Path Integral Quantum Mechanics: from the basics to the latest developments

PI-21

June 14, 2021 - June 18, 2021
On-line, hosted by CECAM-HQ

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1. Description

The topic of this school is the path integral approach to quantum mechanics, which is one of the most computationally efficient methodologies for modeling quantum nuclear effects such as tunneling, delocalization, and zero-point fluctuations. These methods are most useful when describing structural as well as dynamical properties of systems that contain light nuclei such as hydrogen, carbon, oxygen etc. Path integral simulations are best known for studying quantum nuclear effects in large (high dimensional) condensed phase systems, as they provide a favorable compromise between accuracy and computational cost. Thanks to the ever-increasing computational resources, and several new theoretical and computational developments, path integral simulations are being used to answer new questions, and are entering the mainstream of atomistic simulations [1]. The field of path integral simulations is continuously growing with even more young researchers making prominent contributions. Since our last school in 2018, there have been many new developments in the areas of accelerated path integral methods, implementation of approximate methods for studying quantum nuclear effects in solids [2], path integral molecular dynamics for indistinguishable particles [3], accurate as well as accelerated methods for calculating vibrational spectra [4,5], implementation of *ab initio* ring polymer instanton methods [6], combination of path integral methods with machine learning approaches [7], non-adiabatic path integral rate theories [8,9], and many more. These methods are also being made available in an open-source software i-PI, which can connect with a variety of forcefield and electronic structure packages. Beyond the development of new methods, there have also been several notable applications of path integral methods in the areas of materials science, chemistry, and physics, which underscore the importance of path integral methods for atomistic simulations.

Key References

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*[9] J. Lawrence, T. Fletcher, L. Lindoy, D. Manolopoulos, J. Chem. Phys., **151**, 114119 (2019)*

2. Program

Day 1 - Monday June 14th 2021

- 14:00 to 15:00 - Welcome and Introduction
- 15:00 to 16:00 - **David Manolopoulos** – An introduction to path integral methods
- 16:00 to 17:30 - Interactive session: Quantum Statistics
- 17:30 to 17:40 - Coffee break
- 17:40 to 18:00 - **Yoonjae Park** - Electron-hole recombination in hybrid lead halide perovskites from quasiparticle path integral molecular dynamics
- 18:00 to 19:00 - **Venkat Kapil -** Applications of accelerated path integral methods

Day 2 - Tuesday June 15th 2021

- 15:00 to 16:00 - **Sara Bonella -** Real time path integrals
- 16:00 to 17:00 - **Stuart Althorpe -** Matsubara dynamics
- 17:00 to 17:30 - Video Flash Talks
- 17:30 to 19:00 - Poster session

Day 3 - Wednesday June 16th 2021

- 15:00 to 16:30 - Interactive Session: Quantum Dynamics
- 16:30 to 17:30 - **David Manolopoulos -** Ring polymer molecular dynamics rate theory
- 17:30 to 17:50 - **Jinggang Lan** - Simulating the Ghost: Quantum Dynamics of the Solvated Electron
- 17:50 to 18:00 - Coffee break
- 18:00 to 19:00 - **Yair Litman -** Applications of Imaginary Time Path Integral Approaches for Approximate Quantum Dynamics

Day 4 - Thursday June 17th 2021

- 15:00 to 16:00 - **Jian Liu -** Path integral Liouville dynamics
- 16:00 to 16:20 - **Chris Haggard** - Accurate IR spectra using path integrals: the quasicentroid dynamics of polyatomic systems
- 16:20 to 16:30 - Coffee break
- 16:30 to 17:30 - **Jeremy Richardson -** Ring polymer instanton rate theory
- 17:30 to 17:50 - **Nastasia Mauger** - Nuclear Quantum Effects in liquid water at near classical computational cost using the adaptive Quantum Thermal Bath
- 17:50 to 18:00 - Coffee break
- 18:00 to 19:00 - **Nandini Ananth -** Non-adiabatic semi-classical methods

Day 5 - Friday June 18th 2021

- 15:00 to 16:00 - **Barak Hirshberg -** Path integrals for indistinguishable particles
- 16:00 to 16:20 **- Adrien Marjollet** - State-selective scattering cross sections via ring polymer molecular dynamics
- 16:20 to 16:30 - Coffee break
- 16:30 to 18:00 - Interactive session: Q&A and wrapping up
- 18:00 to 18:30 - Poster Awards and closing

3. List of talks

Invited talks

An introduction to path integral methods
David Manolopoulos
Oxford University, United Kingdom

Applications of accelerated path integral methods
Venkat Kapil
University of Cambridge, United Kingdom

Applications of Imaginary Time Path Integral Approaches for Approximate Quantum Dynamics
Yair Litman
MPI for the Structure and Dynamics of Matter, Germany

Matsubara dynamics
Stuart Althorpe
University of Cambridge, United Kingdom

Non-adiabatic semi-classical methods
Nandini Ananth
Cornell University, United States

Path integral Liouville dynamics
Jian Liu
Institute of Theoretical and Computational Chemistry, Peking University, China

Path integrals for indistinguishable particles
Barak Hirshberg
Tel Aviv University, Israel

Real time path integrals
Sara Bonella
CECAM, EPFL, Switzerland

Ring polymer instanton rate theory
Jeremy Richardson
ETH Zurich, Switzerland

Ring polymer molecular dynamics rate theory
David Manolopoulos
Oxford University, United Kingdom

Contributed talks

Accurate IR spectra using path integrals: the quasicentroid dynamics of polyatomic systems
Chris Haggard
University of Cambridge, United Kingdom

Electron-hole recombination in hybrid lead halide perovskites from quasiparticle path integral molecular dynamics
Yoonjae Park
University of California, Berkeley, United States

Nuclear Quantum Effects in liquid water at near classical computational cost using the adaptive Quantum Thermal Bath
Nastasia Mauger
Université Pierre et Marie Curie, France

Simulating the ghost: quantum dynamics of the solvated electron
Jinggang Lan
University of Zurich, Switzerland

State-selective scattering cross sections via ring polymer molecular dynamics
Adrien Marjollet
DESY, France

4. Posters

A comparison of approximated methods for light-elements quantum diffusion

Niccolò Avallone, Riccardo Spezia, Simon Huppert, Philippe Depondt, Fabio Finocchi
Sorbonne Université, France

This work is part of a joint doctoral program in condensed matter physics and theoretical chemistry that aims at simulating the quantum dynamics of light nuclei in materials and molecular systems. The general goal of the project is to develop a mathematical and simulation framework to address quantum reaction rate calculations and quantum-driven diffusion of light nuclei, such as hydrogen.

H atoms show an intrinsic quantum delocalization which can be of the order of chemical bond lengths, so that nuclear quantum effects (NQEs) can have a strong impact. Zero-point energy and tunneling effects allow the exploration of regions of space that would be classically forbidden, with relevant consequences on H diffusion.

First, we considered a simple model for H diffusion in a 2D triangular lattice which uses analytical expressions for the interaction potential. The resulting potential energy surface presents equilibrium points where the H is most likely to be dwelling and saddle points through which the H jumps from one lattice site to the adjacent one.

