

QAMTS2019

**XIXth International Workshop
on Quantum Atomic and Molecular Tunneling
Systems**

[\(<http://qamts2019.phys.uni-sofia.bg>\)](http://qamts2019.phys.uni-sofia.bg)

**17 – 21 June 2019
Borovets, Bulgaria**



Executive Committee

Juergen Eckert, Texas Tech University
Peter Georgiev, University of Sofia, Nađa Došlić, Institut Ruđer
Bošković, Zagreb,
Martin Quack, ETH Zurich

Local Committee

Peter Georgiev and Tsveta Sarafska, The University of Sofia,
Bulgaria



Dear Friends, Speakers, Participants,

Enjoy the science of tunneling and the landscape at QAMTS 2019 in Borovets, Bulgaria!

This is the 19th edition of a highly successful series of international workshops on the topic of Quantum Atomic and Molecular Tunneling in Solids and other Phases, the previous one having taken place in Madison, Wisconsin, USA in 2017 (see also QAMTS history).

The tunnel effect has been a crucial quantum phenomenon starting in the early days of quantum mechanics with the theoretical work of Friedrich Hund (1926/27) on quantum effects in molecular isomerization reactions and George Gamow (1928) on the theory of radioactive alpha decay, both being connected to ‘heavy’ particle motion (of the corresponding He nuclei or ‘atoms and molecules’) and thus fitting into the framework of the QAMTS workshops. Since then, numerous phenomena related to this effect, completely absent, even unthinkable of in classical mechanics have been discovered and continue to be discovered at a regular rate, with also many applications in chemistry and molecular physics. We look forward to learning about some of the most recent and exciting developments in this field.

Slight changes to the program may still be necessary, so please check for the time of your talk. Session chairs will be appointed as we go, so you may anticipate a request to chair a session from one of the members of the executive committee. Note that the free informal discussion afternoon with possible excursions can be either on Wednesday or on Tuesday depending on weather conditions. The lecture program for these afternoons will be exchanged accordingly. **Thus speakers planned for Wednesday afternoon**

should be also prepared to give their talks on Tuesday afternoon instead of Wednesday. The decision on this will be taken on Monday afternoon at the latest, depending on weather forecast.

Remember the unique nature of this series of workshops. As in the past, the hallmark of QAMTS is the highly cross disciplinary nature, which includes work on tunneling of protons and heavier species in condensed or any other phases and in chemical reactions, transport in condensed phases, rotational tunneling, and biological systems, studied by experiment or by theory. Lecture times (45 minutes or 30 minutes) include 10 minute discussion times and it is customary to leave enough time for discussion.

We thank the University of Sofia and in particular the University NIS centre for the financial management, also the Faculty of Physics for hosting our web site.

Borovets, June 2019

The Executive Committee:

Juergen Eckert, Texas Tech University, Peter Georgiev, University of Sofia, Martin Quack, ETH Zurich, Nađa Došlić, IRB Zagreb, and Jernej Stare, KI, Ljubljana.

Local Committee: Tsveta Sarafska, Peter Georgiev

History of the QAMTS workshops

XIX QAMTS 2019

International Workshop on Quantum Atomic and Molecular Tunneling Systems, Borovets, Bulgaria, 16.6. – 20.6. 2019

Juergen Eckert, Peter Georgiev, Martin Quack, Nađa Došlić, Jernej Stare

XVIII QAMTS 2017

International Workshop on Quantum Atomic and Molecular Tunneling in Systems, Madison, WI, USA, 20.5. – 24.5. 2017

Juergen Eckert, Amnon Kohen, Bob McMahaon

XVII QAMTS 2015

International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Phases

Beatenberg/Interlaken, Switzerland 31.5.–3.6.2015

Jürgen Eckert, Beat H. Meier, Frédéric Merkt, and Martin Quack,

<http://qamts.ethz.ch/qamts2015/>

XVI QAMTS 2012

International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Condensed Phases

Santa Fe 10.6. –14.6.2012

Juergen Eckert, Bill Poirier

<http://www.myweb.ttu.edu/lpoirier/QAMTS/Program.html>

XV QAMTS 2010

International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Condensed Phases

Technical University Darmstadt, Germany 5.9. –9.9.2010

Gerd Buntkowsky, Juergen Eckert

http://cgi.chemie.tu-darmstadt.de/QAMTS2010/Getting_There.html

XIV QAMTS 2007

International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Condensed Systems

University of Houston, USA, 28.10. –11.11.2007.

XIII QAMTS 2005

International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Condensed Phases

Antonio Fernández-Ramos, Zorka Smedarchina

University of Santiago del Compostela, Spain, 27.7.–31.7.2005

XII QAMTS 2003

International Workshop on Atomic and Molecular Tunneling in Solids

University of Florida, Gainesville, USA 22.6. –25.6.2003

XI QAMTS 2001

Quantum Atom and Molecular Tunneling in Solids
University of Nottingham, United Kingdom 5.9. –9.9.2001
A. J. Horsewill

X QAMTS 1999

Quantum Atomic and Molecular Tunneling in Solids
Zdzislaw Lalowicz, Zbigniew Olejniczak
University of Krakov, Poland, 26. –30.9.1999

IX QAMTS 1997

Quantum Tunneling of Atoms and Molecules in Solids
Forschungszentrum Jülich, Germany

VIII QAMTS 1995

Quantum Tunneling of Atoms and Molecules in Solids
F. Fillaux, H. G. Büttner, G.J. Kearly, J. Meinel
Institut Laue-Langevin, Château de la Baume, Seyssins/Grenoble 4.10.–
7.10.1995

Proceedings: Physica B: Condensed Matter Vol. 226, no. 1/3
<http://www.sciencedirect.com/science/journal/09214526/226/1-3>

VII QAMTS 1993

Quantum Molecular Tunneling in Solids
Cumberland Lodge, Windsor (UK) 12.7. –15.7.1993
C. J. Carlile, A. J. Horsewill

Proceedings: Physica B: Condensed Matter Vol. 202, no. 3/4 (1994)
<http://www.sciencedirect.com/science/article/pii/0921452694902941#>

VI QAMTS 1991

Castle Ringberg, Tegernsee, Germany

V QAMTS 1988

Turku, Finland

IV QAMTS 1986

Quantum Aspects of Molecular Motions in Solids
Grenoble, France, 24.–26.9. 1986
A. Heidemann, A. Magerl, D. Richter, M. Prager, T. Springer
Proceedings: Springer Proceedings in Physics, Volume 17, 1987
<http://link.springer.com/book/10.1007/978-3-642-71914-1>

III QAMTS 1984, University of Nottingham, United Kingdom

II QAMTS 1982, Braunschweig, Germany

I QAMTS 1981, Institut für Festkörperforschung, Kernforschungsanlage Jülich,
Germany

The scope has widened over the years and in the future the preferred title should be:

Quantum Atomic and Molecular Tunneling Systems QAMTS

The XIXth International Workshop

17 – 21 June 2019, Borovets, Bulgaria

Monday, 17 th June 2019		
9:00 – 9:15	Welcome by Peter Georgiev	page №
9:15 – 10:00	<u>Martin Quack</u> Fundamental and approximate symmetries, parity violation and tunnelling in chiral and achiral molecules	1
10:00 – 10:45	<u>Eli Pollak</u> , Jakob Petersen and Reuven Ianconescu Quantum Reflection, Tunneling Flight Times and Anomalous Quantum Diffusion	2
10:45 – 11:15	Coffee break	
11:15 – 12:00	<u>Brian Kendrick</u> Non-adiabatic quantum tunneling in photodissociation and reactive scattering	3
12:00 – 12:30	<u>Tim Schleif</u> , J.-M. Pérez, S. Henkel, M. Ertelt, W.Sander Heavy-Atom Tunneling in the Cope rearrangement of 1,5-Dimethylsemibullvalenes	page 4
12:30 – 14:00	Lunch	
14:00 – 14:45	<u>Vincent Moliner</u> , S. Martí, K. Świderek, MA. Galmes, J. Javier Ruiz-Pernía, Iñaki Tuñón, Rudolf K. Allemann Towards the design of new biocatalysts from QM/MM computational studies on enzyme catalysis	5
14:45 – 15:30	<u>Nada Došlić</u> Excited state H-transfer in prototypical hydrogen bonded systems	6
15:30 – 16:00	Coffee break	
16:00 – 16:45	<u>Qiang Shi</u> Proton transfer reaction dynamics using the reduced quantum dynamics approach	7

Monday, 17 th June 2019		page №
16:45 – 17:15	<u>Christophe Vaillant</u> High-Accuracy Calculations of Tunneling Splittings in Water Clusters	8
17:15 – Free time and Dinner		
Tuesday, 18 th June 2019		
9:00 – 9:45	<u>Rich Saykally</u> Hydrogen Bond Network Rearrangement Dynamics in Water Clusters: Dramatic Effects of Librational Excitation on Hydrogen Bond Tunneling Rates	9
9:45 – 10:30	<u>Johannes Kästner</u> , J. Meisner, A. Löhle, T. Lamberts Recent Developments in Instanton Theory to Simulate Tunneling Processes in Catalysis, Astrochemistry, and Biochemistry	10
10:30 – 11:00 Coffee break		
11:00 – 11:30	<u>Wei Fang</u> , J.Chen, X.-Z., A. Michaelides, J.O. Richardson Molecular modeling of tunneling effects in adiabatic and nonadiabatic reactions	11
11:30 – 12:00	<u>Alja Prah</u> , Peter Ogrin, Janez Mavri and Jernej Stare Electrostatics and tunneling in monoamine oxidase A enzyme	12
12:30 – 14:00 Lunch		
	Excursion, free time or the Wednesday afternoon talks	
Wednesday, 18 th June 2019		page №
9:00 – 9:45	Tony Pham, Peter Georgiev, and <u>Juergen Eckert</u> Quantum dynamical treatment along with analysis of the potential energy surface for rotational tunneling by bound H ₂ can lead to improved materials	13

Wednesday, 18 th June 2019		page №
9:45 – 10:30	S. Kannath, P. Adamczyk, D. Ferro-Costas, A. Fernandez-Ramos, and <u>Agnieszka Dybala-Defratyka</u> Effect of solvation on kinetic isotope effects on hydrogen abstraction from ethanol in aqueous solution	14
10:30 – 11:00	Coffee break	
11:00 – 11:45	<u>A.I. Kolesnikov</u> , L.M. Anovitz, and S. Irlé Tunneling behaviour of water molecules in bassanite	15
11:45 – 12:30	<u>Claudio Nunes</u> Heavy-Atom Tunneling Reactions on the Slippery Potential Energy Surface of Arylnitrenes	16
12:30 – 14:00	Lunch	
14:00 – 14:45	<u>Antonio Fernandez Ramos</u> The OH + methanol reaction at ultracold temperatures: A tough nut <i>to crack</i> for theory	17
14:45 – 15:30	<u>Katarzyna Świderek</u> , V. Moliner, and A. Kohen Primary and Enzyme Kinetic Isotope Effects in <i>E. Coli</i> Thymidylate Synthase.	18
15:30 – 16:00	<u>Pierre Winter</u> and Jeremy Richardson A More Efficient Method for Thermal Instantons and Development of Microcanonical Rate Theory	19
16:00 – 16:30	Coffee break	
16:30 – 17:15	<u>Bill Poirier</u> , M. Gonzalez, A. Aquino, and J. Eckert Exact Quantum Dynamical Treatment of Hydrogen-material Interactions: $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ and $[\text{FeH}(\text{H}_2)(\text{PH}_3)_4]^+$	20
17:15 – 17:45	<u>Oliver Erhart</u> , P. A. Georgiev and H. Krautscheid Structural Details of the Desolvation Process and Adsorption of Dihydrogen in the Flexible Metal-Organic Framework [Cu(Me-4py-trz-ia)]	21
18:30 -	Dinner	
Thursday, 20 th June 2019		
9:00 – 9:45	<u>Salvador Miret-Artes</u> On non-linear Schrödinger equations for open quantum systems	22

Thursday, 20 th June 2019		page №
9:45 – 10:30	<u>Marko T. Cvitaš</u> , M. Eraković, J. O. Richardson Ground-state tunnelling splittings in water pentamer using instantons	23
10:30 – 11:00	Coffee break	
11:00 – 11:30	<u>Chiara Aieta</u> , Fabio Gabas, Michele Ceotto Parallel Implementation of Semiclassical Transition State Theory and its application to high-dimensional tunneling reactions	24
11:30 – 12:15	<u>Sebastian Kozuch</u> Quantum Tunnelling Instability Computational Detection of Impossible and Transient Molecules	25
12:15 – 14:00	Lunch	
14:00– 14:45	L. Li, N. Seifert, F. Xie, M. Heger, P. Raston, Y. Xu, and <u>Wolfgang Jäger</u> Rotational spectroscopic signatures of tunnel effects in weakly bound complexes and clusters	26
14:45– 15:15	<u>E. Valcheva</u> , K. Lozanova, I. Asenova Resonant Tunnelling in Short Period Strained AlN/GaN Superlattices	27
15:15– 16:00	<u>Ali Hassanali</u> Fluctuations of Hydrogen Bond Networks as a Possible Source of Anomalous Optical Properties in Protein Aggregates	28
16:00 – 16:30	<u>G. Ch. Mellau</u> The pattern of eigenenergies at the saddle point region	29
16:30 – 17:00	<u>Eric R. Heller</u> , L. Schreder, W. Fang, J. O. Richardson Concerted proton-transfer between water molecules in different environments via quantum tunneling	30
Conference Banquet		
Remarks by Peter Georgiev, Juergen Eckert, Martin Quack		

Fundamental and approximate symmetries, parity violation and tunnelling in chiral and achiral molecules

Martin Quack

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Symmetry and asymmetry are concepts, which are used in a wide range of contexts, from the fundamental sciences, mathematics, physics, chemistry and biology to the arts, music and architecture [1]. If asymmetries are small, one may still introduce the concept of approximate symmetries. Symmetries can be associated with constants of the motion. Particularly interesting approximate molecular symmetries are nuclear spin symmetry and parity, resulting in approximate constants of the motion. We shall start with an introductory outline of how symmetries can be applied to the understanding of the time scales in fundamental kinetic primary processes. We then briefly discuss our approach to derive molecular quantum dynamics from high resolution spectroscopy with some selected examples from our recent research including results on molecular tunneling and tunneling switching phenomena in free molecules and including excitation with coherent time dependent fields. Of particular interest is the control of symmetry by external fields. These lead to interesting nonclassical states recently introduced for molecular quantum switches in our work. We shall also report on current progress towards the observation of the theoretically predicted, new process of parity change with time in isolated chiral molecules, which connects the principles of high energy physics with molecular chemical kinetics and potentially the evolution of biomolecular homochirality. We shall present our most recent analyses of high resolution infrared, THz and GHz spectra of relevant chiral and achiral molecules as available at the time of the meeting and relevant in this context. For background reading and some recent results see [1-12], and www.ir.ETHZ.CH.

