG.

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POSTER P29

Quantum tunneling effects on hydrogen transport in lanthanum trihydrides

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Abstract

Ionic conductivity in solids is a topic of great interest in the fields of physics, materials science, and energy applications. Previous studies have primarily focused on the activation energy of ion transport based on classical transition state theory, lacking considerations from the perspective of nuclear quantum effects. Herein, by considering the effects of zero-point energy and quantum tunneling, we examine the quantum behaviors of hydrogen migration in lanthanum trihydrides (LaH_3), through the two dominant pathways—concerted migration and single-ion migration. Our firstprinciples calculations based on instanton rate theory indicate that the quantum rate constants diverge significantly from their classical counterparts at low temperatures. We predict that quantum tunneling becomes dominant over thermal diffusion for concerted hydrogen migration at liquid nitrogen temperature, and emerges even at room temperature when concerted transport is suppressed. We also demonstrate the tuning of migration rates by strain, and the sensitivity of the quantum tunneling rate to the energy barrier geometry. Our findings depict a complete quantum picture of hydrogen transport in lanthanide hydrides and provide a new perspective on ionic conductivity of solid materials.

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POSTER P30

Phase transitions between ice phases VII, VIII, and X

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Abstract

In the high-pressure regime, distinct Roman numerals were historically assigned to the proton-disordered molecular phase (ice VII) and the hydrogen-bond symmetrized atomic phase (ice X). However, the existence of a thermodynamic phase boundary is now heavily debated, and the microscopic origin of the seemingly continuous transformation remains unresolved. Critically, anomalous lattice softening precedes hydrogen-bond symmetrization in compressed ice VII, yet its origin remains elusive[1–3].

Here, utilizing path-integral molecular dynamics (PIMD) simulations with a machinelearning potential, we demonstrate that the experimentally observed lattice softening is a macroscopic manifestation of a classical-to-quantum disordering crossover. This crossover is reminiscent of a Widom line emanating from a hidden critical point obscured by the proton-ordered ice phase (ice VIII). We find that the regime above this crossover is characterized by collective, thermally assisted tunneling that is topologically constrained by the ice rules. Upon cooling, this dynamic state evolves into a stable quantum paraelectric ground state where zero-point fluctuations prevent proton localization. Our findings recast the phase diagram of high-pressure ices as a direct consequence of hydrogen quantum delocalization and its associated structural fluctuations.

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POSTER P31

Instanton Theory for Nonadiabatic Tunneling through Near-Barrier Crossings

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Abstract

Many reactions in chemistry and biology involve multiple electronic states, rendering them nonadiabatic in nature. These reactions can be formally described using Fermi's golden rule (FGR) in the weak-coupling limit. Nonadiabatic instanton theory presents a semiclassical approximation to FGR, which is directly applicable to molecular systems. However, there are cases where the theory has not yet been formulated. For instance, in many real-world reactions including spin-crossover or proton-coupled electron transfer, the nonadiabatic crossing occurs near a potential energy barrier. This scenario gives rise to competing nonadiabatic reaction pathways, some of which involve tunneling through a round-top barrier while simultaneously switching electronic states. To date, no rate theory is available for describing tunneling via these unconventional pathways. Here we extend instanton theory to model this class of processes, which we term the "non-convex" regime. Benchmark tests on model systems show that the rates predicted by instanton theory are in excellent agreement with quantum-mechanical FGR calculations. Furthermore, the method offers new insights into multi-step tunneling reactions and the competition between sequential and concerted nonadiabatic tunneling pathways.

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POSTER P32

Quantum Dissipative Dynamics in a Chiral Phonon Bath

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Abstract

Chiral phonons, quasiparticles in lattice vibrations endowed with angular momentum and handedness, have attracted broad attention in recent years in fields such as spin-lattice coupling and quantum information. In this work, we investigate a chiral phonon system constructed from two interacting degenerate phonon modes, and further introduce a spin degree of freedom to systematically analyze the interaction mechanism between spin and chiral phonons. By treating this system as an open quantum system, we establish the hierarchical equations of motion (HEOM) to describe its dynamical behavior and characterize, within a non-perturbative and non-Markovian framework, the influence of system-environment coupling on the dynamical evolution. The results show that phonon chirality plays a key regulatory role in spin dynamics, and that spin polarization and dynamical evolution are highly sensitive to the directionality and strength of chiral phonons. Meanwhile, environmental dissipation and fluctuation effects significantly affect the stability and observable features of chirality-spin coupling. This work provides a theoretical basis for understanding the microscopic interaction mechanisms between chiral phonons and spins, and lays a foundation for controlling spin states via phonon chirality and for its potential applications in quantum devices.

Keywords: chiral phonon; spin; open quantum system;

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POSTER P33

Excited-state machine-learning framework enabling accurate and efficient nonadiabatic quantum dynamics

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Abstract

Nonadiabatic dynamic coupling of excited electron-nucleus system underpins the microscopic mechanism and rational modulation of diverse photoinduced functional phenomena. We develop an excited-state machine-learning (EML) nonadiabatic molecular dynamics framework, in which electron-temperature evolution is rigorously calibrated from high-precision real-time time-dependent density functional theory (rt-TDDFT) benchmark trajectories, enabling accurate reconstruction of excited-state potential energy surfaces (PESs). This framework natively incorporates the electron-temperature dependence of electron–phonon couplings and intrinsically captures phonon anharmonicity, delivering first-principles-level accuracy for excited-state structural evolutions. Large-scale EML-MD simulations resolve time- and momentum-resolved phonon dynamics in photoexcited bismuth, directly uncovering the competition between coherent photogenerated phonons and thermally induced disordered phonons during phase transition. For selenium photoamorphization, our method simultaneously resolves elusive atomic-scale microscopic dynamics and global structural rearrangement. Balancing high accuracy and efficiency, it offers a versatile paradigm to tackle core challenges in the study of complex excited-state quantum dynamics.

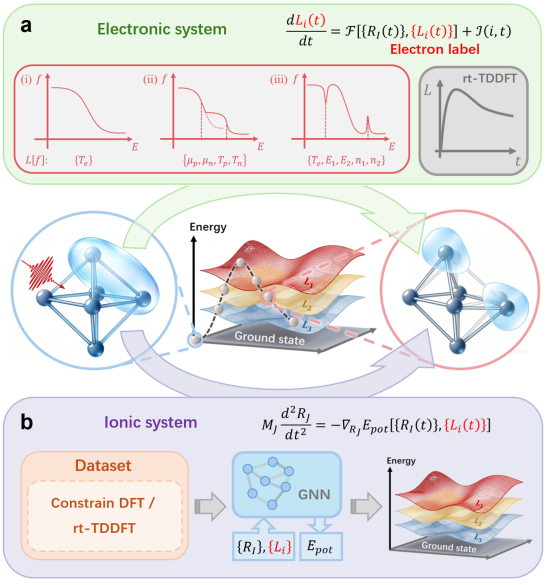

Figure: **Schematic diagram of the workflow of excited state machine learning molecular dynamics (EMLMD). a–b** The evolution equations and the different scenarios that they might describe for the electronic (a) and ionic (b) subsystems, respectively. $\{R_I\}$ and $\{L_i\}$ represent atomic coordinates and labels of electronic structure respectively.

Keywords: excited state; machine-learning potential; non-adiabatic molecular dynamics; light-induced phase transition;