The main dynamical quantity of interest is the diffusion coefficient, which is calculated from the velocity autocorrelation function or from the mean squared displacement using different simulation methods. Classical Langevin thermostat is firstly used to introduce a temperature T in the system. With this method, the diffusion coefficients follow an Arrhenius behavior as a function of temperature: this is considered as reference for a classical system. Note that the frictional coefficient was tuned in order to avoid the overdamped regime.

In order to include the NQEs, in particular the zero-point energy and tunneling, different simulation methods are considered which approximate quantum effects on molecular systems: Quantum Thermal Bath (QTB) [1] also with the recently developed adaptive version (adQTB) [2] and Ring Polymer Molecular Dynamics [3], which is currently one of the most used method to include NQEs in molecular simulations. The interest of QTB and adQTB is that the computing time is largely reduced. They provide accurate results for harmonic systems and the goal of the project is test them in more anharmonic systems.

Preliminary results from these methods show large differences in the diffusion coefficient at low temperature, while the classical Arrhenius regime is recovered at higher temperature. It is now paramount to compare the results with more accurate calculations and/or experimental results and understanding at a deeper level the phenomenon of quantum diffusion.

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[2] E. Mangaud, S. Huppert, T. Plé, P. Depondt, S. Bonella, F. Finocchi, J. Chem. Theory Comput., ***15****, 2863-2880 (2019)*
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Accurate IR spectra using path integrals: the quasicentroid dynamics of polyatomic systems

Chris Haggard, George Trenins, Stuart Althorpe
University of Cambridge, United Kingdom

Quasicentroid Molecular Dynamics (QCMD) [1] is a new path-integral dynamics method that uses curvilinear averages of bead coordinates, rather than the Cartesian averages found in Centroid Molecular Dynamics (CMD). QCMD has been shown to be the most accurate path-integral method for simulating the infrared spectrum of liquid water without suffering from simulation artefacts present in CMD and (Thermostatted) Ring-Polymer Molecular Dynamics (T)RPMD. However, QCMD has not yet been generalized to arbitrary molecular geometries. We explicitly formulate QCMD for tetraatomic geometries and show that it produces an accurate spectrum for gas-phase ammonia. We then use this as a starting point to extend QCMD to larger molecules with a ‘unit-by-unit’ approach.

[1] G. Trenins, M. Willatt, S. Althorpe, J. Chem. Phys., 151, 054109 (2019)

Atomic cluster expansion force fields for organic molecules: evaluation beyond RMSE

Dávid Péter Kovács
University of Cambridge, United Kingdom

The efficient simulation of molecules and materials from first principles is a long-standing challenge in the physical sciences. Machine learned force fields promise to speed up these simulations by several orders of magnitudes whilst being as accurate as high-level quantum mechanics. In the past 3 years several different approaches were proposed to fulfill this promise built on Gaussian Process Regression and Neural Networks. In this poster we demonstrate that highly accurate molecular force fields can be built using the Atomic Cluster Expansion framework and linear least squares regression. Our model is built from body ordered symmetric polynomials which is a natural extension of the traditional molecular mechanics force fields. We show that these relatively simple models are able to achieve state of the art accuracy on the MD17 benchmark dataset of small organic molecules. Furthermore, we also train several other machine learning models like sGDML, ANI and GAP, as well as a classical force field and compare them on tasks such as normal mode prediction and extrapolation to high temperature data. Finally, we fit the potential energy surface of a large flexible organic molecule and compare how well the models reproduce the dihedral torsional energy landscape form as little as 500 reference calculation.

Computer simulations for interpreting muon experiments: the muon spectroscopy computational project

Leandro Liborio, Simone Sturniolo, Eli Chadwick, Alejandra Gonzalez-Beltran, Laura Murgatroyd, Samuel Jackson, Sarah Byrne, Chris Cole, Adam Laverack, Josh Owen
Rutherford Appleton Laboratory, United Kingdom

The STFC Rutherford Appleton Laboratory houses the ISIS Neutron and Muon Sources, which produce beams of neutrons and muons that can be used to study materials at the atomic level. Muons are subatomic particles -produced by bombarding a graphite target with pulses of high-energy protons that originate in a synchrotron- which are 100% spin-polarised and have approximately 1/10 of the mass of a proton. In a µSR experiment, spin-polarized positive muons are implanted in a sample and can be used, among other things, to study hydrogen defects, the magnetic structure of the sample or the organic radicals that may result from adding the muon to an organic sample.

However, the µSR technique has certain key limitations such as not knowing the site of implantation of the muon nor the role of the quantum effects play in the µSR experiments.

Hence, the Muon Spectroscopy Computational Project [1] was stablished to provide support and software tools to address the following outstanding problems in muon spectroscopy:

- Identification of the muon stopping site in different classes of commonly studied systems by means of computer simulations of appropriate level of accuracy;
- Estimation of quantum effects involving the muon and their effect on stopping site stability and spectral dynamics;
- Prediction of frequencies and probabilities of transition between energy levels of muonic atoms. This is a tool that helps with the interpretation of muonic X-ray spectra for elemental analysis;
- Integration of multiple computational tools to create a simplified pipeline from low level theory to experiment simulation.

[1] https://muon-spectroscopy-computational-project.github.io/index.html

Condensed-phase quantum nuclear dynamics with dynamical mean-field theory

Petra Shih[1], Timothy Berkelbach[2]
[1]Columbia University, United States
[2]Center for Computational Quantum Physics, Flatiron Institute, New York, United States

We introduce vibrational dynamical mean-field theory (VDMFT) as a non-perturbative and systematically improvable method for the simulation of anharmonic lattice dynamics. Inspired by its origin in electronic structure theory, VDMFT is a real-space embedding approach that maps the anharmonic dynamics of an extended, periodic lattice onto an impurity problem where the spectral density is self-consistently tailored. We develop VDMFT and its cluster extension with classical and quantum impurity solvers for one-dimensional models. When compared to classical exact molecular dynamics, VDMFT produces spectral function and density of states that precisely captures the frequency shifts, phonon lifetimes, and temperature dependence induced by anharmonicity. With much fewer degrees of freedom in the impurity model than in the full supercell, the approach is expected to converge to accurate results at affordable computational costs.

Contrasting structural proton transport in azole hydrogen bond networks using ab initio molecular dynamics

Austin Atsango[1], Tom Markland[1], Mark Tuckerman[2]
[1]Stanford University, United States
[2]New York University, United States

Understanding the underlying mechanism of proton transport in hydrogen-bonded systems is crucial to a wide variety of applications ranging from voltage-gated proton channels in biological systems to proton exchange membrane fuel cells. Imidazole and 1,2,3-triazole are two promising hydrogen-bonded organic heterocycles that conduct protons via a structural transport mechanism involving intermolecular proton hops. The theoretical study of proton transport in these systems has proved challenging so far because *ab initio* simulations, which model the bond breaking and forming involved in structural diffusion, impose a significant computational cost given the system sizes and timescales needed to converge diffusion properties and hydrogen bond dynamics. Here, we leverage *ab initio* multiple time-stepping, an algorithmic advance that can be used to speed up molecular dynamics simulations, to accumulate *ab initio* trajectories in excess of a nanosecond for imidazole and each tautomer of 1,2,3-triazole. By using correlation function analysis, we decompose the mechanism of proton transport into a series of first-order processes and show that the proton transport mechanism occurs over three distinct time and length scales. We demonstrate that the linearity of hydrogen bond chains formed in imidazole and 1,2,3-triazole is positively correlated with the rate of proton diffusion. We also uncover evidence of a ‘blocking’ mechanism in both tautomers of 1,2,3-triazole, where hydrogen bonds formed by the middle nitrogen atom create a trap that limits the mobility of protons across the hydrogen bond network. Our simulations thus provide insights into the origins of the experimentally observed 10-fold difference in conductivity between imidazole and 1,2,3-triazole.

