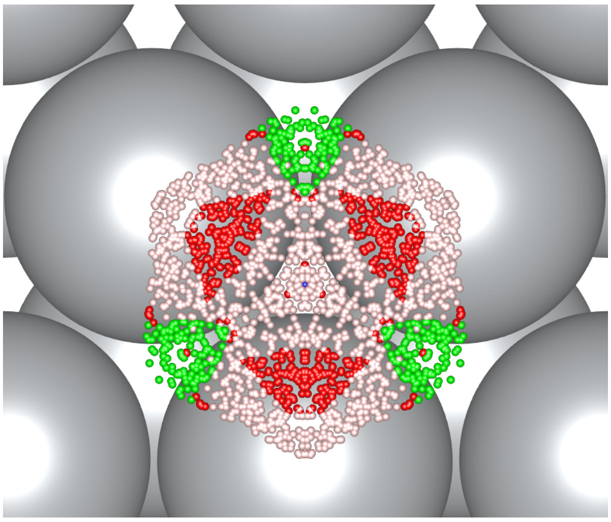
Grand Hôtel d'Orléans, Toulouse (France)



Challenges in reaction dynamics of gas-surface interactions and methodological advances in dissipative and nonadiabatic processes

Organizers: Maite Alducin
Didier Lemoine
Rocco Martinazzo
Peter Saalfrank
Jean Christophe Tremblay

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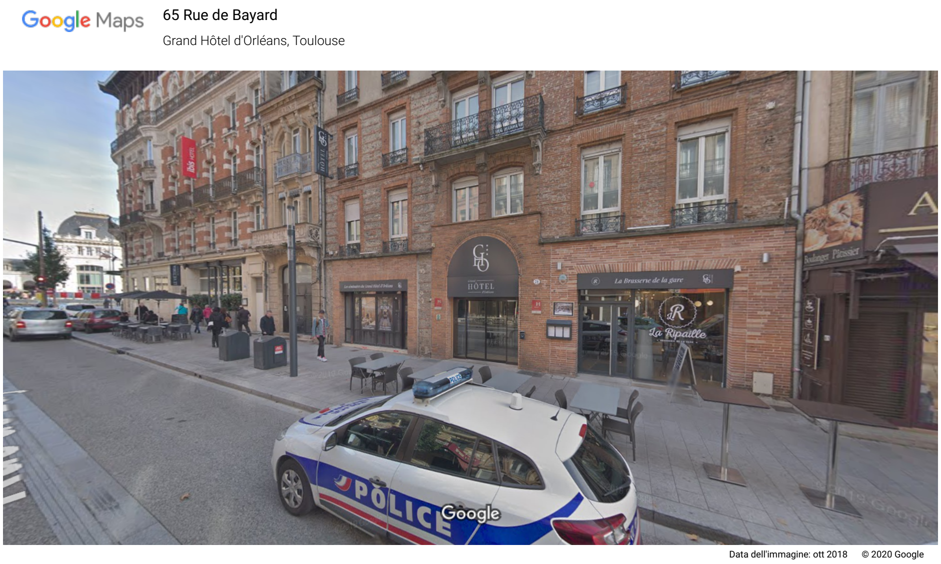
Location

Grand Hôtel d’Orléans, 72 Rue de Bayard, Toulouse. Facade and surface location.



65 Rue de Bayard

Grand Hôtel d'Orléans, Toulouse

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Programme

	Monday, 27th	Tuesday,28th	Wednesday,29th	Thursday,30th
08:00 - 09:00		Adhikari (remote)	Kroes	Miret-Artés (remote)
09:00 - 10:00		Saalfrank	Manzhos (remote)	Mandal
10:00 - 11:00		Maurer Coffee Break	Leccese Coffee Break	D'Agosta Coffee Break
11:00 - 12:00		Díez-Muiño Burghardt (remote)	Spiegelman (remote) Larregaray	Novko Marquardt
12:00 - 13:00		General Discussion	General Discussion	General Discussion
13:00 - 14:00		Lunch	Lunch	Lunch
14:00 - 15:00		Meyer (remote)	Marquetand	Sánchez-Muzas
15:00 - 16:00		Rossi (remote) Behler (remote)	Posenitskiy Benoit	Final Discussion
16:00 - 17:00	Welcome	Coffee Break	Coffee Break	
17:00 - 18:00		Guo (remote)	Jackson (remote)	
18:00 - 19:00		General Discussion	General Discussion	