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Quantum Reflection, Tunneling Flight Times and Anomalous Quantum Diffusion

Eli Pollak , Jakob Petersen and Reuven Iancu

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Ever since the discovery of quantum tunneling, the question how long does it take to tunnel has intrigued the community. Part of the difficulty has been the definition of a time operator in quantum mechanics. We have in recent years noted that one should not resort to formal operators but rather ask what is it that one would measure in a time of flight experiment? [1] Time is a parameter in the Schrödinger equation and all the information should be obtained from the time dependence of quantum wavepackets. Taking this as a point of departure we have studied in recent years what we define as the tunneling flight time [2,3]. Results based on both analytic theory[1] as well as numerical computations [2,3] will be presented showing that the tunneling flight time vanishes. This conclusion has been corroborated only recently, based on attosecond tunneling ionization of the Hydrogen atom [4].

A complementary feature of quantum tunneling is quantum reflection [5]. A study of quantum reflection times reveals differences between coherent and incoherent quantum reflection. The well established phase delay time is not adequate for describing quantum reflection times in the coherent regime.

Finally, quantum reflection has a dramatic effect on quantum diffusion on surfaces. Using a new version of Kramers' turnover theory we verify that quantum reflection can reduce the diffusion coefficient as compared with classical theory, implying an inverse isotope effect [6]. The diffusion of a Deuterium atom can be faster than Hydrogen.

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Non-adiabatic quantum tunneling in photodissociation and reactive scattering

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Non-adiabatic tunneling is a fundamentally new mechanism where the tunneling rate is governed by constructive or destructive quantum interference between two contributing pathways. The two pathways correspond to the minimum energy pathways over two symmetric saddle points associated with a conical intersection which often occurs in photodissociation. The quantum interference can alter the overall tunneling or photodissociation rate by an order of magnitude. The results from recent quantum dynamics calculations for a realistic two-dimensional model of photodissociation will be presented.[1] The effects of isotopic substitution and symmetry on the photodissociation rate will also be discussed. Other examples of non-adiabatic quantum interference effects will be presented from full-dimensional and numerically exact (i.e. no dynamical approximations) quantum reactive scattering calculations of $H + H_2$, its isotopic variants $H/D + HD$, and $Li + LiNa \rightarrow Li_2 + Na$. [2,3] At cold ($T < 1$ K) and ultracold ($T < 1$ mK) collision energies, unique quantum interference phenomena appear which are shown to alter the rotationally resolved ultracold rate coefficients by one to two orders of magnitude and for the hydrogen system up to four orders of magnitude in some cases. A novel control mechanism will be discussed for which the quantum interference can be tuned via the selection of a particular initial quantum state or the application of an external electromagnetic field to govern the outcome of the reaction (a quantum switch!). [4,5]

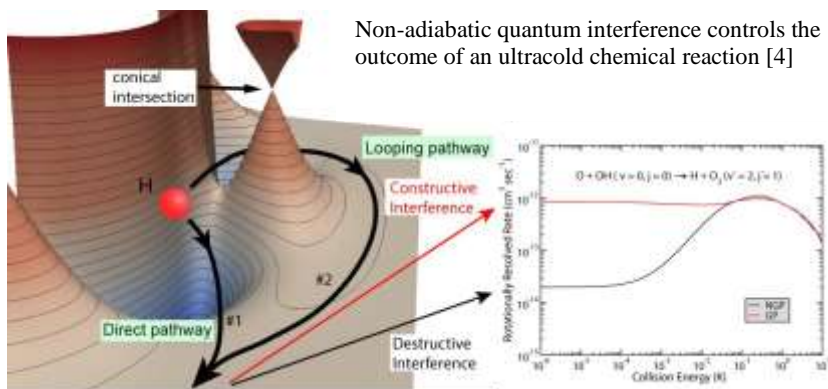
[1] X. Changjian, B. K. Kendrick, D. R. Yarkony, and H. Guo, *JCTC* **13**, 1902 (2017).

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Heavy-Atom Tunneling In The Cope Rearrangement Of 1,5-Dimethylsemibullvalenes

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As an experimental test of the theoretical prediction by Borden et al.^[1] that heavy-atom tunneling is involved in the degenerate Cope rearrangement of semibullvalenes at cryogenic temperatures, mono-deuterated 1,5-dimethylsemibullvalene isomers d^2 -**1a/b** and d^4 -**1a/b** were prepared and investigated by IR spectroscopy using the matrix isolation technique.

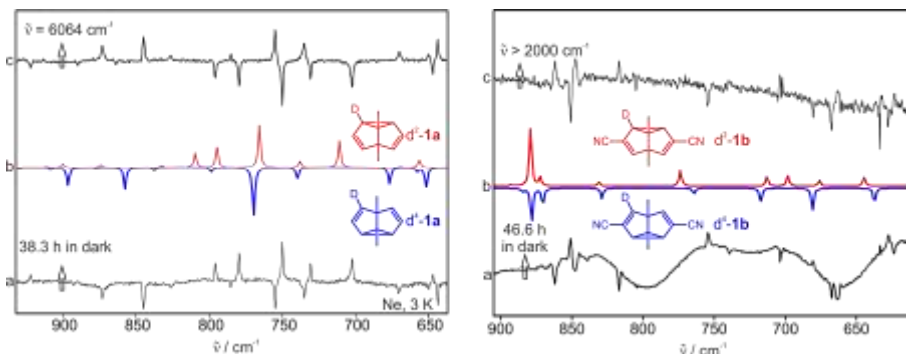


Figure 1. (a) Exp. IR difference spectra obtained after several hours in the dark.^[2] (b) Calc. IR spectra [B3LYP/6-311G(d,p)] for isotopomers. (c) Exp. IR difference spectrum after subsequent irradiation.

As predicted, d^4 -**1a/b** do indeed rearrange to the thermodynamically more stable d^2 -**1a/b** at cryogenic temperatures in the dark (though broadband irradiation with $\lambda > 2000$ cm^{-1} causes an equilibration of the isotopomeric ratio). Since these reactions proceed with rate constants in the order of $10^{-4}/10^{-5}$ s^{-1} despite experimental barriers^[3] of $\Delta H^\ddagger = 4.8/5.6$ kcal mol^{-1} with only shallow temperature-dependences, the results are interpreted in terms of heavy-atom tunneling. This tunneling process curiously does not seem to approach its thermodynamic equilibrium and is inhibited by certain matrix environments, with the potential reasons for these phenomena currently being investigated.

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Towards The Design Of New Biocatalysts From QM/MM Computational Studies On Enzyme Catalysis

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Computational Chemistry techniques based on the combination of Quantum Chemistry and classical Molecular Mechanics (QM/MM) have been extensively applied to the study of enzyme catalysis. Merging these techniques with experimental methods has allowed acquiring a deep knowledge of the reaction mechanisms of these complex but highly efficient biocatalysts at the molecular level.

Recent results obtained in our laboratory in these different lines of research will be summarized in this communication. We will focus in this communication on aspects such as the controversial debate on whether protein dynamics are linked to the chemical reaction step,[1,2] the role of the quantum tunneling and the electrostatic effects contributions to catalysis,[1-3] or the relevance of compression effects in enzymatic methyl transfer reactions.[4] The information acquired from studies of chemical reactions catalyzed by wild type enzymes can be exploited by industry since these giant molecules are able to perform difficult synthetic reactions without the need of extreme temperatures, high pressures or toxic chemicals.[5]

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Excited State H-transfer In Prototypical Hydrogen Bonded Systems

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This lecture focuses on the excited state hydrogen detachment and hydrogen transfer (ESHT) dynamics in three model H-transfer systems.