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Current-induced bond rupture in molecular junctions

Yaling Ke[1], Andre Erpenbeck[2], Uri Peskin[3], Michael Thoss[1]
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[2]Tel Aviv University, Israel
[3]Technion-Israel Institute of Technology, Israel

Establishing a comprehensive and quantitative understanding of mechanical instabilities in single-molecule junctions is a prerequisite for possible applications in nanoelectronic devices. Recent experimental and theoretical studies have revealed a variety of different processes triggering mechanical instabilities, including current-induced heating and nonconservative forces, however, the underlying mechanisms remain largely elusive. In this contribution, we present a fully quantum mechanical investigation of current-induced bond rupture in molecular junctions, employing the

numerically exact hierarchical quantum master equation approach [1]. Based on a generic model for molecular junctions, our systematic study identifies three dissociation mechanisms: (1) ultrafast dissociation induced by the population of anti-bonding electronic states, (2) incoherent stepwise vibrational ladder climbing, (3) coherent multilevel vibrational excitations induced by multiple electronic transitions. Considering a broad range of different regimes and processes, comprising weak to strong electronic-vibrational and molecule-lead coupling as well as vibrational relaxation, we analyze the different mechanisms in detail. Furthermore, strategies for improving the stability of molecular junctions are discussed.

Developing the Feynman variational approximation for polarons in real materials

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We are developing the Feynman variational approximation [1-3] to describe the behaviour of polarons in polar semiconductors. A polaron is a quasi-particle that forms when an electron in a polar material (one with a non-vanishing dipole moment) is localised by a cloud of optical phonons (bosonic quasi-particles corresponding to the out-of-phase movement of the lattice) generated from the electron polarising the surrounding lattice. Polar semiconductors are of interest for developing technological devices, such as photovoltaics and battery electrodes. Experimentally relevant phenomenological properties of materials include charge-carrier mobility, which characterises how far an excited charge can flow through the material under an applied electric field; effective mass, which is an apparent mass a charge-carrier has due to interacting with the lattice; and optical absorption. Predicting temperature-dependent charge-carrier mobility, effective mass and optical absorption is useful in the computational design and identification of materials for potential utility in devices. However, to do so accurately requires us to understand how polaron formation alters the phenomenological properties of materials.

We use Feynman's path integral method applied to Fröhlich's Hamiltonian [4] for large polarons. The resulting density matrix is valid over the full range of electron-phonon coupling strengths, works at arbitrary temperature and provides an accurate approximation for the polaron free energy via the Feynman variational method [1, 3, 5]. Moreover, the Feynman variational solution can provide frequency-resolved temperature-dependent mobility theories [2, 6] and offers considerable scope for expansion and fitting to more complex materials

Using the Feynman path integral and variational method, we derive expressions for the free energy and complex impedance of the polaron at all frequencies, temperatures and coupling strengths, with explicit inclusion of multiple phonon branches. Then, using codes we have written in Julia [7], we use the ground-state energy to evaluate the polaron effective mass and the complex impedance to evaluate a frequency- and temperature-dependent optical absorption and mobility. We show similar behaviour to Mishchenko et al. [8] published diagrammatic Monte-Carlo calculations of frequency-dependent mobility for the Fröhlich polaron. The relative computational ease and fully controlled errors of the Feynman variational approximation suggest that it will be a useful tool to probe frequency- and temperature-dependent mobility in complex polar materials.

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Dissipative quantum dynamics using Matsubara dynamics

Adam Prada, Eszter S. Pos, Stuart C. Althorpe
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Matsubara dynamics is a powerful theory rigorously connecting exact quantum dynamics with classical dynamics that preserves quantum statistics [1] It has been previously used to justify the approximations made by the standard path-integral based dynamics methods of Centroid Molecular Dynamics (CMD) [2] and (Thermostatted) Ring-Polymer Molecular Dynamics ((T)RPMD) [3]. More recently, it has inspired a new method of Quasi-Centroid Molecular Dynamics (QCMD) [4].

All of the path-integral based dynamics methods neglect quantum coherence. This makes them particularly suitable for condensed phase systems, where rapid decorrelation can usually be assumed. However, simulation of large systems is currently not computationally available. One possible solution to this is to employ dissipative quantum dynamics, where the surroundings of the system are abstracted into a bath that is simulated implicitly.

In my research, I am developing an extension to Matsubara dynamics for simulating open quantum systems using dissipative dynamics. This approach may find its use in the calculation of reaction rates and molecular vibrations. In this context, I am also working on overcoming the phase problem that currently prevents Matsubara dynamics from becoming a practical method.

[1] T.J.H. Hele, M.J. Willatt, A. Muolo, and S.C. Althorpe, J. Chem. Phys. ***142****, 134103 (2015)*
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Electrocatalytic proton-coupled electron transfer reactions: the grand canonical ensemble approach

Marko Melander
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Using electrode potential and electrolyte to manipulate reaction thermodynamics and kinetics forms the backbone of all electrochemistry and electrocatalysis. Especially important reactions to understand are proton-coupled electron transfer (PCET) reactions forming the mechanistic basis of *e.g.* oxygen, CO_2, and N_2 reduction and hydrogen evolution reactions. While clever and cheap schemes for evaluating electrochemical thermodynamics and kinetics have been developed, a rigorous treatment is needed to test the accuracy and to define well-controlled computational models.

In my contribution I will present a rigorous theory and numerical techniques to simulate electrochemical solid-liquid interfaces using grand canonical ensemble density functional theory (GCE-DFT) [1] – this approach provides an exact theory and well-defined approximations to compute thermodynamics as a function of the electrode potential and electrolyte concentration. Besides thermodynamics, I will present the newly established generally valid GCE rate theory (GCE-RT) to address PCET reaction kinetics as a function of the electrode potential [2,3]. The GCE-RT can account for (non-adiabatic) proton and electron tunneling which may significantly contribute to PCET kinetics and long-range electron transfer, respectively [3]. Besides theory, I will present how the thermodynamics, kinetics, and nuclear quantum effects of a gold-catalyzed Volmer reaction can be addressed and understood from the atomic scale with GCE-DFT and GCE-RT [2-3].