Description

Energy transfer plays a prominent role in many dynamical processes at surfaces, with important implications in heterogeneous catalysis, corrosion, energy storage, electromobility, and artificial photosynthesis. In close contact with a surface, the internal degrees of freedom (DOFs) of adsorbates typically couple to the substrate phonons. On metals, non-adiabatic coupling to electron-hole pairs (EHP) enhances the energy transfer rate between molecule and environment. These combined effects have been shown to drastically affect the rates and mechanisms of chemical reactions, also when the molecule-metal contact time is only of a few femtoseconds. The presence of dense sets of energy states and the huge number of DOFs renders theoretical treatment of energy transfer in the condensed phase much more challenging than in the gas phase. Fortunately, such complex reactions can usually be separated into a number of elementary steps. Despite significant advances in theoretical modelling of such elementary steps, their reaction mechanism often remains elusive, hindering further experimental progress. Understanding the role of energy transfer in these fundamental reactions is thus of prime importance. In recent years, improved state-to-state molecular beam surface scattering experiments have demonstrated the importance of energy transfer upon molecule-surface collisions. Novel sources of atomic probes (e.g. hydrogen atoms) and high-power coherent light sources in free-electron laser facilities (e.g. Dalian Coherent Light Source) promise to provide even more detailed information about the mechanism of collisional inelasticity. The challenge is now to understand, from first principles, the dynamical implications of the coupling of (de-)excitations in the substrate (EHP and phonons) to the DOFs of atoms and molecules (translation, rotation, vibration, electronic) in the vicinity of surfaces. Translation is intimately related to adsorption and diffusion. Coupling to phonons and/or EHPs can dramatically alter the sticking probability and the mobility of adsorbates on surfaces, which influences the reactivity in subsequent steps. How energy flows in and out of reactive bonds influences the dissociation probability of a molecule, a process which is affected by its coupling to the surface. A freely rotating gas phase molecule becomes constrained in the surface vicinity, leading to strong intramolecular energy redistribution enhanced by coupling to the EHP and phonons. Electronic excitations, either as EHPs excitations or in an initially excited molecule, require proper treatment of nonadiabatic effects beyond the Born-Oppenheimer Approximation.

Two major issues to treat such fundamental reactions are the characterization of the underlying electronic structure and its representation in form of a potential energy surface (PES). Density functional theory is now the established choice for investigating molecule-surface interactions. Recent advances in cluster embedding theories offer the promise of treating even metallic systems systems with wave function methods (coupled cluster, multi-reference configuration interaction), that represent the gold standard for gas phase molecules. In recent years, PES representation has evolved from force fields, interpolation schemes (e.g. corrugation reduction procedure) and rational function design towards neural networks and machine learning representations. Since in most cases only reduced-dimensional PES can be constructed, it becomes important to include environmental effects (EHP, phonons, and neglected molecular DOFs) in the dynamics. To this end, classical molecular dynamics subject to environmental friction within a Langevin formalism is now the most widespread solution, while alternatives such as independent electron surface hopping are also used. Most methods rely on the Markovian approximation (i.e. the absence of memory from the environment) and the assumption of a weak coupling between the molecular DOFs and the surface. For EHP, new theories for the friction tensor in the weak coupling limit have been proposed in recent years. To assess the importance of quantization effects and of non-Markovianity, alternative methods such as Multi-Configuration Ehrenfest (MCE) dynamics, Time-Dependent Discrete Variable Representation (TDDVR), and Stochastic Schrödinger Equations (SSE), have been proposed in the general context of system-bath dynamics. These could help resolve important questions in fundamental surface science, in particular for reactions affected by EHP excitations. For phonon dominated processes, the consensus is that, despite its computational cost, ab initio molecular dynamics with electronic friction (AIMDEF) provides the most balanced description of the dynamics (explicit inclusion of phonons and friction-like EHP coupling). An important advantage of AIMDEF is that it circumvents the pre-computation of a PES. Direct dynamics using moving Gaussian bases has recently seen some great advances for non-adiabatic dynamics in the gas phase, and it could provide a quantum mechanical analogue to AIMDEF for surface processes.

Contents

Abstracts

The effect of surface temperature on the dissociation and scattering of H_2 on and from Cu(111) employing chemically accurate potential energy surface

29 Sept
11:00

Satrajit Adhikari

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The effect of surface temperature on the scattering and dissociation processes of H2(v=0, j=0)-Cu(111) system is investigated by assuming weakly correlated interactions between molecular degrees of freedom (DOFs) and surface modes through a Hartree product type wavefunction. While constructing six dimensional (6D) effective Hamiltonian, we employ: (a) a chemically accurate potential energy surface considering Static Corrugation Model (SCM) [1]; (b) normal mode frequencies and displacement vectors computed with different surface atom interaction potentials within a cluster approximation; (c) the initial state distributions for the vibrational modes by introducing Bose-Einstein probability factors. We perform 6D quantum dynamics [2-5] with such an effective Hamiltonian, and calculate reaction and state-to-state transition probabilities of the diatom. The surface mode vibrations impart substantial effect on the chemisorption process with change of surface temperature. The theoretical outcomes display physically meaningful trend both for sticking as well as transition probabilities compared to experimental [6,7] and other theoretical [1] results.