First, we consider the dramatic effect that binding of a single water molecule has on the excited state dynamics and lifetime of adenine monohydrates. Our nonadiabatic surface hopping simulations provide no evidence of a direct water involvement in the deactivation of adenine monohydrates and no explanation for the observed sub-100 fs excited state lifetime. Puzzled by this discrepancy, we analyse the relevant electron-driven proton transfer reaction pathways and discuss their inaccessibility to trajectory-based nondiabetic dynamics simulations. [1]

Next, we study the excited state dynamics of 1- and 2-naphthols and their water clusters because these systems exhibit very different reactivity. The excited state dynamics of 2-naphthols and 2-naphthol water clusters is mediated by the optically dark $\pi\sigma^*$ state and leads to homolytic cleavage of the OH bond. On the contrary, in 1-naphthol and 1-naphthol water clusters, a highly specific excited state hydrogen transfer (ESHT) to carbon atoms C8 and C5 takes place. The ESHT pathway arises from the intrinsic electronic properties of the $\pi\pi^*(La)$ state of 1-naphthols. [2]

Finally, we explore the photodynamics of malonaldehyde and compare it to that of the homologous acetylacetone. We discuss the mechanisms and time scales of excited state relaxation and the role of H-transfer in these processes. Special attention is paid to the validation of dynamics results against benchmark electronic structure calculations and to the link with experiment. [3]

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Proton Transfer Reaction Dynamics Using The Reduced Quantum Dynamics Approach

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The non-perturbative hierarchical equations of motion (HEOM) method has developed into an important tool to simulate quantum dynamics in condensed phase. I will present its applications to studies of quantum effects in proton transfer (PT) reactions using model systems: (1) The transition from coherent dynamics to rate dynamics for a double-well model coupled to a harmonic bath, and observation of non-Kramers behavior due to quantum tunneling.[1] (2) Effects of the rate promotion mode, which increases rate constant and decrease the kinetic isotope effect.[2] (3) A mixed quantum-classical description of the PT dynamics, where the proton degrees of freedom is quantized, while the other degrees of freedom are treated classically.[3] The hydride transfer reaction in DHFR is also mapped into a double-well/harmonic bath model, and studied using the mixed quantum-classical approach.[5] (4) Quantum effects in photo-induced proton coupled electron transfer reactions, where the effect of vibrational relaxation becomes important.[4]

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High-Accuracy Calculations Of Tunneling Splittings In Water Clusters

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In molecular clusters and weakly-bonded molecules the atoms can undergo large-amplitude structural rearrangements between different degenerate configurations. Tunneling splittings resulting from these rearrangements can be seen in the rovibrational energy levels. The tunneling motions are extremely anharmonic, and the harmonic approximation for treating vibrational energy levels cannot describe these dynamics. Tunneling splittings can be observed in small water clusters, and are a particularly sensitive test of the potential energy surfaces used for calculations of the physical properties of water in various phases.

To date, variational and diffusion Monte Carlo (DMC) calculations have been the methods of choice for calculating tunneling splittings, but both methods can run into difficulties. I will describe how tunneling splittings can be calculated using path integral methods, namely path integral molecular dynamics (PIMD) [1] and semiclassical instanton theory [2,3]. I will show that these methods are able to reproduce the tunneling spectra for the water dimer, trimer, and hexamer, as well as giving an intuitive physical picture for the rearrangement dynamics. I will also show how the methods can be adapted to calculate rotational spectra, and demonstrate the technique on the water dimer [4].

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Hydrogen Bond Network Rearrangement Dynamics in Water Clusters: Dramatic Effects of Librational Excitation on Hydrogen Bond Tunneling Rates

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Theoretical studies of the hydrogen bond network rearrangement(HBNR) dynamics in liquid water have indicated that librational motions initiate the HB breaking/formation processes. We present the results of using a simple time evolution method to extract and compare the hydrogen bond tunneling lifetimes for the water dimer, trimer, pentamer and hexamer from the experimentally measured tunneling splittings in the ground and singly excited intermolecular vibrational states. We find that the specific nature of the intermolecular vibrational excitation does not significantly influence the tunneling lifetime of the dimer, but that excitations of a librational vibration dramatically decrease the water trimer, pentamer, or hexamer lifetimes. Hence, observing and quantifying the enhanced hydrogen bond breaking dynamics for these types of vibrations in water clusters serves as support for theoretical predictions. The specific enhancement of tunneling in larger clusters relative to the dimer also indicates that hydrogen bond cooperativity is a vital element of these dynamics.

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Recent Developments in Instanton Theory To Simulate Tunneling Processes In Catalysis, Astrochemistry, And Biochemistry

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Instanton theory, based on the Feynman path formulation of quantum mechanics, is one way to calculate tunneling rate constants down to low temperature. While it is quite accurate in many cases, it suffered from several shortcomings. We present methodological improvements in several aspects: its accuracy close to the crossover temperature and its limit below that temperature, its convergence properties with the number of images, its temperature-dependence for bimolecular rate constants at low temperature, as well as its dependence on the quality of the potential [1]. Some of these aspects were improved on by using a microcanonical formulation of instanton theory [2].

We applied instanton theory to several reactions of chemical, biochemical, and astrochemical interest [3,4]. Atom tunneling allows reactions to proceed at the cryogenic temperatures of the interstellar medium despite a reaction barrier. These help to explain the formation of water and of the first building blocks of life.

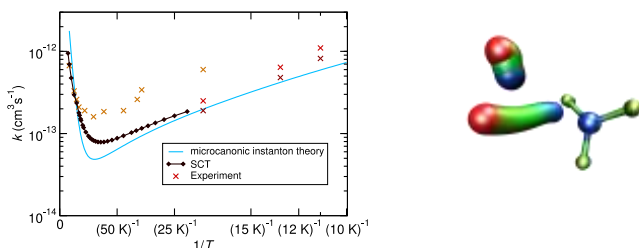


Figure: Rate constants and instanton path for the reaction $\text{NH}_3^+ + \text{H}_2\text{N} \rightarrow \text{H}_4^+ + \text{H}$

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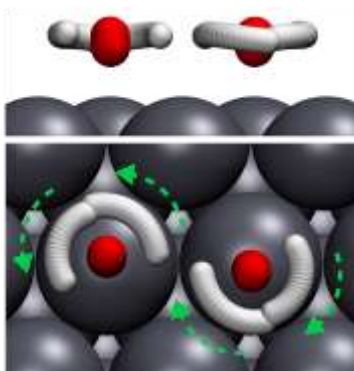
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Molecular Modeling Of Tunneling Effects In Adiabatic And Nonadiabatic Reactions

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Ring-polymer instanton theory [1-3] is a quantum TST-like method, providing insight to favorable tunneling mechanisms and rates via locating an optimal tunneling pathway. Therefore, it can be extensively used to study quantum tunneling in large systems (~100 atoms), describing the electronic structure with ab initio methods. Here I present recent applications of instanton theory to understanding proton transfer reactions in full dimensions, and diffusion processes such as water dimers "waltzing" on metal surfaces. Furthermore, instanton theory can be extended to treat nonadiabatic reactions [4] such as redox reactions, by including tunneling effects to Marcus theory. I also discuss examples of our ongoing work in full atomistic modeling of electron transfer in solution.