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Electron-hole recombination in hybrid lead halide perovskites from quasiparticle path integral molecular dynamics

Yoonjae Park, David Limmer
University of California, Berkeley, United States

Hybrid lead halide perovskites are a class of materials that have unique photophysical properties due to their anharmonic lattices and predominately ionic bonding. High quantum yield, a tunable band gap, high defect tolerance and low binding energy all make perovskites ideal for photovoltaic devices. Lead halide perovskites have exceptionally low rate of electron-hole recombination rates, which is implicated in their high-power conversion efficiencies. However, since both electrons and holes are diffusive and strongly couple to an anharmonicity lattice, elucidating the nature of this phenomena is theoretically difficult and little is known about the mechanism causing low recombination of charge carriers. In this work, we aim to explain the effects of anharmonicity on recombination phenomena and study how photogenerated electron and hole bind, dissociate and recombine by using molecular dynamics simulations. Using an effective mass model of the photoexcited charge carriers, we develop and deploy a quasiparticle based path integral molecular dynamics framework to study recombination. Using an atomistic model for perovskite lattice allows us to capture all orders of anharmonicity, reducing the computational complexity associated with studying this system, which would be intractable from standard solid-state methods.

Energy gap of phase I of molecular hydrogen by ab-initio methods

Mauro Pulzone, Carlo Pierleoni
University of L'Aquila, Italy

TBA

Evaluation of isotope fractionation of boric acid and borate by path-integral molecular dynamics

Amin Alibakhshi
CAU university of Kiel, Germany

Equilibrium constant of isotope fractionation of boron between its two main aqueous species namely boric acid and borate is the main proxy for reconstruction of seawater pH and atmospheric pCO_2 in ancient era. The theoretically evaluated value of 1.0194 reported by Kakihana and coworkers [1] for this equilibrium constant which has been in use for some decades has now been found to underestimate the actual value. More recent theoretical studies based on ab initio vibrational frequency normal mode analysis has reported values ranging from 1.026 [2] to 1.04 [3] for isotope fractionation in pure water.

For theoretical evaluation of isotope fractionation, the two main approaches are ab initio vibrational frequency normal mode analysis and ring polymer path integral molecular dynamics. The main advantage of the later approach is the possibility of explicitly treat the multicomponent solvents and taking into account the anharmonic effects which might have a remarkable contribution in isotope fractionation [4] and are overlooked by normal mode analysis approach.

In the present study, we employ ring polymer path integral molecular dynamics to evaluate the equilibrium constant of isotope fractionation between boric acid and borate in pure and saline water. Our theoretically calculated equilibrium constants for both pure and saline water showed an excellent agreement with the experimentally determined data.

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Feynman diagrams and cohomology of differential forms

Maria Conti[1], Pierpaolo Mastrolia[2], Simone Trevisan[1], Sergio Luigi Cacciatori[1]
[1]Università degli Studi dell'Insubria, Italy
[2]Università di Padova, Italy

A purpose of the current study is to find an alternative approach to the computation of multi-loop Feynman diagrams. Recently, deeper properties of Feynman amplitudes emerged through the study of differential forms. Feynman integrals are rewritten through the Baikov representation, from which it emerges that they form a vector space equipped with a scalar product defined by 'intersection numbers' of differential forms. The integral of interest is then projected onto a basis of 'Master Integrals' of said vector space; the basis was proven to be finite dimensional: its dimension corresponds to the one of the homology group associated to the space of integration, (or of the cohomology group equivalently).The poster includes the following:- the form of a Feynman integral in Baikov representation along with its implications (i.e., the identification of a vector space)- the determination of the dimension of said space from a geometric point of view (along with some explanatory figures)- the topological constructions underlying (along with some explanatory figures)- How the topological constructions lead to some observations related to the identification of a preferred basis of MIs.An extended treatment on these topics will be found in the editorial 'Co-homology of Differential Forms and Feynman Diagrams' (authors: S.L. Cacciatori, M. Conti, P. Mastrolia, S. Trevisan), which has yet to be published.

Finite-temperature, anharmonicity, and Duschinsky effects on the two-dimensional electronic spectra from ab initio thermo-field Gaussian wavepacket dynamics

Tomislav Begusic, Jiří Vaníček
EPFL, Switzerland

Accurate description of finite-temperature vibrational dynamics is indispensable in the computation of two-dimensional electronic spectra. Such simulations are often based on the density matrix evolution, statistical averaging of initial vibrational states, or approximate classical or semiclassical limits. While many practical approaches exist, they are often of limited accuracy and difficult to interpret. Here [1], we use the concept of thermo-field dynamics to derive an exact finite-temperature expression that lends itself to an intuitive wavepacket-based interpretation. Furthermore, an efficient method for computing finite-temperature two-dimensional spectra is obtained by combining the exact thermo-field dynamics [2, 3] approach with the thawed Gaussian approximation for the wavepacket dynamics [4], which is exact for any displaced, distorted, and Duschinsky-rotated harmonic potential but also accounts partially for anharmonicity effects in general potentials. Using this new method, we directly relate a symmetry breaking of the two-dimensional signal to the deviation from the conventional Brownian oscillator picture.

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Formation of van der Waals molecules through direct three-body recombination

Marjan Mirahmadi, Jesús Pérez-Ríos
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In this work, we study the formation of weakly bound van der Waals molecules X-RG (where RG is the rare gas atom) through direct three-body recombination collisions, i.e., X+ RG + RG → X-RG + RG. In particular, the three-body recombination rate for temperatures relevant for buffer gas cell experiments is calculated via a classical trajectory method in hyperspherical coordinates [1,2]. As a result, it is found that the formation of van der Waals molecules in buffer gas cells ($1 \leq T \leq 10$ K) is dominated by the long-range tail (distances larger than the LeRoy radius) of the X-RG interaction. However, for higher temperatures, the potential short-range region starts to play a more relevant role. Moreover, we notice that the rate of formation of van der Walls molecules is of the same order of magnitude independently of the chemical properties of X [2].

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Formic acid adsorption on magnetite (Fe3o4) surfaces - insights from first-principles calculations

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The interface between carboxylic acids, such as formic acid (HCOOH), and magnetite (Fe_3O_4) plays an important role in a variety of applications ranging from hybrid materials to waste water treatment and drug delivery. Furthermore, formic acid is an intermediate in the water-gas shift reaction and in Fischer-Tropsch synthesis, where magnetite is employed as a catalyst. Hence, understanding the binding of formic acid on magnetite can aid the advancement of these applications. On our poster, the latest results on the binding modes, surface stabilities, and vibrational modes of formic acid on magnetite are shown, which were obtained with calculations based on density functional theory. Through the interaction of the molecule with the surface, a restructuring is observed on the important (001) and (111) surfaces of magnetite [1,2]. Thorough sampling of the configurational space and the calculation of vibrational modes allow to compare the computational results with experimental data and to identify which binding modes are present in experimental conditions. At first glance, these properties can be obtained neglecting nuclear quantum effects (NQEs). At second glance, however, several of the identified binding modes are formed with hydrogen bonds, which requires the inclusion of NQEs in future calculations to be represented correctly. Furthermore, including NQEs in future quantum chemical calculations can improve the accuracy of calculated vibrational modes and phase stabilities.