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28 Sept
15:50

Four Generations of Neural Network Potentials

Jörg Behler

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A lot of progress has been made in recent years in the development of atomistic potentials employing machine learning (ML) [1]. In contrast to most conventional potentials, which are based on physical approximations to derive an analytic functional relation between the atomic configuration and the potential-energy, ML potentials rely on simple but very flexible mathematical terms. Due to this bias-free construction they are applicable to a wide range of systems without changes in their functional form, and a very high accuracy close to the underlying first-principles data can be obtained. Neural network potentials (NNPs), which have first been proposed about two decades ago [2], are an important class of ML potentials. While the first generation of NNPs has been restricted to small molecules with only a few degrees of freedom, the second generation extended the applicability of ML potentials to high-dimensional systems containing thousands of atoms by constructing the total energy as a sum of environment-dependent atomic energies [3]. Long-range electrostatic interactions can be added in third-generation potentials employing environment-dependent charges [4], but only recently limitations of this locality approximation could be overcome by the introduction of fourth-generation ML potentials [5], which are able to describe non-local charge transfer using a global charge equilibration step. In this talk the basic concepts of the different generations of NNPs will be introduced and typical applications will be discussed.

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Machine learning strategies for metallic nanoparticles: a few examples

29 Sept
15:50

Magali Benoit

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Metallic nanoparticles or nanocrystals are one of the most important families of functional materials. Their remarkable properties, due to their nanometric dimension, combined with their chemical composition and morphology, have contributed to the increasing development of their use in fields as diverse as electronics, data storage, catalysis, optics, bio-medical etc.

However, due to their small size, the control of their properties depends crucially on the control of their morphology. This is even more critical for nanocrystals formed of several elements for which the chemical order (alloy, core-shell, demixed configuration, etc.) can also influence the morphology, which becomes extremely difficult to predict. For these reasons, many efforts are deployed today to understand, on the one hand, the mechanisms of formation of these objects and, on the other hand, the origin of the stability of the observed morphologies.

Through examples, I will show how machine learning tools can help to tackle these fundamental questions.

28 Sept
11:40

High-dimensional quantum dynamics of exciton and charge migration in functional organic materials: From coherent to diffusive dynamics

Irene Burghardt

Institut fuer Physikalische u. Theoretische Chemie Goethe-Universitaet Max-von-Laue-Str. 7
60438 Frankfurt am Main

We report on quantum dynamical studies of ultrafast photo-induced energy and charge transfer in functional organic materials, complementing time-resolved spectroscopic observations that underscore the coherent nature of the ultrafast elementary transfer events in these molecular aggregate systems. Our approach combines first-principles parametrized Hamiltonians [1], with accurate quantum dynamics simulations using the Multi-Layer Multi-Configuration Time-Dependent Hartree (MCTDH) method [2], along with semiclassical approaches [3]. The talk will focus on (i) exciton dissociation and free carrier generation in regioregular donor-acceptor assemblies [1,4], and (ii) the elementary mechanism of exciton migration [3,5,6] and creation of charge-transfer excitons [7] in polythiophene type materials. Special emphasis is placed on the interplay of trapping due to high-frequency phonon modes, and thermal activation due to low-frequency soft modes which drive a diffusive dynamics [6].

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Theoretical Approaches to dynamical open quantum systems

30 Sept
9:50

Roberto D'Agosta

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Donostia-San Sebastian, Spain

Since long, experience taught us that no system is closed and isolated: after long enough time any system will reach some kind of relaxed state. Understanding and controlling the approach towards this state, and in general how a system couples to its environment, has become of paramount importance for our society. Indeed, to provide a simple example, this coupling is the limiting our predictive abilities of chemical reactions, while it is necessary to setup the initial conditions or driving the reaction in a given direction. More generally, any manipulation of a quantum system takes place through its coupling with an "external" environment.

In this talk, I introduce some of the standard tools that in recent years have been used to investigate the dynamics of open quantum systems. I connect these approaches to other methods to investigate the dynamics of many-body systems and discuss the origin of some relaxation and dissipation processes. To conclude, I introduce a novel model that could be used to enquiry the state of the system without directly affecting the dynamics.

28 Sept
11:00

Electronic friction in dynamical processes at metallic surfaces

Ricardo Díez Muiño

Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, San Sebastián, Spain
Donostia International Physics Center DIPC, San Sebastián, Spain

Understanding and mastering the dynamics of elementary reactive and non-reactive processes at surfaces is a basic ingredient to control many physical and chemical phenomena. The adiabatic approximation, in which electronic non-adiabatic effects are neglected, has been shown to describe reasonably well the dynamics of many of these processes. However, atoms and molecules generate low energy electronic excitations in metal surfaces even at thermal energies. Therefore, dynamical simulations of these systems should in principle incorporate electronic non-adiabatic effects, in order to analyze in which way they affect gas-surface reactions. In many cases, the effect of low-energy electron-hole pair excitations can be included in the theoretical description of the dynamics through an electronic friction coefficient. A widely used model to calculate this friction coefficient is the local density friction approximation (LDFA), which can be directly applied to perform ab initio molecular dynamics with electronic friction (AIMDEF). In this talk, the accuracy of the LDFA approximation will be tested by comparing its predictions with those of a non-perturbative method, namely time-dependent density functional theory (TDDFT). A jellium cluster will be used as a model system for this purpose. A detailed comparison of the LDFA results and the TDDFT results at the cluster surface, a region in which the electronic density is rapidly varying, shows that a local friction approximation provides a satisfactory enough description of the force linked to the excitation of electron-hole pairs. Thus, the LDFA can be described as an efficient framework to calculate the friction coefficient that can be later introduced in multidimensional classical dynamics simulations.