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Electrostatics And Tunneling In Monoamine Oxidase A Enzyme

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Quantum nature of nuclear motion, including tunneling, often represents a constitutive part of enzymatic reactions and can have a strong impact on reaction kinetics. In enzymatic reactions, the established quantity characterizing nuclear quantum effects is the H/D kinetic isotope effect (KIE). Analysis of KIE can provide information on the reaction mechanism and the magnitude of KIE usually reflects the extent of tunneling in the reaction. For enzymatic reactions in which tunneling has little or no role, H/D KIE amounts to about 3-8. On the contrary very large values of H/D KIE are characteristic of reactions mainly driven by tunneling, e.g. soybean lipoxygenase-1 [1, 2].

The focal point of our research are monoamine oxidase (MAO) enzymes that feature relatively modest KIE values of 6-14 [3], which suggests a rather minor role of tunneling. Nevertheless, these enzymes have recently been used as a model system for the investigation of the importance of electrostatics in the catalytic function of enzymes [4]. We developed a simple, yet efficient charge-embedding model, capable of elucidating the role of the electrostatic environment provided by the enzyme on characteristic quantities related to reactivity, which are derived from the DFT-computed electronic structure. Our findings suggest that electrostatics is not only significant, but rather essential for enzyme catalysis.

The present contribution is essentially an extension of the aforementioned approach to quantization of nuclear motion. By using a similar charge-embedding scheme we computed a series of 1D potential energy functions and their pertinent mass-dependent vibrational states along the reaction axis and investigated the effect of charged surroundings provided by the solvated enzyme. We found that the charged environment causes the transition state to occur earlier; the extent of tunneling in the gas phase relative to the enzymatic environment is still under investigation. At the same time, we evaluated the H/D KIE by the quantum classical path (QCP) approach to about 9, yielding good agreement with experimental kinetic data [3] as well as with our earlier study [5].

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Quantum Dynamical Treatment Along With Analysis Of The Potential Energy Surface For Rotational Tunneling By Bound H₂ Can Lead To Improved Materials

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A detailed picture of the nature of the interactions of bound hydrogen with the host materials is of considerable importance for the understanding and further development of areas such as hydrogen storage, proton transfer, and catalysis of a wide range of chemical reactions. These interactions can readily be probed by neutron scattering methods and by NMR, but the results are difficult to interpret in sufficient detail without computational studies. Transitions between the two lowest rotational energy levels of bound hydrogen can readily be observed by inelastic neutron scattering (INS). These can be described as rotational tunneling transitions, and are extraordinarily sensitive to details of the potential energy surface (PES) experienced by the hydrogen molecule. The necessary simulations are, however, challenging, owing to the need to treat quantum dynamical (QD) effects accurately, and the necessity to derive an accurate potential energy surface for the calculation of the rotational energy levels using crystallographic data along with the location of hydrogen molecules determined by simulated annealing. We have carried out an extensive series of INS studies and 2D quantum rotation computational studies on H₂ in a number of porous materials mostly by employing a general purpose materials sorption potential along with explicit many-body polarization interactions. This approach makes it possible to determine which interaction is mainly responsible for the barrier to rotation or the strength of the binding. These studies have pointed the way to the recent realization[1] of a near ambient, sorption based, hydrogen storage material, which has attracted enormous attention for its potential for a viable, inexpensive, on-board hydrogen storage system.

Effect Of Solvation On Kinetic Isotope Effects On Hydrogen Abstraction From Ethanol In Aqueous Solution

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Hydrogen abstraction from ethanol by atomic hydrogen is a well-known reaction which is one of the most important steps in ethanol decomposition.[1] Depending on the temperature this reaction can proceed via three different channels resulting in three different products. It has been shown that at room temperature this reaction goes through only one pathway, however, the reaction can proceed via two transition states (gauche (g) and trans (t)) which interconvert in each other by internal rotation.[2,3] Previous computational study on this reaction was focused on using the simplest presentation of solvent - continuum model of solvation and it was observed that the resulted hydrogen kinetic isotope effects (²H KIEs) deviate from the experimental data which may appear due to the lack of inclusion of specific interactions with the environment. Current research efforts focus on expanding the solvation model in order to test the effect of the explicit presence of water molecules on predicted isotope effects.

²H KIEs were calculated for four different substitution scenarios using two theoretical approaches; multipath variational transition state theory (MP-VTST) [3,4] and a path integral formalism in a form of centroid path integral and free-energy perturbation-umbrella sampling (PI-FEP/UM). [5] The former method allowed for incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which were further used for kinetic isotope effects calculation. The latter method enabled to treat the solvent purely explicitly by using a QM/MM protocol. It was observed that within the MP-VTST approach inclusion of a small number of water molecules did not always improve the predictions and the path integral model succeeded only when the QM region of the model was treated at a DFT level of theory. The influence of environment on the obtained isotopic fractionation as well as the contribution of various factors like conformation of the transition state and the position of water molecule directly interacting with the solute were analyzed and discussed.

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Tunneling Behaviour Of Water Molecules In Bassanite

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Recently, using inelastic neutron scattering (INS), we observed quantum tunnelling of water confined in ~ 5.1 Å diameter channels of mineral beryl (hcp structure) [1]. The study reveals that at low temperatures water does not have hydrogen bonds and water protons tunnel between 6-fold equivalent positions in ab-plane. In the present work we studied dynamics of bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, monoclinic structure, space group I121 [2]), a structure of which has channels formed by CaO_8 and CaO_9 polyhedra with water molecules residing in the channels and occupying two different positions. The INS spectra of bassanite measured in wide range of energy transfer, showed that at low temperature ($T=5$ K) intramolecular O-H stretching modes of water are at high energy, around 445 meV (compared to 410 meV in ice-Ih), and the intermolecular librational band is at significantly low energies, 35 – 90 meV (65 – 125 meV in ice-Ih), indicating weak hydrogen bonds acting on water molecules. At lower energies, we observed a peak at about 1 meV which shows the behaviour of tunneling mode (see Fig. 1): its intensity decreases with temperature increase (from 5 to 35 K) and intensity increases as a function of neutron momentum transfer (nonmagnetic peak). In addition, we observed two peaks at about 4.5 and 5.5 meV (both have vibrational type), and the intensity of the first peak grows with temperature increase (and it rises faster than it should be due to Bose population factor), while the intensity of the second peak decreases. Therefore, a possible phase transition or at least change in water position in the bassanite channels occurs at around 15 K. In the talk we will discuss the observed INS results and attempt to explain the tunneling of water molecule, which was not observed before in other INS experiments involved confined water molecules in the presence of hydrogen bonds.

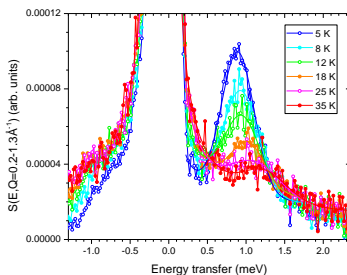


Figure 1. Temperature dependence of the dynamical structure factor $S(E,Q)$ for bassanite measured with $E_i=4$ meV.

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Heavy-Atom Tunneling Reactions On The Slippery Potential Energy Surface Of Arylnitrenes

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Quantum mechanical tunneling (QMT) of heavy-atoms like carbon or nitrogen for the longest time has been considered very unlikely, but recent evidences suggest it occur more frequently than assumed and that it can have serious implications for chemistry and biology [1]. In this lecture, I will address our discoveries of heavy atom QMT on the potential energy surface (PES) of aryl nitrenes.