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Fundamental studies on the role of nuclear quantum effects in terephthalic acid

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Multiple proton transfer (MPT) is the movement of several protons along hydrogen bonds with interesting manifestations in a variety of chemical and biological processes. From proton hopping in water to proton transfer in DNA base pairs, the science of MPT is crucial and needs detailed investigation. As a lot of factors affect the nature of proton transfers in complex systems, we decided to study a less complex prototypical molecular crystal, terephthalic acid (TPA). TPA molecule is a dibenzoic acid with the carboxyl groups at the para position of the benzene. In the solid state [1], each TPA molecule binds to two neighbouring TPA molecules through O-H---O bonds to form linear chains. Multiple chains experience weak C-H---O hydrogen bonds to form a sheet and eventually multiple sheets stack on top of each other through weak van der Waals interactions to form the crystal. Existing experimental reports [2,3,4,5] suggest the hydrogen atoms along the O-H---O bond shuttles between the two TPA molecules. This double proton transfer (DPT) is believed to onset around 70 K and is commonly termed as the order-disorder transition. In order to theoretically understand the nature and characteristics of the DPT in TPA, we performed *ab initio* molecular dynamics simulations at multiple temperatures ranging from 70 K to 500 K. The nuclear quantum effects (NQE) were included through the generalized langevin equation-based path integral molecular dynamics [6,7] (PIGLET) simulations to get exact static properties. Additionally, thermostatted ring polymer molecular dynamics simulations [7,8] (*t*-RPMD) were also performed to approximately understand the dynamics of the DPT.

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Gaussian processes for finite size effect extrapolations

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TBA

Hamiltonian operator for coupled internal motion of HO_2.

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Hamiltonian operator can be explicitly expressed in terms of Cartesian coordinates. However, this system of coordinates is non-ideal for studying systems with direct forces among the atoms. Therefore, we express the Hamiltonian in terms of internal coordinates. To express the kinetic energy operator in terms of internal coordinates has turned out to be a tedious task. In the current work, we suggest the use of Generalized Fourier Functions (GFF) with complex exponentials to express the metric tensors. The use of GFF allows to invert the metric tensor without need of a computer algebra software. In addition to this, we can also solve the integral elements of Hamiltonian matric analytically. In this project the above-mentioned methods are employed to formulate the Hamiltonian operator for HO_2 Radical.

How many water molecules are needed to solvate one?

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The comprehension at the molecular scale of the processes involved during solvation still remains a challenge in chemistry. Remarkably, the question concerning how many solvent molecules are necessary to solvate a solute one is still open. By exploring several water clusters of increasing size, we employ semiclassical spectroscopy [1-5] to determine on quantum dynamical grounds the minimal number of surrounding water molecules to make the central one display the same vibrational features of liquid water. We find out that the minimal structure eventually responsible of proper solvation is made of 21 water molecules, and that particular care must be reserved to the quantum description of the combination of the central monomer bending mode with network low-frequency librations [6]. The results obtained with the accurate ab initio potential are then compared with the popular Caldeira-Leggett one to rationalize whether a simplified model can qualitatively and quantitatively describe the solvated system behavior [7]. An ongoing study on how genetic algorithms [8] and adiabatically switched trajectories [9] can help to deconstruct the complex spectrum of the formic acid dimer will be also presented.

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Hydrogen adsorption and abstraction on the C/Si interface: a combined density functional theory and quantum dynamical study

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The C/Si interface [1] has drawn an ever-increasing interest in the last years because of its peculiar features that makes it appealing from both a fundamental and applied perspective. Such interface consists of two carbon layers grown on the SiC(0001) surface - a "buffer", which is strongly bound to the substrate, and a "graphene" layer, which is in turn only weakly bound to the buffer [2].

Hydrogenation of the buffer layer is particularly attractive since it completely decouples the graphene layer, thereby making the latter really free-standing. Furthermore, the corrugation of the buffer layer, which is due to a different strength of the C-Si interactions across the lattice, has shown to have a considerable effect on the energetics of the hydrogen adsorption, that combined with the known flexibility of graphene makes the C/Si interface a possible candidate for a new generation of hydrogen storage devices [3,4].

The passivation of the buffer layer that lies at the heart of the aforementioned decoupling strategy is ruled by the competition between the adsorption of H atoms and the reactivity of adsorbed species towards abstraction processes, *i.e.* the reaction between an adsorbed H and a gas-phase H that produces molecular hydrogen. In the latter case, the so-called Eley-Rideal recombination, the reaction is barrier-less, and the rate is governed to a large extent by its exothermicity.

At present, modeling of the substrate and of the H adsorption energetics has been limited to small-sized systems with a limited ability to accommodate the long-range features of the substrate (its curvature) and of the surface reconstruction that takes place upon adsorption [5].

Here we present a combined energetic and dynamical investigation of the hydrogenation of the buffer layer. DFT calculations were performed on the (minimal) structure comprising 1310 atoms that is known to describe the observed reconstruction of the clean buffer surface. We scrutinized the H adsorption energetics on the buffer layer and related it to the local geometry of the surface around the binding site. Next, we investigated the Eley-Rideal reaction on a number of representative sites of the buffer-layer using a fully quantum approach (a time-dependent wavepacket method). To this end, we employed the rigid-surface approximation that reduces the problem to a tractable 3D one and a model LEPS potential, parametrized with first-principles data, to solve the time-dependent Schrodinger's equation for the ensuing wavepacket describing the evolution of the heights of the two H atoms above the surface and their lateral separation [6,7]. By means of this approach, we were able to assess the role of hydrogen adsorption site on the rate (cross-section) of the abstraction process.

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Modeling electronic structure, dynamics and properties of conducting polymers for optoelectronic applications

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Conducting organic polymers have continued to receive considerable attention for their potential applications in electronic and spintronic device technology and photovoltaic applications [1-3]. In organic photovoltaic cells the interaction between a polymer chromophore and some other material at the donor–acceptor interface is crucial for efficient charge separation [1-4]. The efficiency of optoelectronic devices composed of conducting polymers is determined by several parameters such electron/hole mobilities, charge transfer/hopping integrals, and differences in electrochemical potentials/onsite energies. One of the key profiles of conducting polymers is that the building-block molecule contains conjugated π orbitals, which are electronically coupled with each other, allowing for efficient charge transport along the polymer chain.[5] We focus on polythiophenes and particularly on P3HT which is one of the prototypical materials in the organic semiconductor family. Optoelectronic properties of bulk P3HT depend sensitively upon intra- and inter-polymer chain interactions, crystallinity and grain boundaries, which greatly affect its charge transport properties. Surprisingly, selective deuteration of polythiophene backbone vs alkyl side chains can lead to a distinct optoelectronic response of the photovoltaics [1-2] revealing the importance of quantum nuclear effects [4,6]. While it is tempting to use solid-state density functional theory (DFT) approaches designed to model electronic structure in crystals and exploit its periodicity, crystalline polymers are far from ideal crystals. Typically, a high level of polycrystallinity with a large number of very small, nanometer sized crystal grains is observed with the individual chains consisting about ~60 thiophene units which critically affects device performance [6], We discuss our development and progress towards understanding charge transport, dynamics and optoelectronic properties of conducting polymers employing large scale electronic structure methods, quantum nuclei [6-7] and electron dynamics [3-5] as well as perturbation theory [8].