Dynamics of Surface Scattering and Reactions

28 Sept
17:00

Hua Guo

Department of Chemistry and Chemical Biology, University of New Mexico

Chemical reactions at gas-solid interfaces are of great importance in many heterogeneous processes such as catalysis, corrosion, and material fabrication. In this talk, dynamics of several prototypical surface processes, including scattering and recombinative desorption, are explored theoretically on metal surfaces. Ab initio molecular dynamics (AIMD) is used to explore the dynamics of bond breaking/formation and energy transfer. High-dimensional potential energy surfaces including the surface degrees of freedom are constructed from on-the-fly AIMD trajectories and static DFT calculations. These potential energy surfaces allow a $\sim 10^6$ acceleration for dynamical calculations, which is vital for studying rare events such as trapping. Energy dissipation due to electron-hole pairs is also considered, using the local density friction approximation. I will focus on our recent work on CO scattering from Au(111)[1,2] and CO oxidation on Pt surfaces.[3,4]

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29 Sept
9:10

Methane dissociation on stepped Ni, Pt and Ir surfaces

Bret Jackson

Department of Chemistry, University of Massachusetts, Amherst MA 01003, USA

A quantum model based on the Reaction Path Hamiltonian is used to compute state-resolved dissociative sticking probabilities for methane colliding with metal surfaces. We assume that the potential energy surface is harmonic with respect to displacements away from the minimum energy path (MEP), but only for the strongly bound internal vibrations of the molecule. DFT is used to map out the MEPs for these reactions, and Hessian calculations along each MEP give us both the potential energy surface and the vibrationally nonadiabatic couplings needed to define the kinetic energy operator. The total molecular wave function is expanded in the adiabatic vibrational states of the methane molecule and evolved in time. Sudden models are used to treat lattice motion and molecular translation parallel to the surface. We explore the dynamics of direct dissociation on the steps and terraces of Ni(211) and Pt(211) [1-3] and on Ir(111) [4], finding good agreement with experiment. For a reactor at 500 K, we show that sticking on the (211) surfaces is dominated by collisions within a few tenths of an Å of the minimum barrier site on the step edge, and by molecules with either one or two quanta of bending vibration excited, with translational energies of about 0.10 - 0.35 eV, or 0 - 0.2 eV, respectively. To dissociate at these low energies requires both a significant conversion of vibrational energy into motion along the reaction path and a puckering of the lattice atom over which the molecule dissociates. We also examine the indirect precursor-mediated reaction of methane on Ir(111), and consider the effects of step defects on this pathway[4].

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Towards a Chemically Accurate Description of Reactions of Molecules with Transition Metal Surfaces

29 Sept
8:30

Geert-Jan Kroes

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Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. Unfortunately, currently no first principles methods can be relied upon to deliver the required accuracy. As a first step to solving this problem, in 2009 we came up with a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). While the original procedure was restricted to cases where the Born-Oppenheimer static surface (BOSS) model could be used (H_2 with surfaces), we can now also use it for heavier molecules interacting with metals. For this, we can combine SRP-DFT with Density Functional Molecular Dynamics (DFMD). Also, thanks to a collaboration with Jörg Behler (University of Göttingen) we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons, for polyatomic molecules interacting with metals. Furthermore, the effects of electron-hole pair excitation can be modeled with the local density friction approximation (LDFA) and with orbital dependent friction (ODF). We are increasingly turning to systems for which DFT at the generalized gradient approximation (GGA) or meta-GGA level would seem to be insufficiently accurate. Examples that will be discussed include HCl + Au(111) (in a collaboration with Alec Wodtke and Jan Geweke from the MPI Göttingen) and O_2 + Al(111). From the latter two systems, we now have evidence that the accuracy for systems that are characterized by low values of (Φ - EA) (the work function of the metal surface minus the electron affinity of the molecule) can be described more accurately with screened hybrid density functionals than with GGA functionals. Also, for such systems (which are treated inaccurately with GGA-DFT) meta-GGA functionals already give results that are improved over GGA results. Finally, I will discuss quantum Monte-Carlo results for H_2 + Al(110), that were obtained in a collaboration with Katharina Doblhoff-Dier. These results suggest that GGA-DFT correctly describes the energetic corrugation of the barrier heights (how they vary with impact site), while the absolute number of the minimum barrier height is tunable; with these findings the success of SRP-DFT can be explained on the basis of the hole model.