Although research on aryl nitrenes (reactive intermediates) is a mature field, with more than 50 years of literature reports, their slippery and electronically intricate PES still hides fascinating reactions. To explore such challenging surface, one powerful approach is to use a combination of a cryogenic matrix environment and tunable narrowband radiation source [2]. In this way, we have uncovered interesting cases of heavy atom QMT reactions [3,4], such as the competitive carbon vs nitrogen tunneling in benzazirine rearrangement to cyclic ketenimine and aryl nitrene, respectively (Figure 1). Experimental and theoretical results providing support for the occurrence this and other heavy-atom tunneling reactions will be discussed.



Figure 1. Two competitive tunneling reactions from the same chemical species, carbon vs nitrogen tunneling in benzazirine to ketenimine and aryl nitrene, respectively.

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The OH + Methanol Reaction At Ultracold Temperatures: A Tough Nut For Theory

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Laval nozzle experiments are state-of-the-art in the study of chemical reactions at low temperatures. One prominent example is the hydrogen abstraction reaction of methanol by the OH radical. It was found that the thermal rate constants for this reaction behave abnormally at temperatures below 200 K [1, 2]. Specifically, it was found that the thermal rate constants increase substantially as the temperature is lowered. Quantum mechanical tunneling was considered the cause of this highly non-Arrhenius behavior. The low-pressure and low-temperature conditions of the experiment and the striking results led to some researches to conclude that Laval nozzles could be used to simulate the conditions of the interstellar space. This idea is very attractive because involves to have a lab able to reproduce reactions that occur in the outer space.

The initial theoretical calculations that made use of the master equation failed to reproduce the experimental results [1]. Further studies by Siebrand et al. [3], that included RRKM, quasiclassical trajectory calculations, and kinetic Monte Carlo simulations indicated that the sudden increase of the thermal rate constants needs the presence of a third body (for instance another molecule of methanol). This theoretical interpretation was heavily criticized by some experimentalists on the ground that the presence of, for instance, methanol dimers would modify the kinetics. In an attempt to clarify the situation, Gao et al. [4] performed new theoretical calculations using a version of variational transition state theory which can deal with several reaction bottlenecks (canonical unified statistical (CUS) theory). These authors concluded that the only way to reconcile theory and experiment is by assuming that the experiments are already in the high-pressure regime. Under these conditions, the pre-reactive complex is stabilized, so tunneling can play an important role in the reaction. This high-pressure effect is also compatible with the participation of a third body, as indicated by Siebrand et al.

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Primary And Enzyme Kinetic Isotope Effects In *E. Coli* Thymidylate Synthase

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Given the ubiquitous character of hydride transfer reactions in enzyme catalyzed processes, a deep understanding of this step is crucial not only from the foundations point of view but also for the implications in pharmaceutical and biotechnology applications. In the present communication, the hydride transfer step catalyzed by thymidylate synthase (TSase) has been studied by means of hybrid QM/MM potentials with semiempirical Hamiltonians and the M06-2X hybrid density functional. Calculations of the protium and tritium transfer at different temperatures have allowed calculation of the temperature dependence of primary kinetic isotope effects (KIE). Dynamics and quantum tunneling effects are revealed to have little impact on the reaction-rate but are most significant in determining the KIEs and their temperature dependence. The small temperature dependence of quantum tunneling corrections and the quasiclassical contribution term cancel each other, while the recrossing transmission coefficient appears to be temperature independent over the 5–40 °C interval in wild type ecTSase.

Similar simulations carried out on the isotopically substituted protein, have revealed small but measurable enzyme kinetic isotope effects. Deep analysis of this results have rendered conclusion of the dynamic role of the protein on the rate limiting step.

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A More Efficient Method For Thermal Instantons And Development Of Microcanonical Rate Theory

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Instantons describe the tunnelling pathways that dominate molecular dynamics at low temperatures [1,2,3]. They can be used to calculate thermal rate constants in systems where the full quantum description would be too demanding by discretizing the tunnelling pathway with a number of ring-polymer beads. We have developed a new Divide-and-Conquer method for thermal instanton rate calculations which reduces the computational scaling required to compute the prefactor by avoiding the diagonalization of a very large matrix [4]. This opens the door for calculation of thermal rate coefficients for low-temperature reactions where many ring-polymer beads are required. Our new method is benchmarked on the full-dimensional H + CH₄ reaction for which a fitted PES is readily available [5]. This method is also applied to the unimolecular hydrogen transfer reaction in the syn-CH₃CHO Criegee intermediate for which the PES was calculated on-the-fly.

We also present recent developments in using instantons to calculate microcanonical rate coefficients as well as how to incorporate instanton tunnelling corrections into statistical RRKM theory [6]. Lester and coworkers have performed experiments as well as RRKM calculations with Eckart corrections on the unimolecular syn-CH₃CHO reaction [7]. In this case, we find that their energy-dependent rate coefficients agree well with those calculated using our RRKM-instanton approach. Future work will consist of extending the RRKM-instanton formulation to calculate microcanonical rate coefficients for reactions which exhibit barriers that are poorly described by Eckart tunneling corrections.

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Exact Quantum Dynamical Treatment Of Hydrogen-material Interactions: Fe(H)2(H2)(PEtPh2)3 And [FeH(H2)(PH3)4]+

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Hydrogen, H₂, is arguably the most well understood molecule. Yet remarkably, our mechanistic understanding of hydrogen-material interactions remains limited—despite much interest, e.g., in the contexts of hydrogen fuel storage, catalysis, etc. Simulations are challenging, owing to the need to treat quantum dynamical (QD) effects accurately. Conversely, NMR and inelastic neutron scattering (INS) experiments provide useful data, but are difficult to interpret properly without theory.

This talk addresses the fundamental QD interactions of hydrogen in two specific coordination complexes of the “Kubas” variety: (1) Fe(H)2(H2)(PEtPh2)3; (2) [FeH(H2)(PH3)4]+. Both a density functional theory (DFT) and QD investigation are conducted. For the first complex [1,2], just the rotation of the dihydrogen ligand is investigated explicitly, albeit in full QD dimensionality. Ground and excited state tunneling splittings are computed, and excellent agreement with experiment is achieved with no adjustable parameters. Rotation is the most important dynamical player at low temperature, but is also expected to play an important role in the fluxional reorganization of all hydrogen ligands in (1) via quantum tunneling. As a precursor to the latter calculation, H atom transfer in the simpler, theoretical complex (2) is also investigated. To our knowledge, this represents the first QD study of the benchmark “H+H₂ reaction in a complex” to be performed, although at present, only the DFT portion of this investigation has been conducted.

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Structural Details Of The Desolvation Process And Adsorption Of Dihydrogen In The Flexible Metal-Organic Framework [Cu(Me-4py-trz-ia)]

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The flexible metal-organic framework (MOF) [Cu(Me-4py-trz-ia)] features outstanding uptake properties for H₂ and CO₂ at ambient pressure.^[1] Depending on solvent molecules present in the framework this material shows different X-ray powder diffraction patterns (Figure 1) under varying activation conditions indicating several structural transitions before reaching the fully desolvated phase **1e**. Interestingly, post-synthetic solvent exchange prior to activation alters the structural transition path that is passed during the desolvation providing a faster and energy-efficient activation of this MOF. Following up these result, we present a detailed structural insight into the behaviour of this flexible MOF after different solvent exchange procedures and during activation by combination of single crystal structure analyses, Rietveld refinement and DFT simulations. Additionally, the interaction of dihydrogen with this framework was investigated by DFT calculations and inelastic neutron scattering (INS) experiments.