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Modeling vibrational strong light-matter interactions with cavity molecular dynamics simulations

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Vibrational strong light-matter interactions have attracted great attention during recent years. By confining a large ensemble of liquid-phase molecules in a Fabry-Perot microcavity and when a vibrational mode of molecules is resonant with a cavity mode, the formation of vibrational strong coupling (VSC) not only demonstrates a peak splitting, or Rabi splitting in the IR spectrum, but also selectively modifies the ground-state chemical reaction rates [1] and intermolecular vibrational energy transfer rates [2]. To model these intriguing VSC-related phenomena, we have developed a cavity molecular dynamics (CavMD) scheme which self-consistently simulates the coupled dynamics between realistic molecules and cavity modes with classical mechanics. Currently, our CavMD approach can correctly model (i) the Rabi splitting [3], (ii) polariton (hybrid light-matter state) relaxation dynamics [4], (iii) polariton-enhanced molecular nonlinear absorption [4], and (iv) the dark-state dynamics in the cavity [5]. Moreover, CavMD also reveals an important possibility [6]: by exciting a polariton of the solvent molecules, the input energy can mostly excite the solute molecules to high vibrational states and leave the solvent molecules barely excited; outside the cavity the same pulse fluence can only weakly excite the solute molecules and the selectivity is low. We thank the interface of I-PI which enables a fast implementation of CavMD.

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Multipole polarizabilites of positron and positronium molecular systems

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Positron (e^+) has many intriguing fundamental properties and it is also useful in many applications based on the electron-positron annihilation, but besides that process, positron may form metastable states with atomic and molecular systems [1]. These bound states might be formed due to the polarization of the electronic cloud by the presence of the positron. Moreover, the positron can take one electron forming the Positronium atom (Ps: e^-e^+), which can be also polarized by the residual ion [2]. Yet, the description of the positron-electron correlations in these metastable molecular states is still a challenge for quantum Chemistry methods. We can observe these difficulties on the theoretical predictions of positron and positronium binding energies to atoms [5] and molecules [1], in particular for either nonpolar or only weakly polar molecules where the positron binding energies can vary between 1 meV to 300 meV at most. Even more challenging is the study of other electronic and positronic properties, such as the polarizability which is crucial to understand the interactions with other charged or neutral species. Examples of the above can be found for the dipole polarizability of PsH, where a discrepancy of a factor by three has been reported [4]. Furthermore, the positronium dimer (Ps_2; a two positronic complex, two significantly different values for the C_8 dispersion coefficients have been reported: ≈16000 [6] and zero [7], giving rise to the question of whether the Ps_2 system can be considered as an atomic or molecular structure. In this work, we apply quantum Monte Carlo methods to integrate an ansatz which includes a set of electron-positron geminal orbitals to explicitly account for the interparticle correlation. Through this novel approach we present first calculations on binding energies, and polarizabilites for a set of positronic atoms and molecules, comparing them with other quantum Chemistry methods and analytical results [3]. The later reveal that for Ps only the odd order polarizabilities are non-zero (dipole, octupole and so on) suggesting that dipole-dipole approximation could be enough to describe the interactions between matter and antimatter.

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Nonadiabatic instanton rate theory – quantum tunnelling beyond the Born-Oppenheimer approximation

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The accurate prediction of (quantum) rates and rate mechanisms is key to advance our understanding of chemical reactions in a variety of disciplines, ranging from astrophysics to biology. In many cases the Born-Oppenheimer approximation is a valid choice and molecular reactions are well described on a single electronic surface.

Semiclassical instanton theory, which is commonly used to accurately predict rates within the Born-Oppenheimer approximation, is based on locating the optimal tunnelling pathway (the instanton) on the adiabatic surface using the stationary-action principle, and can therefore predict the tunnelling rate as well as its mechanism.

In the nonadiabatic limit, where the Born-Oppenheimer approximation breaks down, Golden-Rule Instanton (GRI) theory is the method of choice. In GRI-theory, the instanton is optimised on the two weakly-coupled diabatic states. A priori however, the distinction into adiabatic and nonadiabatic regimes i.e. strong or weak coupling of the two diabatic states is only valid in limiting cases, and in general a more universal rate theory would be desirable. Towards this aim, we developed the Nonadiabatic Ring-Polymer Instanton (N-RPI) theory.

N-RPI theory bridges the gap between the adiabatic and nonadiabatic limit by constructing the effective electronic surface on which to optimise the tunnelling path from the two coupled diabatic states. It is therefore ensured that the instanton path cannot be dominated by the optimal path residing entirely on either diabatic surface. NRPI-theory hence overcomes pitfalls of other quantum instanton theories that aim for applicability to arbitrary coupling strengths.

In order to demonstrate the predictive power of our newly developed N-RPI theory, we investigate the linear crossing model, which is the most fundamental nonadiabatic curve-crossing system. We show that N-RPI theory successfully predicts the rate for this system in both the adiabatic and the nonadiabatic limit and crucially also for intermediate coupling strengths.

Nuclear quantum effects in small alkali-cation-doped he clusters from path-integral molecular dynamics simulations

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The investigation of helium nanodroplets has received a great deal of attention during the last few years, being a challenge for both theoreticians and experimentalists. Such nanodroplets have emerged as a new and exciting medium for studying the isolation of otherwise hardly accessible molecules, allowing detailed study of a wide variety of molecular dopants, neutral or charged. In this context, alkali ions have attracted particular attention because of their strong binding to helium.

The main focus of this work is to analyse thermal and nuclear quantum effects in various He_N-A_2^+ clusters, with A=Li-Cs, as the size of the system changes, and their effect on the molecular ions' microsolvation process, related with slow mobility of such ions observed experimentally in ultra-cold He-droplets [1]. For this purpose, pure helium clusters containing up to 100 atoms and doped with an alkali dimer cation have been studied through thermostatted PIMD (Path Integral Molecular Dynamics) simulations in the NVT canonical ensemble, at a low temperature of 2K, using the open i-PI code [2]. The description of the total interaction between the A_2^+ cation and the He atoms is based on a sum-of-potentials approach containing accurate three-body *ab initio* terms, plus two-body He-He interactions [3,4]. The most stable structures, as a function of the number of solvent He atoms, were determined by employing an evolutionary algorithm [3]. New insights into energetics, that control the stabilization of specific compact-structure conformers from such quantum simulations will be discussed.

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Nuclear quantum effects on the hydrogen bond donor-acceptor exchange in water-water and water-methanol dimers

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We present results from Path Integral Molecular Dynamics simulations that describe effects from the explicit incorporation of nuclear quantum fluctuations on the topology of the free energy associated to the geared exchange of hydrogen bonds in the water-water dimer. Compared to the classical treatment, our results reveal important reductions in the activation energy and changes at a qualitative level in the overall profile. Most notably are those manifested by a plateau behavior, ascribed to nuclear tunneling, that bridges reactant and product states, contrasting with the usual symmetric double well profile. The characteristics of the proton localizations along the pathway are examined. An imaginary time analysis of the rotational degrees of freedom of the partners in the dimer at the vicinities of transition states shows a clear "anticorrelation" between intermolecular interactions coupling beads localized in connective and dangling basins of attractions. As such, the transfer is operated by gradual concerted inter-basin migrations in opposite directions, at practically no energy costs. Modifications operated by partial deuteration and by the asymmetries in the hydrogen bonding characteristics prevailing in water-methanol heterodimers are also examined.