29 Sept
11:40

Translational Inelasticity of Hydrogen Atoms Scattering off Hydrogen- Covered W(110) Surfaces

Raidel Martin Barrios[1,2], Oihana Galparsoro[1,2,3], Aliezer Martinez Mesa[1,2], Llinersy Uranga Piña[1,2], Pascal Larregaray[1,2]

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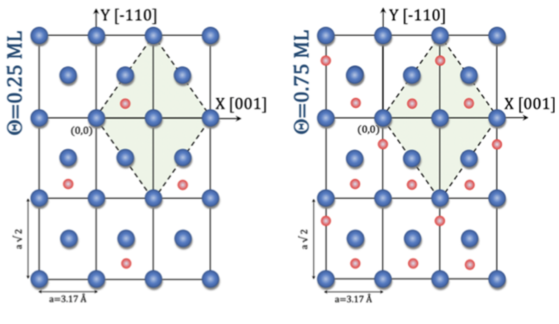
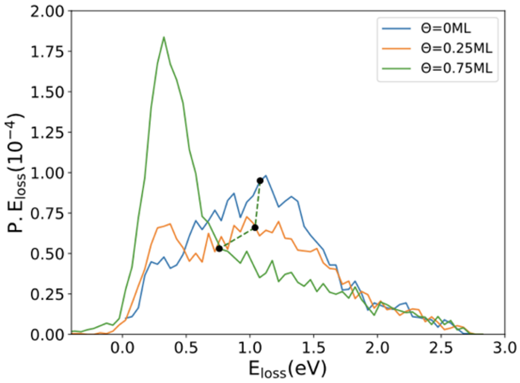
Quasi-classical trajectory simulations are performed to investigate the energy transfer upon scattering of hydrogen atoms off hydrogen-covered (110) tungsten surfaces. For hydrogen atoms impinging clean metal surfaces at energies of the order of few electronvolts, translation energy loss has been recently demonstrated to be mainly mediated via electron-hole pair excitations. The present theoretical approach scrutinizes the effect of coverage by hydrogen pre-adsorbed atoms. Scattering can be rationalized in terms of three distinct dynamical mechanisms, the contribution of which changes with coverage. These allow in particular to understand why the shape of the energy loss spectra critically depends on whether scattering is analyzed in the whole space or at specular angle.



Position of the adsorbed H atoms (red points) on W(110) at Θ=0.25 ML (left) and Θ=0.75 ML (right).



Energy loss spectra for atoms scattered at specular angle, for Θ=0 (blue), 0.25(orange) and 0.75(green) ML. The distributions are normalized to the total number of trajectories. Black circles represent the average energy loss.

Hydrogen adsorption and abstraction on the C/Si interface: a combined DFT-quantum dynamical study

29 Sept
9:50

Mirko Leccese[1], Didier Lemoine[2], Rocco Martinazzo[1]

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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 make it appealing from both a fundamental and an applied perspective[2]. Such interface consists of two carbon layers grown on the SiC(0001) surface - a "buffer" layer strongly bound to the substrate and a "graphene" layer which is weakly bound to the buffer[3]. Hydrogenation of the buffer layer is particularly attractive since it completely decouples the graphene layer, thereby making the latter really free-standing. In addition, the corrugation of the buffer layer, which arises from the variation of the C-Si interaction strength over the moiré supercell, makes the C/Si interface an ideal system for studying the effects of corrugation on the H adsorption energetics (*e.g.* for hydrogen storage applications[4]). The passivation of the buffer layer lies at the heart of the aforementioned decoupling strategy and is ruled by the competition between the adsorption of H atoms and the reactivity of adsorbed species towards abstraction processes. In the latter case, 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 accomodate 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 (1310 atoms) that is known to describe the observed reconstruction of the clean buffer surface. We scrutinized the H adsorption energetics 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 wave packet method within the flat-rigid surface approximation and a model LEPS potential, parametrized with first-principle data[6,7]. In this way, we assessed the role of the adsorption site on the rate of the abstraction process.

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30 Sept
9:10

An Implementation of the Stochastic Multi-Configuration Time-Dependent Hartree Method

Souvik Mandal[1], Jean Christophe Tremblay[1], Roberto Marquardt[2], Fabien Gatti[4,5,6]

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[3] Laboratoire : Institut des Sciences Moléculaires d'Orsay (ISMO), Université Paris-Saclay, France

We propose an implementation of the Monte Carlo Wave Packet (MCWP) method in the Multi-Configuration Time-Dependent Hartree (MCTDH)[1] code to allow studying dissipative quantum dynamics.[2-4] A minimal two-dimensional model is parametrized to represent O_2/Pt(111): the internal stretching mode – at higher frequency, typically with a stronger probe signal – and the distance to the surface – describing the adsorption strength. A dissipation operator is formulated which obeys the Lindblad form of a stochastic master equation that is designed to reach thermal equilibrium in the long time limit. We investigate the thermalization behavior and the interplay between intramode coupling and dissipation. The convergence of our stochastic Multi-Configuration Time-Dependent Hartree (sMCTDH) approach is benchmarked with respect to the number of MCWP realizations at different temperatures and for different initial conditions. A potential coupling term is introduced and varied to systematically investigate relationships between intramode coupling and the relaxation rate. It appears that the model represents proper thermal behavior in the weak coupling case, but the modes become populated inequally in the high coupling regime.

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Rectangular collocation as a promising approach for accurate computational vibrational spectroscopy of molecules on surfaces

29 Sept
17:00

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The rectangular collocation approach allows solving the Schrödinger equation, electronic or nuclear, without converging integrals. The rectangular nature of the matrix equation facilitates basis optimization and, when applying the KEO numerically [1], it is easy to use any basis functions, even non-integrable [2]. As a result, the method can handle problems which pose difficulties with the variational approach such as calculation of vibrational spectra at interfaces, where potential energy surfaces (PES) are usually unavailable and ab initio calculations are costly [3]. The absence of the requirement to converge integral allows reducing the volume of space sampled by the collocation points and to use relatively small point sets which could be computed ab initio, obviating the need for a PES. At the same time, numeric application of the exact KEO much simplifies calculations without introducing approximations. All these properties make rectangular collocation particularly attractive for molecules on surfaces. As the method solves the Schrödinger equation directly, it does not require potential representations over orders of coupling like VSCF and does not break down at resonances like PT. I will review results of previous applications of rectangular collocation to molecules on surfaces and present recent advances in the method which have the potential to significantly contribute to computational spectroscopy at surfaces, such as sampling only selected parts of the configuration space [4] or machine learning optimization of the collocation point set [5].

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30 Sept
11:40

Diffusion without friction

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In essence, diffusion is the result of many body interactions. Nevertheless, the delocalized nature of the quantum mechanical state of a single particle inherently reflects the diffusive character of its motion. Fuerth [1] related this character to the uncertainty principle. The thermal probability density of a single adsorbate, for instance, is extremely delocalized on the adsorption substrate. Under these circumstances it seems worth to investigate how the temporal evolution of the mean square deviation of an independent particle's position looks like, when its dynamics is described entirely by quantum mechanics, say, from the solution of the Liouville-von-Neumann equation for a thermal state. In this contribution, the mean square deviation $\langle (x(t) - x(0))^2 \rangle$ of the position x of an independent particle of mass m in thermal equilibrium is evaluated quantum mechanically in the presence of a periodic potential. When the potential is constant, the problem is solved analytically. The result is an initial ballistic motion of the particle which then goes over to Brownian diffusion with the diffusion coefficient $\hbar/2m$ after some time. The problem is also treated numerically by solution of the time dependent Schrödinger equation for an initial thermal wave packet. As an application, the diffusion of a CO molecule along the $\langle 100 \rangle$ direction of a Cu(100) substrate is calculated in the independent particle formalism. It is shown that the method captures essential features of experimental observables. The diffusion coefficient agrees semi-quantitatively with the result obtained from helium-3 spin-echo experiments [2] despite the neglect of friction, showing that the quantum nature of the particle's motion might itself and to a large extent account for the observed phenomenon.

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Nonadiabatic machine learning molecular dynamics

29 Sept
14:30

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The development and application of machine learning potentials for excited states [1-3] will be presented, aiming at fast and accurate nonadiabatic molecular dynamics simulations. The dynamics is simulated with our surface hopping approach SHARC (surface hopping including arbitrary couplings), which is able to treat not only kinetic dynamical couplings but also any other arbitrary coupling on an equal footing [4]. Consequently, machine learning is employed not only for potentials and forces but also for nonadiabatic couplings, spin-orbit couplings [5-7] and dipole moments [8]. These developments open up the possibility to simulate time scales in the nanosecond regime compared to a few picoseconds in conventional approaches [5].

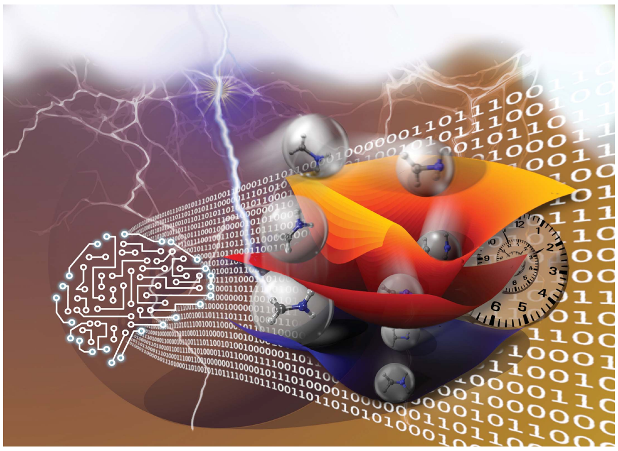

Figure 1: Machine learning enables long time scale molecular photodynamics simulations

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28 Sept
9:50

Quantifying the limits of ab initio electronic friction theory to predict dynamics at metal surfaces

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Nonadiabatic effects that arise from the concerted motion of electrons and atoms at comparable energy and time scales are omnipresent in thermal and light-driven chemistry at metal surfaces. Excited (hot) electrons can measurably affect molecule-metal reactions by contributing to state-dependent reaction probabilities. Vibrational state-to-state scattering of NO on Au(111) has been one of the most studied examples in this regard, providing a testing ground for developing various nonadiabatic theories. [1] This system is often cited as the prime example for the failure of electronic friction theory. However, the exact failings compared to experiment and their origin from theory are not established for any system, because dynamic properties are affected by many compounding simulation errors of which the quality of nonadiabatic treatment is just one. I present our recent efforts to combine a tensorial representation of electronic friction based on Kohn-Sham Density Functional Theory [2] with high-dimensional machine-learning-based representations of energy and friction landscapes to perform molecular dynamics with electronic friction (MDEF) simulations. [3] This allows us to perform a comprehensive quantitative analysis of the performance of nonadiabatic molecular dynamics in describing vibrational state-to-state scattering of NO on Au(111) and compare directly to adiabatic results. [4] We find that electronic friction theory accurately predicts elastic and single-quantum energy loss, but underestimates multi-quantum energy loss and overestimates molecular trapping at high vibrational excitation. We provide a detailed analysis of the origin of these failings and conclude with an outlook on future method improvements.

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Hydrogen adsorption and dissociation on small copper clusters: importance of fluxionality?

28 Sept
14:30

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The adsorption of molecular hydrogen onto metal surfaces is an important benchmark for understanding catalytic processes. Its application lies for instance in hydrogenation and methanation processes that are part of sustainable production of fuels from CO2 and H2. Whereas the adsorption of hydrogen molecules on single-crystal surfaces is well-studied, the active site of a catalyst is typically far from such an idealized surface. To obtain a fundamental understanding of the interaction between H2 and more complex surfaces, we use copper clusters as a model for real catalysts. In these systems, energy dissipation is intrinsically connected to the 'hot' topic of cluster fluxionality [1], the fact that cluster isomers may interconvert from one to another under the influence of temperature and because of exothermic reactions of adsorbates.

Here, we present a combined experimental and theoretical investigation of the adsorption of H2 on small cationic copper clusters in the gas phase. Measured IR spectra of clusters with a controlled number of H2 molecules adsorbed are interpreted with the help of a systematic global search [2] for preferential isomers and adsorption configurations at the DFT level [3]. We find a mixture of both dissociative and molecular binding, dependent on the cluster size and shape [4]. Structural fingerprints originally developed in the context global optimization [5] allow us to overcome the otherwise factorial time complexity to "measure" the similarity to different isomers during ab initio molecular dynamics trajectories. I will discuss the resulting isomer populations and their implications for the aforementioned cluster fluxionality.

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30 Sept
8:30

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. 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. If we have time, in the fourth and last example, we analize a quite unknown pure quantum effect, the so-called quantum backflow.

Dynamics of adsorbates on metal surfaces under equilibrium and non-equilibrium conditions

30 Sept
11:00

Dino Novko[1], Jean Christophe Tremblay[2], Ivor Lončarić[3], Maite Alducin[4,5], J. Iñaki Juaristi[4,5,6]

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Understanding the fundamental processes that bring about the specific time scales of surface reactions is a long-standing aim in surface science. The resonant infrared absorption and ultrafast time-resolved vibrational spectroscopies constitute an invaluable tool for exploring the equilibrium and non-equilibrium surface dynamics, respectively. Here we bring forth consistent nonadiabatic ab initio theories that clarify the microscopic intricacies behind thermal and nonthermal vibrational relaxations of CO on metal surfaces, bringing us a step closer to the above-mentioned goal. First, the result for the vibrational lifetime of the CO internal stretch (IS) mode on Cu(100) in equilibrium condition will be shown. Recent first-principles studies showed how the standard Fermi's golden rule formula for nonadiabatic coupling is unable to explain the experimental lifetimes of the CO IS. Here we present the theory of electron-mediated vibrational intermode coupling that is able to resolve this issue [1]. Namely, the results demonstrate a strong electron-mediated coupling between the internal stretch and low-energy CO modes, but also a significant role of surface motion. Further, we introduce the first robust theoretical framework [2] that successfully explains the observed nonthermal frequency and linewidth changes of the CO IS mode on Cu(100) induced by subpicosecond laser pulses [3]. Our results show how the nonadiabatic coupling underlies the nonthermal frequency shifts, while electron-mediated vibrational mode coupling gives rise to linewidth changes. In fact, under highly nonequilibrium condition hot electrons promote an intramode coupling between coherent and incoherent internal stretch modes, while after the first picosecond coupling with low-energy modes prevail. Furthermore, surface modes are also decisive and stay active until equilibration. At the end, we show our results for the vibrational relaxation of physisorbed CO on Au(111)[4]. It is shown that the nonadiabatic theory reproduces the long CO lifetime measured in Au(111) [5] provided the molecule–surface interaction is properly described.

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29 Sept
15:10

On Application of Deep Learning to Simplified Trajectory Surface Hopping

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Deep Learning is applied to simulate non-adiabatic molecular dynamics of phenanthrene based on Time-Dependent Density Functional based Tight Binding (TD-DFTB) [1] approach for excited states combined with mixed quantum-classical propagation. Starting from the Tully's fewest-switches trajectory surface hopping [2] algorithm coupled to TD-DFTB, we examine the simplified surface hopping scheme based on the Landau-Zener approximation and Deep Learning potentials for excited states. We first assess the accuracy of the TD-DFTB approach upon comparison with experimental and higher-level theoretical data. Using the recently developed SchNet [3,4] architecture for Deep Learning applications, we train several models and evaluate their performance with respect to TD-DFTB. The main focus is given to the analysis of the electronic population of low-lying excited states computed with the aforementioned methods. We determine the relaxation timescales and compare them with experimental data. Our results show that the simplified approach considered in this study may yield a relatively accurate description of the electronic relaxation in phenanthrene as compared with the reference data. Furthermore, the SchNet performance allows high-throughput analysis at a negligible cost. We finally highlight potential numerical artefacts arising with the use of single precision SchNet models in simplified trajectory surface hopping simulations. [5]

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Nuclear quantum effects in intramolecular hydrogen dynamics

28 Sept
15:10

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The inclusion of nuclear zero-point-energy and tunneling effects in high-dimensional anharmonic systems represents a considerable challenge in atomistic simulations. I will discuss methodology based on the path integral formalism, that can give access to reaction rates and vibrational spectra, including nuclear quantum effects and that is fully applicable to systems where a high number of anharmonic degrees of freedom are relevant. As a paradigmatic example, I will show results for the intramolecular hydrogen transfer dynamics of the porphycene molecule. I will discuss how we unraveled the contribution of different tunneling paths to the reaction rates at lower temperatures [1], explained an unusual temperature dependence of its vibrational spectrum [2] and discovered that surface fluctuations can enhance the intramolecular hydrogen tunneling rate by orders of magnitude when these molecules are adsorbed on metallic surfaces [3]. I will finish with considerations about the impact of electronic friction on hydrogen tunnelling reactions in metallic environments, providing physical insight on the effects of this non-adiabatic process in tunnelling events.

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28 Sept
9:10

Photochemistry and spectroscopy of molecules at surfaces: Insights from ab initio molecular dynamics

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The interaction of adsorbates on solid surfaces with light is central to surface spectroscopy, surface photochemistry, and non-adiabatic surface science in general. In the present contribution, light-driven molecular adsorbates will be modelled by ab initio (in one example, semiempirical) molecular dynamics. Three examples will be highlighted:

First, we consider femtosecond laser (FL) pulse driven chemistry at metals, e.g., FL-induced, hot-electron mediated desorption or diffusion. We describe these processes by (Langevin) Ab Initio Molecular Dynamics with Electronic Friction (AIMDEF) based on Density Functional Theory (DFT), and random forces obtained from a two-temperature model. Our focus is on associative desorption of H2 and isotopomers from Ru(0001) and its "dynamical promotion" [1], as well as on desorption, diffusion and the time-resolved vibrational response of CO on Ru(0001) and Cu(100) [2], respectively.

A second example illustrates how vibrational (IR and Sum Frequency Generation (SFG)) spectra of water-covered aluminum oxide surfaces can be determined with the help of auto- and cross-correlation functions computed from DFT-based AIMD [3].

Third, the step towards explicitly non-adiabatic surface dynamics is taken in the form of semiclassical, AM1/CI-based "surface hopping". Specifically, we consider cis-trans isomerizations in densely packed, ordered azobenzene layers, and how they are influenced by excitonic and steric effects [4].

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Photo-induced desorption dynamics of CO from Pd(111) simulated with a complex neural Network potential

30 Sept
14:30

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The correct description of photo-induced dynamics and reactivity of adsorbates on metals presents a challenging scenario for current state of the art theoretical methods. This kind of systems not only require the inclusion of laser-excited electrons effects, but they require in many cases the incorporation of complex adsorbate-excited surface lattice effects, and even out of phase adsorbate-adsorbate interactions [1,2].

Very recently, the desorption of CO from Pd(111) surfaces induced by short femtosecond laser pulses has been successfully modeled with the use of ab initio molecular dynamics with electronic friction and two temperature model thermostats in what is known as the (T_e,T_l)-AIMDEF method [2]. However, the exhaustive statistical analysis needed for the disentanglement of the role of the aforementioned complex interactions during dynamics is hindered by the high computational cost of this methodology. Taking advantage of the available (T_e,T_l)-AIMDEF dynamics information, we have developed a high-dimensional embedded atom neural network (EANN) [3] potential energy surface that is able to reproduce the available DFT data for an extensive range of surface temperatures (90 to 1000 K) and varying CO coverages caused by numerous desorption events.

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28 Sept
8:30

Non adiabatic molecular dynamics and friction dynamics in the framework of Density Functional based Tight Binding theory

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The Density Functional based Tight Binding theory (DFTB) [1-4] is an approximation of DFT. Obviously, DFTB has the same drawbacks as DFT, plus the effects of its own inherent approximations that need to be probed. However, DFTB is 100 to 1000 times faster than DFT, which makes it a computationally-efficient tool in large scale molecular or materials science simulations, enabling the investigation of larger systems, at longer simulation times, with better trajectory sampling, or the use of larger cells in calculations for periodic systems. Since it remains a quantum theory for electrons, it keeps the ability to describe electronic structure changes and excitations. Developments and applications of the coupled electron-nuclei dynamics using the Time-Dependent DFTB (TD-DFTB) framework and Tully's Trajectory Surface Hopping algorithm will be exemplified. In particular, molecular dynamics simulations focusing on the non-adiabatic relaxation of highly-excited electronic states of polyacene systems, emphasizing the influence of system size and morphology [5,6], will be presented. Also, developments of DFTB to incorporate the effect of electron-hole pair excitations in atom/molecule-metallic surface dynamics via a friction tensor [7] determined on-the-fly will be reported. Preliminary applications to the collision of H with a silver surface using this alternative DFTB strategy will be shown.

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