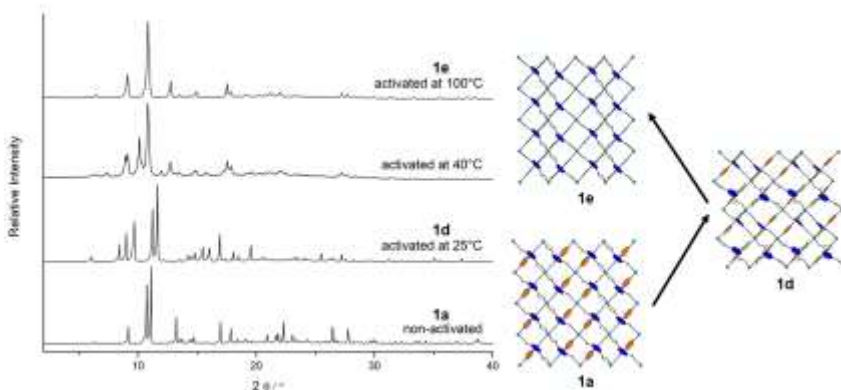


Figure 1, left: X-ray powder diffraction pattern of the as-synthesized, non-activated phase **1a** of [Cu(Me-4py-trz-ia)] and after activation at different temperatures for 24h under vacuum; right: schematic representation of the frameworks of the phases **1a**, **1d** and **1e** (view along [010]).

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On Non-Linear Schrödinger Equations For Open Quantum Systems

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Recently, two generalized nonlinear Schrödinger equations have been proposed by Chavanis [Eur.Phys. J. Plus 132 (2017) 248] by applying Nottale's theory of scale relativity relying on a fractal space-time to describe dissipation in quantum systems. Several existing nonlinear equations are then derived and discussed in this context leading to a continuity equation with an extra source/sink term which violates Ehrenfest theorem. An extension to describe stochastic dynamics is also carried out by including thermal fluctuations or noise of the environment. These two generalized nonlinear equations are analyzed within the Bohmian mechanics framework to describe the corresponding dissipative and stochastic dynamics in terms of quantum trajectories. Several applications of this second generalized equation which can be considered as a generalized Kostin equation have been carried out. The first application consists of dissipative tunneling by an inverted parabolic barrier by means of scaled trajectories. After, the so-called Brownian-Bohmian motion is investigated by calculating classical and quantum diffusion coefficients. And as a third example, transmission through a transient (time dependent) parabolic repeller is studied where the interesting phenomenon of early arrival is observed even in the stochastic dynamics although the magnitude of early arrival is reduced by friction.

Ground-State Tunnelling Splittings In Water Pentamer Using Instantons

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Ring-polymer instanton (RPI) method [1] can be used to calculate tunneling splittings between symmetric wells in high-dimensional molecular systems. It approximates the tunnelling dynamics using an optimal tunnelling path along which the quantum process predominantly takes place. The method has been generalized to treat systems with multiple wells [2]. This enabled the calculation of tunnelling splitting patterns in water clusters in full dimensionality and their interpretation through the rearrangement motions in the cluster.

The RPI method consists of three time-consuming steps: locating of the minimum action path (MAP) in full dimensionality, the calculation of Hessians along the path and the calculation of the so-called fluctuation prefactor. We present our numerical methods to reduce the computational effort involved in each of the above steps.

We developed the string method [3] for locating instantons (MAPs) in order to reduce the number of path discretization points. In the quadratic string method [4], we optimize the path in local quadratic estimates of the potential energy surface (PES) to reduce the number of iterations. We also extend the Mil'nikov-Nakamura original multidimensional formulation of the instanton method [5] to treat the asymmetric paths, which regularly appear in the studies of water clusters, to avoid the matrix diagonalization in the prefactor calculation, and apply it in Cartesian coordinates, to retain the simplicity of the RPI method.

Finally, we calculate the ground-state tunnelling splitting pattern in water pentamer using our methods and identify the important rearrangement motions that appear in the spectrum.

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Parallel Implementation Of Semiclassical Transition State Theory And Its Application To High-Dimensional Tunneling Reactions

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Semiclassical Transition State Theory (SCTST) can incorporate the non-separable coupling between degrees of freedom (DOFs) of reactive systems and include the effects of reaction path curvature and anharmonicity, as well as quantum tunneling contributions in the rate constant. The rate expression is derived by relying on a perturbative expansion for the vibrational energy which makes it possible to express the semiclassical cumulative reaction probability in a convenient way, without any further assumptions about the separability of the DOFs.[1-4]

The main goal of the talk is the extension of this semiclassical methodology to systems of increasing dimensionality upon computation of the densities of states for the reactants and the transition state by means of a convenient parallel implementation of the Wang-Landau algorithm.[5-6]

The new strategy is implemented into two codes, “paradensum” and “parsctst”, which are currently distributed with the open source MultiWell program suite for chemical kinetics.[7] The needed input information is just the reaction barrier height, the normal mode frequencies, and the anharmonic force constants, which are routinely calculated by suitable electronic structure packages.

After describing the codes and demonstrating their computational accuracy and efficiency, the new implementation is applied to estimate the rate constant of the proton transfer isomerization of the 2,4,6-tri-tert-butylphenyl to 3,5-di-tert-butylneophyl, a reaction involving 145 degrees of freedom and showing a clear tunneling regime below 250K.[6]

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Quantum Tunnelling Instability

Computational Detection Of Impossible And Transient Molecules

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One of the hardest, but also most rewarding task in chemistry consists in the generation of any molecule we can envision. As Hoffmann stated "...the literature of organic chemistry has contained characterizations of molecules as unstable, strained, distorted, sterically hindered, bent and battered. Such molecules are hardly seen as dull; on the contrary, they are perceived as worthwhile synthetic goals, and their synthesis, or evidence of their fleeting existence, acclaimed. What is going on here? Why this obsession with abnormal molecules? Is this molecular science sadistic at its core?"[1]

This raises the question: is it even in the realm of possibilities to generate all those extreme molecules? On this matter computational chemistry has the upper hand: it can predict with high confidence the stability of any system whether in kinetic or thermodynamic terms. Moreover, it can predict the probability of decomposition of such molecules by a quantum mechanical tunnelling mechanism[2,3] in what we can call "Quantum Tunnelling Instability" (QTI).

In this talk we will discuss the preliminary analysis of several cases of "impossible molecules", systems which should be synthesizable and stable at low temperature, but their half-lives are in fact extremely short due to unavoidable quantum tunnelling effects (from the ground state or in thermally activated tunnelling).

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Rotational spectroscopic signatures of tunnel effects in weakly bound complexes and clusters

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One of our research interests is the study of intermolecular interactions using microwave, rotational spectroscopy of gas-phase complexes and clusters that are prepared in a molecular expansion. Intermolecular motions sometimes involve tunnelling, which can manifest itself as splitting of lines in the rotational spectra. From the splittings or possible observation of tunnelling transitions in combination with electronic structure calculations, information about tunnelling barriers, tunnelling paths, and zero-point energies can be derived.

In this presentation, I will discuss two different types of clusters/complexes. The first are relatively strong, hydrogen-bonded complexes. One example is formic acid – hydrogen peroxide (Fig. 1), which undergoes a complicated tunnelling motion involving the torsional degree of freedom of the H₂O₂ subunit. I will show how the transient chirality of H₂O₂ is imprinted onto the complex and the tunnelling motion.