Numerical evaluation of Rényi entropy based on Path-integral formulation

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The Renyi entropy has shown to be a very useful tool for analyzing quantum phase transitions and out of equilibrium phenomena. In the last decade, some numerical methods have been proposed for measuring entanglement Renyi entropy in Path Integral Monte Carlo simulations of spin systems, as well as experimental setups for measuring it. Here we will introduce a new method for studying entanglement Renyi entropy extending previous approaches to realistic systems at finite temperature, like high-temperature superconductors, where we suspect that quantum phase transition of the protonic wave function takes place.

Parallel implementation of anharmonic constants to speedup semiclassical transition state theory rate constant calculations

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Calculations of reaction rates in theoretical chemistry is still a challenging task. Rigorous and dynamical approaches are complicated by the low probability of reactive events occurring in a time span of dynamics. Moreover, quantum effects, such as tunneling and zero point energy, are recognized to have a significant impact on the rate constant value. An effective way to include these effects with a statical approach is the Semiclassical Transition State Theory (SCTST).
The main bottleneck of this approach is the computational time required for anharmonic constants calculations. I devised an algorithm that allows to efficiently compute these constants and I've applied it to some organic reactions involving Heavy Atom Tunneling.

Parametrization and testing of a highly accurate potential energy surface for C2H3 in helium

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Protonated Acetylene (PA), $C_2H_3^+$, is known for its unique dynamics. Its PES possesses six equivalent global minima and six more local minima. All of these are separated by extremely shallow energy barriers which can be overcome by zero point energy alone. These highly sensitive properties make it an ideal testing tool for the effect on helium on molecular dynamics.

In this work, we are preparing the tools necessary to simulate PA in helium clusters of varying size at the CCSD(T) level of theory. This is achieved my training a neural network on a limited set of configurations, from which the NN accurately interpolates any configurations encountered during simulation.

Also, we are showing first results which demonstrate that helium indeed has an effect on the structure of PA.

Quantum-confinement of hydrogen isotopes inside the Buckminster-Fullerene

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Deuterium is an important raw material for industry and research; for example, it plays an important role in nuclear power plants, fusion reactors and analytical chemistry. Currently, deuterium is mainly produced by the very energy-intensive Girdler sulfide process, which requires about the power consumption of an average German household to enrich 1 kg of heavy water.

A new approach was provided by Beenakker et al. [1] in 1995 with the concept of "Kinetic Quantum Sieving" (KQS). It was calculated that for pores of the order of the de Broglie wavelength of a molecule, the zero-point energy of the molecule is crucial for the adsorption strength. This concept has been widely used for hydrogen isotope separation because deuterium has lower zero-point energy than hydrogen due to its higher mass and is thus preferentially adsorbed. The materials investigated are mainly one-dimensional and two-dimensional materials such as CNTs (carbene nanotubes) and graphene, but some zeolites and MOFs (metal-organic frameworks) have also been tested for this phenomenon. In this bachelor thesis, the investigated materials were extended to zero-dimensional ones by simulating the confinement of H_2 and D_2 in the Buckminster-fullerene. A simplifying assumption was made that the entrapped molecules can be treated as particles in a three-dimensional spherical box. The fullerene wall was approximated with different central potentials, such as an infinite wall or even an exponential potential. Since no analytical solution is available for the latter potential, a numerical algorithm was developed and implemented in MATLAB to compute both ground states and sophisticated excited states. It was shown that the exponential potential is an excellent approximation of the pore wall and the hard-wall potential is unfavorable, although it is common in the literature [1] to describe pore walls with it. Furthermore, by establishing an angle-dependent potential that takes into account the atomic positions of the carbon atoms in the C_{60}-Buckminster-fullerene, it could be shown that a central potential is a good approximation for low-energy states. In addition, the deuterium molecule was found to be more stable in the C_{60} than the hydrogen molecule by a zero-point energy difference of 0.53 mEH.

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Ring polymer molecular dynamics for unimolecular fragmentation

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Aim: The project concerns the inclusion of nuclear quantum effects (NQEs) in simulating gas phase fragmentation. At this aim we used a simple model of CH_4 fragmentation which analytical potential was developed and studied by Hase and co-workers [1]. The NQE of interest is the difference in zero point energy between reactant and products which modifies the dissociation barrier: 109.46 kcal/mol vs 98.89 kcal/mol for classical and quantum surfaces.

Context: Molecular dynamics simulations are one of the common tools to study the dynamical properties of a chemical system. The most common approach, due to computational effort, is to describe nuclei as classic particles, allowing the study of reactivity of relatively large systems. However, NQEs like tunneling and zero point energy can be important in the description of different phenomena. Different

methods were developed in last years to include these effects in the context of atomistic simulations being accessible to relatively large systems, like Ring Polymer Molecular Dynamics (RPMD) [2], Centroid Molecular Dynamics (CMD) or Quantum Thermal Bath (QTB) [3].
Methods: We have implemented RPMD in Venus code with different thermostats: γ-TRPMD (γ is the centroid friction parameter), TRPMD (which has γ = 0), γ-RPMD (which has the same friction on the centroids and on the beads normal modes) and NVE-RPMD. This reaction was recently studied with QTB [4] and we compare it here with RPMD results. We tuned the γ and the number of beads (between 1 and 64) for temperatures in the 2800 K – 4500 K range which allows fragmentation for simulation time-lenghts up to 5 ns. For each set of parameters between 100 and 500 trajectories were run in order to have enough reactivity to extract reaction lifetimes.
Results: RPMD simulations with finite γ on the centroid can be successfully fit with generalized-Arrhenius equation, thus allowing to extract the corresponding fragmentation threshold. The classical quantum barrier difference (which from the model is 10.57 kcal/mol) was estimated from the different parameters, finding that γ-TRPMD with smallest γ agrees better. TRPMD simulations with γ = 0 seem to follow a micro canonical kinetics: we are thus considering semiclassical-RRKM theory to describe it and obtain threshold values.

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Scalable distributed memory implementation of the quasi-adiabatic propagator path integral

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The accurate theoretical treatment of quantum dynamics subject to a non-Markovian environment is a cornerstone in describing numerous physical processes, ranging from excitation energy transfer in biomolecules to the interaction among qubits in quantum computers. The most general Quasi-Adiabatic Path Integral [1] (QUAPI) formalism is widely applicable beyond high-temperature and weak system-bath coupling limits. Nevertheless, despite significant progress in the simulation of small model quantum systems, the application of the path integral approach to complex quantum systems is still highly challenging due to the exponentially growing number of paths. Several physical approximations have been recently proposed [2, 3, 4] to facilitate the numerical treatment of more complex systems in the QUAPI formalism. Even though such approximations significantly reduce the memory bottleneck of the method, they are not straightforward to implement and may even negatively affect the performance.
Here we present a scalable parallel implementation of the Mask-Assisted Coarse Graining of Influence Coefficient (MACGIC) QUAPI method [4, 5] that allows expanding the range of the treatable systems through more effective utilization of computational resources. In our implementation, we employ a hybrid MPI-TBB programming model. The Intel MPI library is used to distribute propagation paths over multiple computing nodes, which allows to mitigate the memory bottleneck of the method. Shared memory parallelization as implemented in the task-based Intel TBB library is employed for the proper performance scaling within each node. The fast lookup based on the hash map data structure and a novel mask pre-merging scheme further improves the numerical performance of the MACGIC approximation. The advantage of the parallel implementation and its scaling are demonstrated for a range of quantum systems of increasing complexity.

