

Simulating chemical processes from scratch: classical and quantum molecular dynamics

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Abstract

La chimica è una scienza quantitativa nella quale i processi cinetici giocano un ruolo fondamentale: non solo essi determinano la scala dei tempi delle trasformazioni molecolari, ma anche i prodotti preferenziali di complicati sistemi di reazione, come quelli presenti negli ambienti biologici, all'interfaccia gas-solido di un sistema catalitico, nell'atmosfera terrestre e nel mezzo interstellare. Nonostante questo, lo studio quantitativo della cinetica di reazioni chimiche è un campo di ricerca relativamente giovane. Questo è dovuto sia alle intrinseche difficoltà nell'ottenere funzioni di energia potenziale sufficientemente accurate per studi di dinamica, sia alle difficoltà nel seguire i processi dinamici in sé. In questo contributo riassumiamo il nostro recente lavoro in questo campo entusiasmante. Cominciamo mostrando come i metodi accurati della chimica quantistica possano essere utilizzati per mappare i potenziali d'interazione che governano la dinamica di sistemi piccoli, ma ciononostante complessi, dove la comune approssimazione di Born-Oppenheimer cessa di valere. Successivamente, mostriamo come la dinamica molecolare classica possa essere applicata per predire il comportamento di atomi e/o molecole che urtano su una superficie, una questione di primaria importanza nella catalisi eterogenea. La dinamica molecolare quantistica diventa d'obbligo quando sono coinvolti sistemi intrinsecamente quantistici, e quindi evidenziamo come le tecniche odierne permettano di risolvere esattamente l'equazione di Schrödinger dipendente dal tempo per sistemi molecolari semplici. Infine, mostriamo i nostri recentissimi risultati nella descrizione dell'interazione e dissipazione di energia in sistemi quantistici semplici, accoppiati ad un bagno termico. Questi rappresentano le prime simulazioni di dinamica quantistica in tempo reale di sistemi decisamente estesi.

Chemistry is a quantitative science in which rate processes play a major role. Not only they determine the time-scale for molecular transformations, they also

determine the preferential outcome of complex reaction networks, such as those occurring in biological environments, at the solid-gas interface of a catalytic system, in the earth atmosphere and in the interstellar medium. Despite this, the quantitative study of the rate of chemical reactions is largely a young field of research. This is due to both inherent difficulties in obtaining accurate potential energy functions for dynamical simulations and in following the dynamical processes themselves. In this work we summarize the efforts we have made in recent years in this exciting field. We start showing how accurate quantum-chemistry methods can be used to map the interaction potentials governing the dynamics in small, yet complex systems where the common Born-Oppenheimer approximation ceases to be valid. Then, we show how classical molecular dynamics may be applied in predicting the behaviour of atoms/molecules impinging on a surface, an issue of paramount importance in catalysis. Quantum molecular dynamics is mandatory when inherently quantum systems are involved, and we show how present-day techniques allow to solve exactly the time-dependent Schrödinger equation in simple molecular systems. We finally show our very recent results in describing interaction and energy dissipation of simple quantum systems coupled to a heat reservoir. These represent the first real-time quantum dynamical simulations in very large systems.

Keywords Quantum chemistry; Molecular Dynamics; Quantum dynamics; Time-Dependent Wave Packet Dynamics; Interstellar Chemistry; System-Bath Quantum Dynamics

Chemistry in space: exotic reactions and the CH⁺ mystery

The interstellar space is a rather complex environment with a rich, largely unexplored chemistry [1]. Very low-density clouds of gaseous molecular species (comprising hydrogen, helium and traces of heavier elements) and not-well characterized solid particles evolve because of gravitational attraction, stellar radiation fields, cosmic ray bombardment, and supernovae explosions. Collapsing clouds form protostellar globules, which in turn may lead to star formation. Star death releases heavy elements and dust grains, which undergo complex chemical transformations. High energy ionization of very stable atoms (e.g. He) induces cascades of complex ionic reactions, which in turn lead to polyatomic molecules. Photostimulated processes are very active in dissociating molecular systems and in triggering chemical transformations through unusual paths.

Experimental informations on interstellar chemistry may only come from rather crude observations of the sky above earth. Laboratory chemistry is not currently able to reproduce the very low density (from 1 to 10⁶ atoms per cubic centimeter), yet complex environment of the interstellar medium. Therefore, simulations of individual chemical processes thought to occur in such macrosystems has become a valuable tool for understanding cloud evolution. Chemistry plays a key role in determining the physical properties of these clouds and their macroscopic dynamics. Heat capacity is largely controlled by the fraction of atomic species which has become molecular. Even the very first step in star formation requires that part of the

gas becomes molecular and radiates energy, otherwise a gravitationally collapsing cloud reaches a stationary situation in which thermal pressure counterbalances gravity. Chemistry itself benefits of this complex environment, and large hydrocarbon molecules and aminoacids are formed. These might represent the first steps toward life evolution.

In this environment, carbon networks are of fundamental importance for chemical evolution [2]. Simple carbon bearing species react with the abundant molecular hydrogen, and recombine to form large molecules *via* radiative association processes [3], i.e. direct molecular adduct formation through radiative stabilization $A+B \rightarrow AB + \gamma$ (where γ is a photon). This is an exotic process which, on earth, can only be studied in complicated, expensive apparatuses, such as ion accelerating rings [4]. The reason is that at typical earth densities three-body recombination (i.e. third-body collisional stabilization of AB) is much more efficient than radiative recombination.

At the very first step of this carbon chain, the observed abundance and ubiquity of the simple CH^+ species cannot be explained by standard chemical routes [2], and a complex mechanism has been hypothesized long ago [5] but yet not confirmed by quantum chemical calculations. This mechanism involves formation of the stable CH_2^+ molecular ion which subsequently may undergo photodissociation to form CH^+ . CH_2^+ formation is thought to occur via recombination of C^+ and H_2 , a process that actually requires (i) a non-adiabatic transition through a conical intersection, (ii) a non-adiabatic transition through a Renner-Teller intersection and (iii) a radiative transition. This makes the radiative association reaction that forms CH_2^+ an enormously difficult problem, which still waits for solution. Accurate exploration of the low-lying adiabatic energy landscapes is a prerequisite for a multistate quantum dynamical calculation of the emission probability during the collision of reaction partners.

We have used a standard quantum chemical code available at CILEA, the open-source GAMESS-US code [6], to perform highly accurate electronic structure calculations of the three lowest states of the triatomic systems for more than one thousands of geometrical arrangements of the three nuclei. These calculations are of the so-called Multi Reference Configuration Interaction (MRCI) type, and are based on a large Multi Configuration Self-Consistent Field (MCSCF) reference space and a very large atomic basis set. In this approach, for a fixed nuclear geometry the eigenvalue problem which determines the electronic energy levels (the electronic Schrödinger equation) becomes a standard (though computationally expensive) matrix eigenvalue problem which is iteratively solved for the lowest energy solutions. Large Hamiltonian matrices (with more than $10^6 * 10^6$ elements) were required to obtain a global accuracy within chemical needs ($<1 \text{ kcal}\cdot\text{mol}^{-1}$). Calculations made extensive use of the parallel implementation of the code, which was needed both to make the required computational time reasonable and to allow storage of the above Hamiltonian matrices ($>100 \text{ Gb}$).

Figs 1,2 summarize the results so far obtained, in the most important “ C_{2v} ” configuration, that is when the carbon atom approaches the midpoint of the H-H bond, perpendicularly to it. They represent the energy of three lowest electronic

states as a function of the distance of the carbon atom from the H_2 molecule and of the interatomic H-H distance. At short distances, molecular formation is signalled by deep wells, which occur both in the 2A_1 state (the ground-state) and in the 2B_1 state. These two states become degenerate when the molecule has a linear configuration, since they represent the two components of a Π state. This is a well-known case where the famous Born-Oppheimer approximation fails, and it is called a Renner-Teller interaction, after Renner and Teller who first described this situation. Other “critical” points in the energy landscape occur at non-linear geometries, where the 2A_1 and 2B_2 surfaces cross each other. This critical region (a line for a triatomic system) is called the seam of a conical intersection (CI), a “diabolical” object in nuclear configuration space [7] where exotic processes may take place: conical intersections act as funnels in non-radiative decay of photo-excited molecular species, may resonantly enhance specific reactive pathways, and lead to quantum interference between reaction paths with common endpoints [8]. It is now accepted that conical intersections in molecular systems are much more common than previously thought and that they actively take part in important biological processes, e.g. the process of vision. In this simple system, the conical intersection controls the overall recombination process: when a carbon atom impinges on a hydrogen molecule, it can only access the barrierless 2B_2 state; then, a transition through the CI is needed to bring the system in the 2A_1 state, and a second transition through the Renner-Teller interaction to the 2B_1 state, where finally radiative decay may occur back to the 2A_1 state.

Computed properties (geometries, energy barriers, and binding energies) are in very good agreement with the few available experimental data on this system, and suggest that the above mechanism is indeed possible [9]. This is a good starting point for the more challenging quantum dynamical problem, which is currently under investigation.

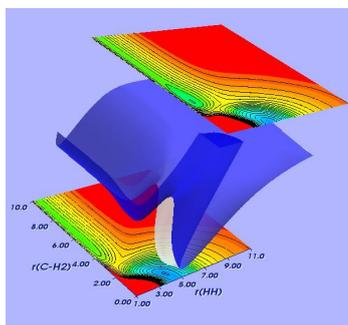


Fig.1 The $^2A_1/{}^2B_1$ Renner-Teller intersection in the CH_2^+ system, shown in the C_{2v} configuration. White color for the 2A_1 and blue for the 2B_1 Potential Energy Surface (PES), respectively.

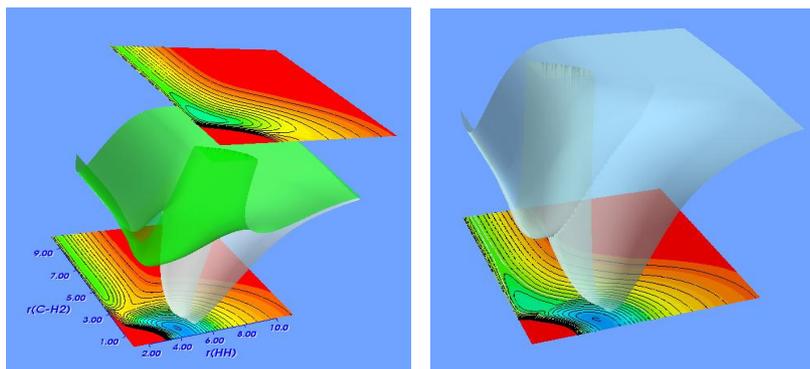


Fig.2 The ${}^2A_1/{}^2B_2$ conical intersection in the CH_2^+ system. On the left the 2A_1 (white) and the 2B_2 (green) Potential Energy Surfaces in C_{2v} configuration. On the right the lowest lying PES.

Dynamics at surfaces: interaction of hydrogen atoms on metal surfaces and the new economy

Surfaces of condensed phases exhibit unusual chemical and physical properties, thanks to the fact that surface atoms are undercoordinated compared to atoms in the bulk. This very unique environment makes surfaces so special and so important in a wide variety of fields, with deep impact both on economy and on fundamental science. Surface science is a young, very active area of research, with contributions both from the physical and chemical communities.

Theoretical surface science [10] occupies a special position in this field. Because of its attitude in explaining surface processes at the atomic scale resolution, it is of valuable help in rationalizing experimental data, and with the ever increasing availability and reliability of predicting theories, models, software tools and computational power, its importance is being recognized even by the more skeptical.

Atomic and molecular hydrogen interacting with metal surfaces has long been used as prototypical model for heterogeneous catalysis. The way in which the bond of an H_2 molecule dissociates on a metal surface is a paradigm for dissociative chemisorption, the first step in any catalytic process. Interest in hydrogen-metal systems themselves is enormously grown in recent years, because of its fundamental importance in a hydrogen-based new economy. This has led to a wealth of *first-principle* (of the Density Functional Theory (DFT) kind) electronic structure studies of metal-hydrogen interactions, comprising full potential energy function evaluations for H_2 on both smooth and stepped surfaces, analysis of surface reconstructions/relaxation following adsorption, analysis of hydrogen absorption properties of metal substrates, and studies of absorption induced modification of bulk physical properties.

In general, in this kind of studies one focuses on the electronic properties of a “slab” containing a number of metal atom layers and the interesting adsorbate species, and periodic boundary conditions are applied to simulate the bulk material. Depending on the system, hundreds of atoms (several thousands of electrons) may

be required, and for long time this made the problem of determining from first-principles the interaction forces within these systems an hopeless task. It was only relatively recent, that the advent of DFT-based methods made possible reasonably accurate studies of the energetics in these systems. In turn, dynamical studies of molecular dissociation/formation could be performed on accurate potential energy surfaces and directly compared to detailed experimental data such as molecular beam studies [11].

In this field, we have focused on the hydrogen-on-nickel system, and have used a DFT-like, many-body potential energy function to study a number of issues concerning both molecular hydrogen formation and dissociation, with a fully mobile surface, at a quasi-classical level. In particular, we have focused on the so-called hot-atom formation, i.e. on the formation of highly mobile species which undergo hyperthermal diffusion. This unique kind of diffusion is ubiquitous in hydrogen-metal systems: hydrogen atoms bind to metal surfaces with strong (2.6-2.8 eV), non-directional bonds, and therefore they may travel across the surface with an energy well in excess to the diffusion barrier. This is the case when *atomic* hydrogen adsorbs on surfaces, but it is also the case when molecular hydrogen dissociatively chemisorbs on metals at room temperature, since the reaction exothermicity is still much larger than thermal energy.

We have performed quasi-classical calculations to model collisional and diffusion dynamics in hydrogen-nickel systems with our own parallel, gas-surface code TRAJ. In our code, the substrate is modelled by a number of layers of metal atoms, subjected to periodic boundary conditions, and classical Hamilton's equations are solved for a huge number of initial conditions. The latter are chosen to sample, in a Monte-Carlo sense, the relevant classical equilibrium distribution functions, and to mimic the quantum nature of hydrogen atoms according to the known quasi-classical prescription. The adopted interaction potential is an accurate Embedded-Diatomics-In-Molecules model [12, 13], which includes true many-body effects through the (approximate) calculation of atomic densities. Our implementation of this model potential makes use of modern techniques of molecular dynamics simulations, which greatly allow to reduce the computational effort when thousands of atoms are involved. It can also be easily extended to include approximately a variable number of hydrogen atoms, and therefore to study surface coverage effects. Energy dissipation to the bulk is modelled by adding dissipative and fluctuating forces at the bottom atoms of the slab, according to a Langevin prescription.

We first considered hot-atom formation when an atomic hydrogen beam impinges on a H covered Ni(100) surface, and compared hot-atom dynamics with Eley-Rideal dynamics [14], i.e. direct molecular hydrogen formation. Though we limited the study to the single-adsorbate case our results clearly illustrated the importance of hot-atoms in hydrogen recombination reaction on metal surfaces, in agreement with previous theoretical and experimental studies. It further compared in details all the possible dynamical routes and gave insights into hot-atoms properties, and the effect of corrugation and temperature on them. Then, we studied dissociative chemisorption of hydrogen molecules on the same surface, and the subsequent hot-

atom dynamics of the product atoms [15]. Representative results are reported in Figs 3, 4.

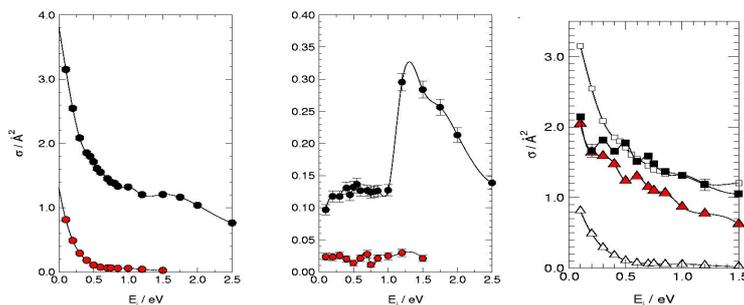


Fig.3 H-atom scattering on H adsorbed on Ni(100). Left: stable hot-atom formation cross-section for impact in the occupied (black) and nearest neighbor cell (red), in the rigid-surface model. Center: Eley-Rideal reaction cross-sections (colours as in the left panel). Right: long-lived Hot-atom formation cross sections in the realistic mobile surface model at $T=120$ K (colours as in the left panel). Eley-Rideal cross-sections are very similar to the rigid-surface results [14].

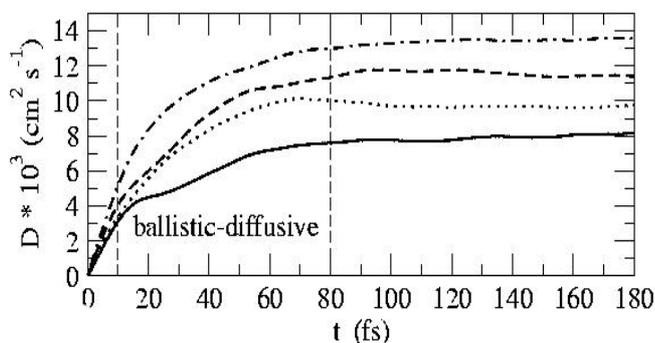


Fig.4 The averaged squared displacement per unit time, $D = \langle |x(t) - x(0)|^2 \rangle / 4t$ of hydrogen atoms following dissociative chemisorption of H_2 molecules on Ni(100), for several values of the collision energy (solid, dotted, dashed and dashed-dotted lines for 0.1, 0.2, 0.3 and 0.5 eV, respectively). Vertical lines approximately

mark the different regimes of hot-atom motion: leftmost region is for ballistic motion and rightmost region for diffusive motion [15].

Dynamics at surfaces: how does molecular hydrogen form in the Universe?

In recent years there has been an ever growing interest in the dynamics of hydrogen atoms on graphite surfaces. Apart from its importance in fusion reactors [16, 17], and for the study of hydrogen storage in graphite nanostructures [16, 18, 19], much of the current research has been motivated by the formation of hydrogen molecules in the interstellar medium (ISM). It was hypothesized long ago that the molecular hydrogen abundance even in the most diffuse clouds (with 10^2 atoms per cm^3) may only be explained by a recombination process on the surface of interstellar dust particles [20-22]. It is now generally accepted that cosmic dust is composed of very small particles of different sizes and nature [23-25]: in diffuse clouds, the largest particles (0.1 μm in size) are composed of a silicate core covered by an “organic refractory” mantle, whereas smaller particles are carbonaceous (0.03 μm) and even smaller particles are simply large Polycyclic Aromatic Hydrocarbons; in cold molecular clouds H_2O and CO_2 ice mantles are formed on the silicate core-organic refractory particles, and incorporate also the previously mentioned carbonaceous particles. Thus, at least in diffuse clouds, molecular hydrogen may be formed on carbon surfaces of dust particles, being either the refractory mantle or the smaller carbonaceous particles or PAH molecules. This has stimulated much of the recent experimental and theoretical investigations on hydrogen interaction with graphite (0001).

In the ideal, defect-free graphite surface, hydrogen atoms may adsorb on the surface either chemically or physically. First-principles electronic structure calculations [26-28] agree on the fact that hydrogen chemisorption occurs on top of a carbon atom and requires substantial lattice reconstruction, with the carbon beneath the H atom puckering out of the graphite plane by about 0.4 Å. The carbon atom needs to rehybridize its valence orbitals, causing partial loss of the aromatic character of the graphite plane, and a barrier to chemisorption of about 0.2 eV appears. This barrier indicates that sticking of H atoms in the chemisorption well hardly occurs -*via* direct dynamics- at the conditions typical of diffuse clouds ($T \leq 100$ K), although it may occur for example in the so-called photo-dissociation regions [29]. On the other hand, physisorption of hydrogen atoms may occur at very low energy and leads to formation of weakly bound species far apart from the surface (at about 4 Å). In this case, DFT calculations are not accurate enough to describe the interaction and the physisorption binding energy has been estimated to be ≈ 40 meV from selective adsorption experiments [30]. Only recently, a correlated quantum chemistry calculation (of the so-called Møller-Plesset Perturbation Theory kind) on the H-Coronene model system has nicely confirmed the measured

physisorption binding energy, and has given a quantitative estimate of the diffusion barrier [31].

Once hydrogen adsorption has occurred, two different mechanisms for forming molecular hydrogen are possible. In the first, so-called Langmuir-Hinshelwood (LH) mechanism, molecular formation occurs when two adsorbed collide during their diffusive journey on the surface. Since diffusion is activated, this process requires the thermal energy to be comparable with the height of the diffusion barrier, which in turn depends on the nature of bonding between hydrogen atoms and the surface. In the second mechanism, the so-called Eley-Rideal (ER) one, an atom from the gas-phase directly impinges on a previously adsorbed species and forms the reaction product. This is one of the possible Collision Induced processes which occur in gas-surface collisions.

Hydrogen atoms are light atoms, for which usually a quantum description is necessary. This is particularly the case for hydrogen-graphite systems where, in contrast to hydrogen-on-metal ones, there is no accelerating potential in front of surface which allows the atom to enter the classical regime. Also, since formation of hydrogen molecules in interstellar space occurs in cold clouds ($T = 1-100$ K), the main interest here is in the *cold* collision energy regime, where any system needs a quantum description. This makes the problem a quite challenging computational task, since the exponential scaling of current quantum dynamical methods prevents a complete description of the adsorbate-surface dynamics. Fortunately, in studying hydrogen formation reasonable approximations can be introduced that reduce the problem to a tractable one.

We have used the rigid-flat surface approximation [31] to quantumly study the Eley-Rideal reaction, and a number of possible other Collision Induced processes, between a gas-phase hydrogen atom and an H atom adsorbed on graphite. The rigid approximation allows to reduce the dynamical problem to a small dimensional one; it prevents energy exchange with the surface, but this is reasonable since the impinging atom is light, the substrate is stiff, and the dynamics is direct (i.e. fast). The flat approximation further reduces the dimensionality of the problem, since it allows to factor out three more degrees of freedom, the molecular translations on the surface plane and the molecular rotations around an axis perpendicular to it. This is reasonable too, since the dynamics is governed by the “entrance channel” potential, and this, in turn, is mainly determined by the H-H interaction. It is worth noting at this point, that six-dimensional quantum calculations on gas-surface systems are nowadays possible, but only when studying dissociative chemisorption events; the difficulties in studying CI processes arise from the need to sample wide regions of space and, at the same time, to correctly describe the high reaction exothermicity.

We studied the scattering problem by solving the Time-Dependent Schrödinger Equation (TDSE) for the H-H/graphite system. This approach has been becoming very popular in recent years, when compared to traditional, Time-Independent (TI) approaches, thanks to a number of recent advances in this field. It is also much more appealing than the historical, TI one, since it allows to study time-dependent phenomena, not-energy-conserving processes (e.g. dissipation), and also to directly map reaction dynamics, as seen for example in pump-probe experiments in the

femtosecond domain (the so-called femtochemistry)[33]. Briefly, in this approach one represents the wavefunction (and the corresponding quantum mechanical system operators) on a grid of points or on an appropriate (equivalent) basis-set, and solves numerically the first-order TDS equation. Explicitly unitary, energy conserving algorithms which prevent explosions or implosion of the wavefunction have been developed, and absorbing potentials at the grid edges have been introduced and optimized in order to prevent unphysical reflections from the grid boundaries.

We used a full grid representation of the wavefunction, in conjunction with a split-operator propagation algorithm, and the recently introduced Transmission-Free absorbing potentials. In this scheme application of the Hamiltonian operator on the wavefunction requires fast-Fourier transforms along two cartesian coordinates and a (unfortunately not-fast) Discrete Bessel transform along the radial coordinate. Our own code, HAWP, extends the previously developed ERWP code of Jackson and Lemoine [34,35], in that it allows energy-resolved calculation of *all* possible collision induced cross-sections [36]; it further codes our recently developed Two-Wavepacket approach which allows time-dependent calculations in the cold collision energy regime [37].

We studied on a wide energy range all the possible collision induced processes resulting from the scattering of a gas phase H atom off an adsorbed H atom [36,38,39]. The accurate, first-principles Potential Energy Surface of Sha and Jackson [35] was adopted, and several initial states of the adsorbed H atom were sampled, both for the physisorbed and the chemisorbed case. A number of interesting results are worth mentioning (Fig.s 5,6): we quantally studied for the first time the collision induced desorption of atoms from a surface, showing quantum features in the corresponding cross-sections; we showed the existence of quantum effects at high collision energies in a barrierless reaction dynamics (the Eley-Rideal one), which we interpreted as manifestation of “product quantization”; we confirmed formation of vibrationally hot product molecules; we showed how efficient is the adsorbate-induced trapping of H atoms when impinging on a physisorbed species, thereby suggesting a possible role of Hot-Atom dynamics in hydrogen formation. More recently [40], we have studied these processes for the first time in the cold collision energy regime, and we have shown that Eley-Rideal formation in this regime may only occur out of a physisorbed hydrogen atom (Fig.7). This is an important result since it sets constraints on the possible routes to hydrogen formation in the interstellar medium.

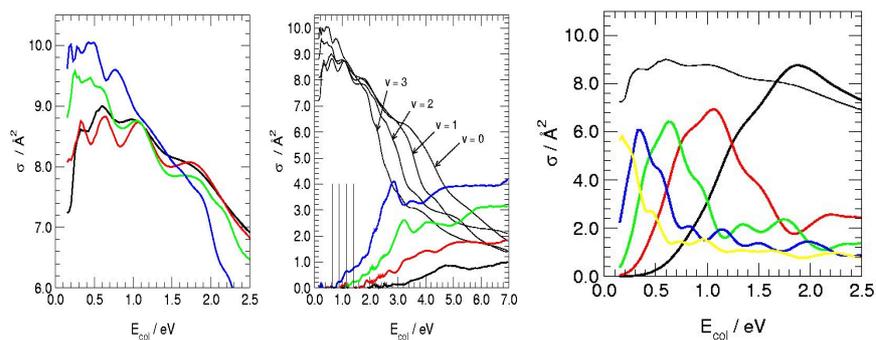


Fig.5 Quantum cross-sections for H scattering on H atoms adsorbed on graphite. Left: Eley-Rideal reaction cross-sections for several value of the target vibrational quantum number (black, red, green, blue for $v=0-3$, respectively). Center: Collision Induced Desorption cross-sections, compared with ER ones (dashed lines). Colours as in the left panel. Right: the total, $v=0$ ER cross-section is compared with vibrationally resolved cross-sections (multiplied by a factor of 2). Black, red, green, blue, yellow for $\text{H}_2(v')$ ($v'=0-4$), respectively [38].

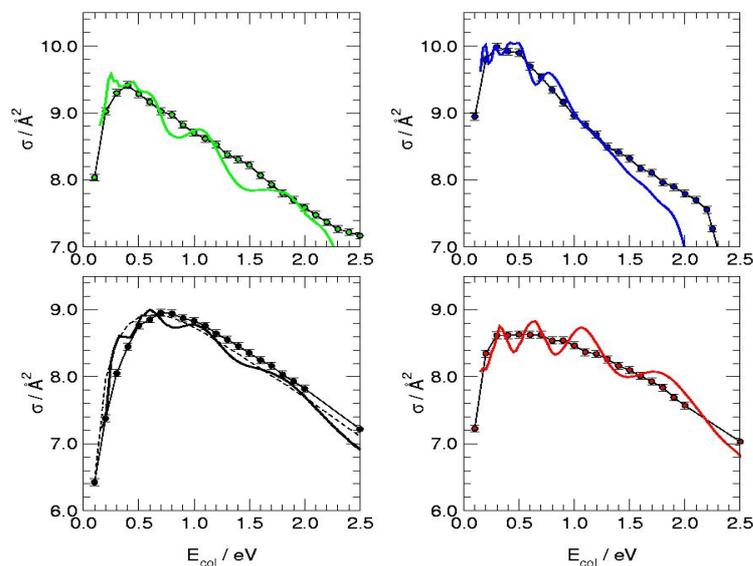


Fig.6 Quantum (full lines) and QCT (points connected by lines) Eley-Rideal cross-sections, showing the existence of quantum undulations. Colours as in Fig.5, left panel [36,38].

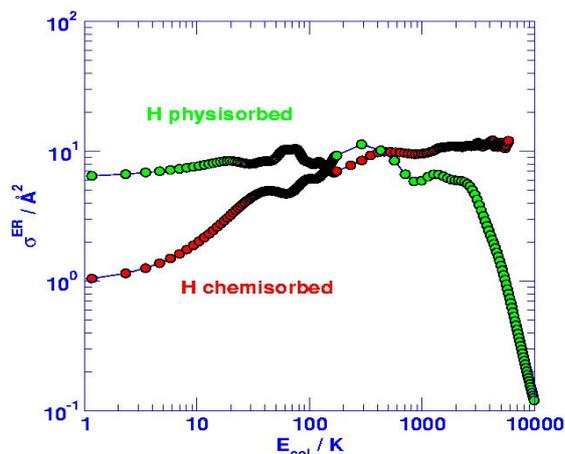


Fig.7 Quantum Eley-Rideal cross-sections in the cold collision energy regime, for target atoms initially chemisorbed (red) and physisorbed (green) on graphite, in their ground vibrational state [40].

Quantum dissipative dynamics: real-time quantum dynamics in large systems

The problem of how a small system interacts with and dissipates energy to a thermal reservoir is a very common one in chemistry and physics. Even with very large molecules, chemical reactions always involve a few number of atoms at a time, the remaining ones being only “spectators” in the process. The latter, however, are not passive: they determine the way for the excess reaction energy to be dissipated and/or they provide fluctuations needed to thermally activate the reagents.

This kind of problems in classical mechanics has been long subject to theoretical investigation, and very important analytical results have been obtained [41,42] since Einstein’s work on Brownian motion. Kramers[43] developed long ago a theory for chemical reactions in condensed phases (now known as Kramers’ theory of reaction rates) which treats the reservoir as a dissipative medium and the reaction dynamics as damped motion along the reaction coordinate. According to this theory the reaction rate undergoes a turnover as a function of the damping (being vanishingly small for both strong and weak damping), a result which has been subjected to experimental verification[44]. On the other hand, classical computational studies with thousands (millions) atoms are nowadays possible, and this allows to directly simulate complex systems, even when usual assumptions cannot be made, e.g. the Markov approximation.

In quantum dynamics the situation is more complicated. Here, the need of a quantum description arises when studying inherently quantum systems (e.g. light

atoms, tunnelling mediated processes, etc..) and/or heat reservoir at low temperatures. Among them, the ubiquitous hydrogen atom transfer in biological relevant environments, sticking of low-energy atoms/molecules on low temperature surfaces such as that occurring in the interstellar medium, radiative association processes at low collision energies when photon emission cannot be treated perturbatively with the famous Fermi's golden rule. Current approaches rely either on the quantum Langevin equation or in the reduced density matrix theory. The latter, in particular, is a very elegant and promising approach but it is currently restricted to small dimensional problems, and more importantly to severe approximations. For example, the simple positivity is not guaranteed unless a so-called Lindblad form for the dissipative functional is adopted; locality in time is usually introduced with the help of the Markov approximation, that is in the limit of a vanishingly small bath relaxation time.

We have recently attacked this problem from another point of view, since we realized that a brute force approach to explicitly simulate the dynamical behaviour of a small system coupled to large dimensional baths would be free of any such problem. Then, because of the exponential scaling of exact quantum dynamical methods, we introduced an approximate description of the bath degrees of freedom, what we called the Local Coherent-State Approximation (LCSA) to the system-bath dynamics [45, 46]. Specifically, we used system Discrete Variable Representation and bath Coherent-State sets to write down a multiconfiguration expansion of the total wavefunction appropriate to describe the system at $T=0$ K, and we employed the Dirac-Frenkel variational principle to get simple equations of motion. The latter comprise a kind of Schrödinger-Langevin equation for the system coupled to pseudo-classical equations of motion for the bath degrees of freedom. This approximation allows to properly describe the important system-bath correlations and, at the same time, gives rise to a quantum method which scales *linearly* with respect to the number of bath degrees of freedom[46].

We applied the method to a number of model problems, ranging from tunnelling to vibrational relaxation dynamics, in systems with up to 80 bath degrees of freedom, and compared the results with those of exact MultiConfiguration Time-Dependent Hartree (MCTDH)[47] calculations, the most efficient quantum dynamical method today. We have shown that quantitative agreement can be obtained between LCSA and MCTDH results, but using much less computational power. Indeed, we have shown in practice how baths with thousands of degrees of freedom can be used to model dissipation in complex environments[46], see Fig.8,9.

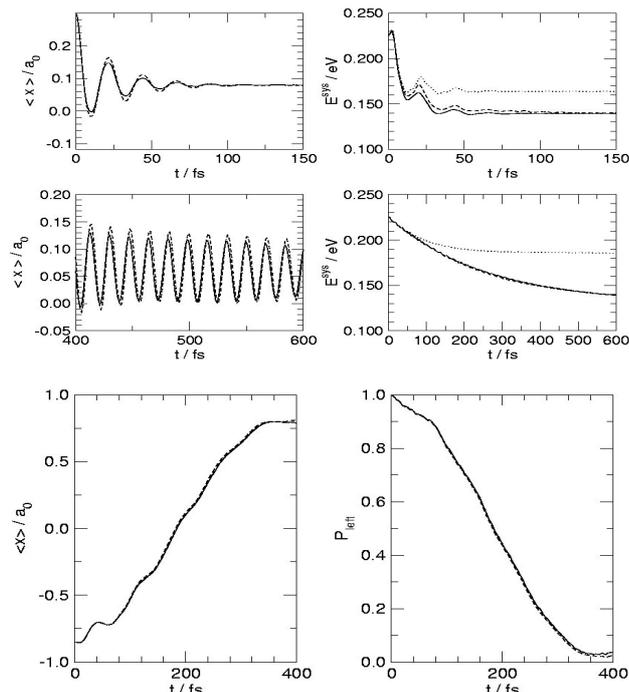


Fig.8 LCSA (dashed) and exact MCTDH (full lines) results for model system-bath problems. Upper panels: vibrational relaxation of a Morse oscillator coupled to a discretized Ohmic bath with 50 harmonic oscillators. Average position ($\langle x \rangle$) and subsystem energy (E^{sys}) for different values of the Ohmic relaxation time, $\gamma^{-1} = 8, 200$ fs, top and bottom row respectively. Bottom row: tunnelling dynamics in the double-well problem coupled to a heat bath. Average position $\langle x \rangle$ and occupation probability P of the initially occupied well. The system is coupled to an Ohmic bath with 50 harmonic oscillator and $\gamma^{-1} = 50$ fs. [46]

More recently, we have used the above LCSA to describe dissipative quantum dynamics at $T > 0$ K in a Langevin-wavefunction framework[48]. Specifically, a classical, secondary bath has been coupled to the primary bath (i.e. that in direct contact with the system of interest) and, following a standard procedure, its dynamics has been factored out in the form of dissipative and fluctuating forces acting on primary bath degrees of freedom. This allows to simulate real-time dynamics at non-zero temperature by means of independent propagation of LCSA-like wavefunctions. The resulting ‘‘Monte Carlo LCSA’’ is currently being parallelized, and will furnish the first real-time simulations of the quantum dynamics of very large systems at $T > 0$ K.

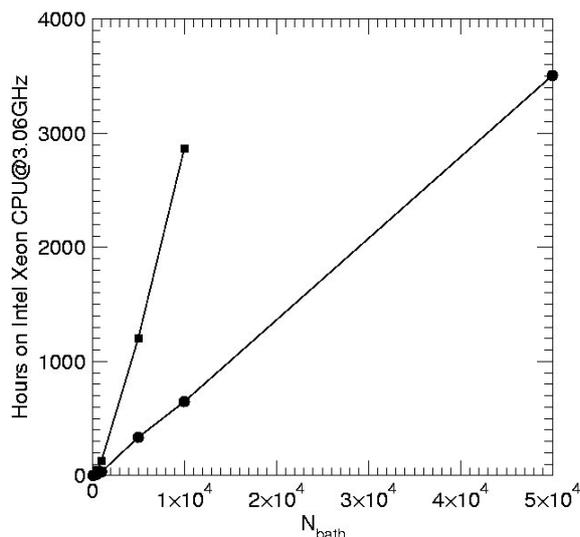


Fig.9 Computer time required to solve the LCSA equations for a model vibrational relaxation dynamics as a function of the number of bath oscillators. Circle and square symbols for 50 and 100 system DVR states, respectively [46].

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