The other type of clusters are non-linear molecules solvated by helium atoms. The ultimate goal in this research direction is to find indicators of superfluid behaviour at the microscopic or mesoscopic size regime. An intriguing example are pyridine – He_N clusters (Fig. 2 shows the structure of benzonitrile – He₅), with contain up to $N = 20$ helium atoms. Transitions of some of the clusters show splitting patterns, which we tentatively assign to different conformers or tunnelling of a helium atom from one side of the aromatic ring to the other.

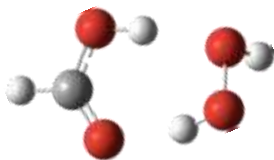


Figure 1. Lowest energy conformer of the formic acid – hydrogen peroxide dimer.

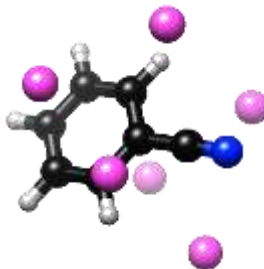


Figure 2. Structure of the benzonitrile – He₅ cluster.

Resonant Tunnelling In Short Period Strained AlN/GaN Superlattices

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Electronic conduction in short period strained GaN/AlN superlattices is studied. The mechanisms of current transport perpendicular to the superlattice layers are explored both theoretically and experimentally, with an emphasis on the elastic and inelastic tunnelling through the AlN barriers. The calculations are performed in the framework of envelope-function approximation and the transfer-matrix based formalism [1]. The current and the conductance show nonlinear oscillatory character. The observed characteristics are interpreted as sequential resonant tunnelling through AlN barriers and reveal negative differential conductivity (NDC). The results are important as NDC in semiconductor superlattices is the origin of various proposals for compact THz wave sources.

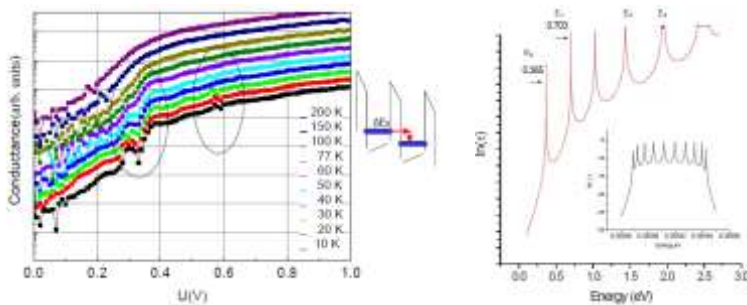


Figure 1. (a) Volt-conductance characteristics of GaN/AlN superlattice measured at 10- 300K, NDC regions are marked; (b) Transmission coefficient τ calculated in below-barrier condition versus the incident electron energy of the superlattice. The fourth minizone in superlattice is inserted in order to demonstrate the fine structure of all the minizones.

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Fluctuations of Hydrogen Bond Networks as a Possible Source of Anomalous Optical Properties in Protein Aggregates

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Textbook physical chemistry tells us that the optical activity of peptide aggregates originates in fluorophores characterised by aromatic groups. Recent experimental work has challenged this notion, finding that amyloid proteins devoid of aromatic amino acids, are capable of absorbing low energy photons and subsequently fluorescing. In this talk, I will highlight some of our recent theoretical work in trying to understand this phenomenon. In particular, using a combination of ab initio molecular dynamics (AIMD) and path-integral molecular dynamics on various model amyloid systems, we find that protons along the hydrogen bond network in the aggregates are susceptible to proton transfer. These proton transfer fluctuations are quite sensitive to nuclear quantum effects (NQE) - in the case of glutamine aggregates, NQE make proton transfer barrier less, and are also coupled to other vibrational modes in the system. We demonstrate further that these vibrational modes are coupled the changes in the optical activity suggesting the existence of a **“structural chromophore”**.

The Pattern Of Eigenenergies At The Saddle Point Region

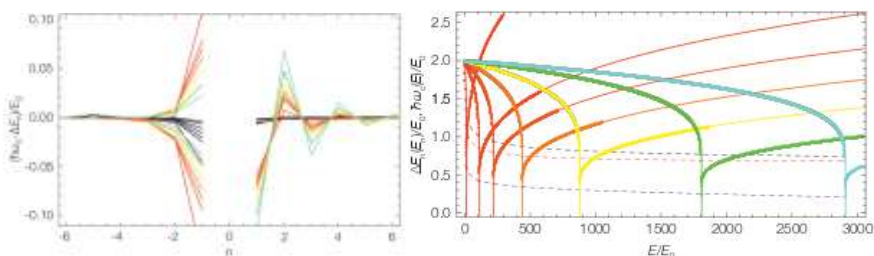
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The tunnel effect for bound states is described in the frequency domain by a set of wave functions and corresponding eigenenergies. Inspection of the wave functions allows us to interpret the tunnel effect. The question arises whether there is a specific pattern of eigenenergies that corresponds to the tunnel effect ?

To answer this question, I will show how the saddle point region, which connects two potential minima, is encoded in the eigenstates of the model symmetric double-well quartic potential. The analysis is based on the correspondence principle between the classical oscillation frequency $\hbar\omega_c(E)$ and the energy spacing $\Delta E_n(E_n)$ of the eigenenergies and allows to set up an approximate analytical model for the level positions at the saddle point. Eigenstates at the saddle point region show some characteristic features: The spacing of the eigenenergies with the energy is decreasing to a specific value at the saddle point, the eigenstates with the smallest spacing are localized at the saddle point and the localization factor $\Delta x\Delta p$ has a local minimum at the saddle point. These results are related to the concept of the excited state quantum phase transition emerged from the study of nuclear eigenstates.

Finally, I will present some applications of this model system, especially in the context of the description of the molecular isomerization based on bound eigenstates of the molecular potential energy surface.



The difference between the classical and quantum frequencies in the neighborhood of the saddle point and the plot of the classical oscillation frequency and the corresponding exact $\Delta E_n(E_n)$ for color-coded increasing barrier heights.

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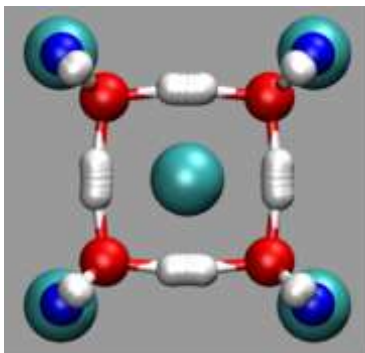
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Concerted Proton-Transfer Between Water Molecules In Different Environments Via Quantum Tunneling

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Proton tunneling through hydrogen bonds governs a wide range of physical, chemical and biological issues such as enzyme-catalyzed reactions or proton ordering and hydrogen-bond symmetrization in high-pressure ice. Recently Meng et al. elucidated the role of concerted tunneling in a cyclic water tetramer, coupled through four hydrogen bonds, by scanning tunneling microscopy[1]. To further improve the underlying understanding of concerted tunneling in complex systems[2], we utilize semiclassical instanton rate theory[3] to investigate proton tunneling in different hydrogen bonded systems. Therefore we calculate rates of proton transfer reactions between water molecules in vacuum, on salt surfaces and as part of bulk ice. We identify significantly increasing tunneling factors for the water clusters on the surface and in ice compared to the same clusters in vacuum. Furthermore we observe that tunneling, included in the instanton rate, changes the reaction pathway in ice from a stepwise, in the classical case, to a concerted mechanism. In each instance we were able to draw conclusions about the effect of quantum tunneling while retaining a simple, semiclassical picture of the reaction (see Figure 1).



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