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Special Displacement method as an approximation to path integrals for lattice dynamics

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Typical first-principles calculations in quantum nanostructures are performed by describing the nuclei as classical particles clamped at their crystallographic positions. This approximation undermines the accuracy of predicting condensed matter properties at finite temperature, missing quantum nuclear and thermal effects [1]. Recent advances in nonperturbative approaches to quantum nuclear dynamics, including path integral (PI) and finite differences simulations, aim to provide an efficient in-silico solution to this problem. Recently, we have developed an ex-novo approach, namely the special displacement method (SDM) [2,3], to include these effects in state-of-the-art electronic-structure calculations. In this school, I will demonstrate how SDM can advance the field of electronic-structure calculations to explore novel emergent phenomena arising from the interplay of electron-phonon interactions. I will also show that SDM represents an exact single-point approximant of an imaginary-time Feynman's path integral for the lattice dynamics. Finally, I will discuss the limits of SDM applicability compared to PI.

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State-selective scattering cross sections via ring polymer molecular dynamics

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Structure prediction calculations of carbon nitride polymorphs with CN2 stoichiometry

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Carbon nitrides exhibit versatile properties interesting for sustainable energy applications, such as water splitting, visible-light sensitivity and catalytic activity, while being chemical robust and available at low cost.

With our work we aim to find new, thermodynamic- and kinetically stable Polymorphs with x-CN2 stoichiometry, hoping for the high nitrogen content to enhance the photocatalytic performance compared to graphitic carbon nitride (g-C3N4) [1].

The minima-hopping method, based on density-functional tight-binding (DFTB), was used initially to sample the potential energy landscape of CN2. The obtained structures were further equilibrated and evaluated with DFT-PBE and sorted according to their total energy. The kinetic stability of systems with low energy was then assessed with MD simulations, conducted by an artificial neural network (FLAME [2]).

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The energy dissipation process of hydrogenation reactions of atomic nitrogen on water ice surfaces

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In the colder (10-20K) regions of interstellar medium, the icy surfaces of interstellar grains serve as solid state supports for chemical reactions [1][2]. Among the plausible roles of these surfaces, that of third body is advocated, in which the formation energy of surface reactions can be dissipated among the grain causing the stabilization of the product [3]. This energy dissipation process is poorly understood at the atomic scale and it can have a tremendous impact on astrochemical surface processes like chemical desorption and diffusion [4]. In this work, we studied the formation of NH_3 via successive H-addition to atomic nitrogen on crystalline and amorphous ice surfaces. We first characterized the potential energy surfaces of the hydrogenation reactions and of possible competitive processes (i.e., H abstractions) using static quantum chemical calculations. Subsequently, the partitioning of the nascent energy released by the hydrogenation reactions between the newly formed species and the surface has been elucidated by means of ab initio molecular dynamics (AIMD) simulations. Results indicate that the H-additions on N are largely favorable reactions at 10 K, being barrierless and exhibiting large negative reaction energies, as opposed to the competitive H-abstractions, which are either endothermic or present high activation energies. AIMD simulations show that such favorable nascent energies are, in large part, quickly absorbed by the ice surfaces and their dissipation can be accelerated by mechanisms which involve an H exchange between the surface and the newly formed species.

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Vibrational calculations and Au/Ag SERS-activity

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The search for fast, accessible and inexpensive way to mass-testing SARS-Cov-2 infectious disease COVID-19 is an essential task. The actual gold-standard for COVID-19 screening is RT-PCR. However, its high false-negative rate (~ 29%) and poor sensitivity (~ 71%) limits the action of medical care units in special in high-morbidity cases.[1] Since it demands complex preparing and lab-site measurements in samples it is not a point-of-care method of test. Thus, new diagnostic methods need the tailored in order to overcome the RT-PCT limitations. Evidences had been presented relating COVID-19 mortality might to viral driven hyperinflammation.[2] In this way iron-based dosages metabolite dosages had been recommended to probe the fatality rate.[3] The detection of hepcidin hormone available in saliva is an option to be considered and the Surface Enhanced Raman Spectroscopy (SERS) technique is an interesting possibility to address this problem. The SERS has great potential for point-of-care applications in diagnosis and screening in biofluids like saliva. Thus, one emerging question relates to sensitivity of SERS detect hepcidin.[4] Thus the present project aims calculate the Raman-active vibrational modes and electrostatic potential mesh (MEP) of hepcidin biomolecule using Density Functional (DFT) calculations and the corresponding SERS activity over Au and Ag surfaces.

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Vibrational spectrum of asymmetric well systems using a combination of VCI and instanton theory

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Systems which possess multiple symmetry-related minima separated by finite potential energy barriers have split vibrational energy levels. The splittings of vibrational levels are a consequence of tunneling and delocalization of vibrational wavefunctions across multiple minima. If minima are not symmetry-related, but have different energies (in case of different conformers) or different zero-point energies (in case of partial isotopic substitutions), vibrational spectrum can be decomposed into a combination of two contributions: the vibrational energies of the wavepackets localized in the minima and the interaction due to tunneling between the minima. If asymmetry is sufficiently large, vibrational levels of one minimum can be shifted between the vibrational levels of the other minimum. In this case, the interactions between different vibrational levels of the two minima have to be taken into account and vibrational structure becomes complex.

In our contribution, we show that the Jacobi field instanton method (JFI) [1] can be used to compute the tunneling contributions in such systems and describe the interaction between the different vibrational states of two minima via tunneling matrix elements. These matrix elements can be used along with the vibrational energies obtained using vibrational configuration interaction (VCI) [2] to construct Hamiltonian matrix of the system in the basis of the localized wavepackets. We show that the eigenvalues of this matrix give the vibrational spectrum with great accuracy. The above approach is used to compute the spectrum of partially deuterated malonaldehyde, which is a real-life system with such properties.

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X-ray absorption spectral calculations of Fe(CO)5 and substituted Fe(CO)x.

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The calculation of Fe L-edge X-ray absorption (XAS) spectra for $Fe(CO)_5$ presents a theoretical challenge. The ground state L-edge spectrum of $Fe(CO)_5$ consists of a trade-off between inclusion of static correlation (RASSCF) and dynamic correlation (RASPT2), where the former provides a set of reference orbitals to calculate the core excitations. Furthermore, the need for spectral convergence by means of averaging over many states presents an additional computational cost that needs to be considered. We present a formalism to calculate accurate L-edge spectra for both the ground and excited singlet states of $Fe(CO)_5$ and substituted $Fe(CO)_x$ with applications to recent experimental and theoretical results.

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6. Additional Information

CECAM website for this workshop:
https://www.cecam.org/workshop-details/1032

Notes: