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Abstracts of Invited Lectures
Although the molecular dynamics (MD) simulation method is well developed, it is totally based on classical mechanics and no quantum mechanical effects are taken into account. It is well known now that quantum mechanical effects such as non-adiabatic transition and tunneling play crucial roles in various large-scale chemical and biological systems [1,2]. Here, we propose a new method which can take into account these quantum mechanical effects by running classical trajectories [3].

(1) Nonadiabatic transitions at conical intersections of potential energy surfaces can be dealt with by using the analytical Zhu-Nakamura theory that enables us to treat even classically forbidden transitions. It is possible to clarify the non-adiabatic dynamics from tri-atomic systems to reactions in solutions [1,4,5].

(2) Quantum mechanical tunneling effects can be taken into account by detecting caustics along classical trajectories and finding optimal tunneling paths from there [3,6,7]. The trace of caustics makes a caustic hyper-surface that provides the boundary between classically allowed and forbidden regions. The caustics can be detected by finding zero elements of the following matrix $A$ that is propagated along classical trajectories: $A_{ij} = \left\{ \frac{\partial p_i}{\partial q_j} \right\}^{-1}$, where $p$ ($q$) is a momentum (coordinate). This matrix satisfies a Riccati type differential equation which can be solved stably. The optimal tunneling path can be detected geometrically by expanding the coordinates in terms of a parameter $z$ as $q_j(z) = q_j^C + \sum_{n=1}^{\infty} C_{jn} z^n$, $z \in (0,1)$, where $q_j^C$ is the coordinate at caustic. The coefficients $C_{jn}$ are determined variationally.

In this talk, our method mentioned above will be explained, mainly focusing on the tunneling effect. Some simple numerical examples will be presented and future perspectives will be discussed.

References
Quantum-corrected classical trajectory approach to chemical dynamics

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Several quantum corrections to the classical trajectory approach of chemical reaction dynamics [1] will be considered in the light of the semiclassical theory of molecular scattering [2,3].

References


IL 3

Mixed quantum-classical simulations of nonequilibrium heat transport in molecular junctions

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Abstract

The study of nonequilibrium heat transport in molecular junctions has gathered much attention in recent years due to its crucial role in the field of molecular electronics. Understanding the details of this process can aid in the fabrication of nano-sized electronic devices. Approximate quantum dynamical methods have been successfully used to calculate heat currents and to gain insight into the factors affecting the heat transport in a prototypical model molecular junction [1]. This model, known as the nonequilibrium spin-boson (NESB) model, consists of a two-level system in contact with two harmonic oscillator baths at different temperatures. Recently, a mixed quantum-classical framework for studying heat transport in molecular junctions was developed, which could enable the simulation of heat transport in realistic systems with many degrees of freedom [2]. In this work, we assess the ability of a recently developed mixed quantum-classical dynamics method, known as Deterministic Evolution of Coordinates with Initial Decoupled Equations (DECIDE) [3], for calculating the steady-state heat current in the NESB model in a variety of parameter regimes. Our results are compared and contrasted with those obtained using the numerically exact multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) approach [4], and using approximate methods, including mean field theory, Redfield theory, and adiabatic mixed quantum-classical dynamics. Despite some quantitative differences, the DECIDE method performs quite well, is capable of capturing the expected trends in the steady-state heat current, and, overall, performs the best out of the approximate methods. These results hold promise for DECIDE simulations of nonequilibrium heat transport in more realistic systems.

References

On dynamical traps and transition to statisticality: classical and quantum perspectives

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Meticulous experimental and theoretical studies over the past two decades have resulted in the identification of several classes of reactions that exhibit non-statistical dynamics. In such systems the phenomenon of intramolecular vibrational energy redistribution (IVR) can no longer be `wished away” and takes on centre stage in any attempt to gain insights into the reaction mechanisms. More interestingly, nonstatisticality implies that there are preferred IVR pathways and hence rekindles the hope of being able to effect mode-specific dynamics using rationally designed external fields.

In order to identify the dominant IVR pathways one needs to map out the possible anharmonic resonances and their connectivity at the energy of interest. For isolated molecules with three or more degrees of freedom this presents a formidable challenge. Fundamentally, it is this network of resonances that is ultimately required to uncover the conditions for transition to statisticality as well.

This talk presents various ways of constructing and visualising the classical analog of the resonance network. Our studies on model Hamiltonians [1] as well as spectroscopic Hamiltonians [2] for specific molecules bring out the key features on the resonance network that regulate the energy flow dynamics. A feature of particular interest is the so called resonance junction wherein several independent resonances intersect. Such junctions, somewhat counterintuitively, act as dynamical traps that result in the decoupling of a subset of the vibrational modes over chemically significant timescales. This talk provides evidence for the role of such junctions in the observed non-statistical dynamics. Moreover, we show that the quantum IVR dynamics [2], including dynamical tunnelling effects [3], is exquisitely sensitive to the features on the classical resonance network.

References

A conceptual understanding of roaming and chaotic pathways in reaction based on the stereodynamical stability

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Abstract

The recent investigation by experiment and theory has provided a clear evidence of roaming pathway in the photodissociation of methyl formate in which the conical intersection acts as an essential role. [1,2] In addition to such deterministic roaming trajectories, we have proposed a new type of roaming trajectory with chaotic behavior suggested from the action-angle diagram in the H + H₂ collinear reaction. [3,4] For the purpose of generalization in order to include roaming pathways, we have proposed a new reaction scheme based on so-called the stereodynamical stability(SDS). [5] The SDS originates from higher terms of Taylor expansion of potential energy functions. [6] In the new scheme, we have to handle non-equilibrium steady-state using the flux distribution for the excited state of a system on 2D plane together with the reaction-diffusion formula of KPP (Kolmogorow-Petrovsky-Piskounov). We show how to link the new reaction scheme with a 3D Polanyi rule as the extension of the well-established 2D Polanyi rule. [7] In the 3D Polanyi rule, the curvature and torsion of Frenet-Serret formulas by use of three independent interatomic distances (R_AB, R_BC, and R_AC) in the non-linear A + BC reaction, should provide us a key concept in understanding reaction dynamics including molecular rotation. We also considered the collapse of superposition of wave functions as the first step in the new reaction scheme. Therefore, we may touch on stereographic interpretation of the collisional decoherence for the coherent-NO + Ar collision, for instance, by employing the catastrophe bifurcation theory [8].

References

Quantum Roaming in the complex forming mechanism of the reactions of OH with Formaldehyde and Methanol at low temperature and Zero Pressure: a ring polymer molecular dynamics approach

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The quantum dynamics of the title reactions are studied[1] using the ring polymer molecular dynamics (RPMD) method from 20 to 1200 K using recently proposed full dimensional potential energy surfaces[2,3] which include longrange dipole–dipole interactions. A V-shaped dependence of the reaction rate constants is found with a minimum at 200–300 K, in rather good agreement with the current experimental data[4,5,6,7]. For temperatures above 300 K the reaction proceeds following a direct H-abstraction mechanism. However, below 100 K the reaction proceeds via organic-molecule···OH collision complexes, with very long lifetimes, longer than 10−7 s, associated with quantum roaming arising from the inclusion of quantum effects by the use of RPMD. The long lifetimes of these complexes are comparable to the time scale of the tunnelling to form reaction products. These complexes are formed at zero pressure because of quantum effects and not only at high pressure as suggested by transition state theory (TST) calculations for OH + methanol and other OH reactions. The zero-pressure rate constants reproduce quite well measured ones below 200 K, and this agreement opens the question of how important the pressure effects on the reaction rate constants are, as implied in TST-like formalisms. The zeropressure mechanism is applicable only to very low gas density environments, such as the interstellar medium, which are not repeatable by experiments.

References

DYNAMICS vs KINETICS – ACTIVATION AND TRANSITIVITY

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This lecture examines the phenomenological information from both laboratory experiments and computational simulations, that is enlarging our understanding of the temperature dependence of rates of chemical transformations and transport phenomena at low temperature range: there deviations from linearity of Arrhenius plots (so arguably from Maxwell-Boltzmann statistics) are ubiquitous. Modern approaches and techniques in quantum mechanics and collisional scattering experiments have consolidated mechanisms for reactive processes, probing images of single microscopic events and so interpreting and predicting kinetic and related parameters occurring in a variety of environments. Our statistical mechanics approach evaluates the effect of temperature on chemical reaction rates in cold environments using venerable mathematical concepts arising from “criteria for choices”: Bernoulli-like urn distribution and Euler’s formula for the exponential as limit of a succession for events, corresponding in statistics to the Pareto-Tsallis statistical weights. From statistical mechanics perspectives[1,2], the transitivity concept was introduced as a measure which regulates transit in physicochemical transformations, not necessarily involving reference to transition-state hypothesis of Eyring. The Transitivity plot is defined as the reciprocal of the apparent activation energy vs reciprocal absolute temperature[3] which permits a representation of non-Arrhenius behavior in a “geometrical scale” and make explicit a positive or negative linear dependence of transitivity for several deviation cases: (i) the super-Arrhenius kinetics, where transport phenomena accelerate processes as temperature increases; (ii) the sub-Arrhenius kinetics, where quantum mechanical tunnelling propitiates low temperature reactivity; (iii) the anti-Arrhenius kinetics, where processes with no energetic obstacles are rate-limited by molecular reorientation requirements. Furthermore, a very successful tool of theoretical kinetics, Eyring’s Transition-State Theory (TST) is modified considering the behavior of the transitivity function at low temperatures, introducing the ‘d-TST’ formulation which describe deviation from Arrhenius behavior under quantum tunneling regime [4]. The information presented here is accounts for a systematization of the foundations and tools developed over the last ten years[5] to handle the kinetics of non-Arrhenius processes, while a poster at this conference will document application in a variety of contexts.

Low temperature collisions: from modeling spin-control of reactions to unraveling scattering resonances using ab initio potentials

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Achieving control of chemical reactions using external electromagnetic fields has long been a goal in collision dynamics studies. At low temperature regime one can use for example laser-cooled and trapped molecules, such as CaF, SrF or polyatomics SrOH, SrOCH\textsubscript{3} and bring them in contact with ultracold alkali atoms to study spin-selective chemistry. However, the role of hyperfine interactions and DC magnetic fields in determining control mechanisms has remained elusive. We present an extended coupled-channel statistical theory of barrierless atom-diatom chemical reactions, and apply it to elucidate the effects of magnetic fields and hyperfine interactions on the ultracold chemical reaction Li(\textsuperscript{2}S\textsubscript{1/2}) + CaH(\textsuperscript{2}Σ) \rightarrow LiH(\textsuperscript{1}Σ) + Ca(\textsuperscript{1}S\textsubscript{0}) on a newly developed set of \textit{ab initio} potential energy surfaces (PESs)[1,2]. We observe large field effects on the reaction cross sections, opening up the possibility of controlling ultracold barrierless chemical reactions by tuning the hyperfine states of the reactants with an external magnetic field.

The second part of the talk will focus on the appearance of resonances in transitions between spin-orbit states of Carbon atom in collisions with He atoms and H\textsubscript{2}/D\textsubscript{2} molecules. We will present collision energy dependent cross sections calculated on our recently developed diabatic C-He[3] and C-H\textsubscript{2} [4] PESs. Theoretically calculated cross sections are compared to experimental results performed at University of Bordeaux and an excellent agreement is found between the two approaches.

References

Non-adiabatic quantum reactive scattering with applications to ultracold chemistry

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An electronically non-adiabatic quantum reactive scattering methodology for A + BC reactions is presented based on hyperspherical coordinates and a time-independent coupled-channel approach. A diabatic electronic representation is used where the nuclear motion kinetic energy operator is diagonal and the diabatic potential matrix includes off-diagonal coupling between the electronic states. The methodology is full-dimensional (6D), numerically exact (i.e. no dynamical approximations are used), and is parallelized to run efficiently on a variety of computational platforms from workstations to supercomputers. The full state-to-state scattering matrix is computed as a function of collision energy for each value of total angular momentum, inversion parity, and identical particle exchange symmetry. The methodology is applied to several triatomic molecules where the two lowest-lying electronic states exhibit a conical intersection in the interaction region. Recent scattering results will be presented for the ultracold hydrogen exchange reaction H + H₂, its isotopic variants H/D + HD, and the O + OH → H + O₂ and Li + LiNa → Li₂ + Na reactions. The geometric phase is 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 new signature of the geometric phase is also seen in the appearance of a prominent shape resonance for H + H₂(v=6). The origin of these large geometric phase effects is due to a new quantum interference mechanism which is unique to ultracold collisions. Experimentalists might exploit this effect to control a chemical reaction through the application of external fields or by the selection of
Quantum mechanical study of the $\text{H}^+ + \text{H}_2/\text{HD}$ reactions for the primordial universe chemistry

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Most of the kinetic models employed in astrochemistry assume molecular populations in thermodynamic equilibrium. However, recent investigations have shown that deviations from these equilibrium conditions are relevant in the primordial Universe [1]. Therefore, a precise knowledge of the rovibrational structure and the state-to-state chemistry of first molecules, namely $\text{H}_2$ or $\text{HeH}^+$ and deuterated versions, is crucial.

In order to understand the physical and chemical evolution of the primordial gas, which leads in particular to the formation of the first stars, it is necessary to have quantitative information about the chemical reactions involving the different rovibrational levels of the reactants and the products, so-called state-to-state reactions [2].

Integral cross sections and rate coefficients at high temperatures for the

\[
\text{H}^+ + \text{H}_2(v, j) \rightarrow \text{H}^+ + \text{H}_2(v', j')
\]

and

\[
\text{H}^+ + \text{HD}(v, j) \rightarrow \text{D}^+ + \text{H}_2(v', j')
\]

reactions have been computed [2,3]. They will serve as input for chemical networks which, coupled to radiative hydrodynamics models, describe the evolution of the primordial universe.

References

Adiabatic Quantum Trajectory Capture Method for Ultra-cold Chemical Reactions

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Cold atoms and molecules offer unique possibilities for fascinating new experiments in ultracold chemistry in the gas phase [1]. Chemistry in the ultracold temperature regime (i.e. with temperatures as low as mK-nK) may be expected to be completely different from what is observed in the typical laboratory temperature range of 200-400K, with long-range interactions and quantum effects such as tunneling playing a dominant role. In addition, for complex-formation reactions, in particular, the relevant length, energy, and time scales all change by orders of magnitude, once the colliding partners are close enough to form a complex. These features all conspire to make accurate quantum dynamical calculation difficult.

In this context, the wavefunction-free formulation of quantum mechanics [2,3] has proven to be a quite useful and numerically efficient method. This exact approach relies on a trajectory-based Lagrangian action principle to derive exact evolution equations for an ensemble of interacting quantum trajectories (in the present context, a single trajectory suffices). Moreover, symmetry conservation laws that manifest only in the quantum trajectory context are used to greatly improve numerical convergence—as is a newly discovered conserved action quantity (the pertinent quantum trajectory evolution equations were recently discovered to be completely integrable).

The above theoretical and methodological results will be discussed in the context of the Li(2S) + CaH (X ^2Σ\textsuperscript{+}) reaction, down to μK [1,4]. More recent theoretical developments, including the incorporation of constraints, will also be discussed if time permits.

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Recent investigations on $O(1D)+D_2$ and $C(1D)+H_2$ reactions and isotopic variants

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We have carried out theoretical calculations to study the dynamics of $X+H_2$, where $X = O(1D)$ or $C(1D)$, reactions and isotopic variants where hydrogen atoms are substituted by deuterium at low temperature by means of a statistical quantum method [1]. Integral cross sections at the low energy regime and rate constants [2, 3] have been obtained and compared with results obtained by means of exact quantum mechanical approaches and phase space theory. In addition to this, recent experimental investigations on these processes constituted a useful benchmark to test both the theoretical predictions and the role played by different electronic potential energy surfaces.

References

Probing complex quantum dynamical behaviors on weakly bound molecular systems

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We use first principles treatments to investigate the structure, the spectroscopy and the dynamics of weakly bound complexes. We consider molecular systems in their electronic ground states (such as the atmospherically important (CO$_2$)$_2$, CO$_2$-N$_2$, CO$_2$-CO dimers) or electronically excited states (such as DABCO molecule embedded into Ar cluster).

We use different ab initio methods to compute the multi-dimensional potential energy surfaces of these systems. These include standard coupled cluster, complete active space self-consistent-field, internally contacted multi reference configuration interaction and the newly implemented explicitly correlated (CCSD(T)-F12 and MRCI-F12) methods. Then, we carry out quantum dynamical computations on these multidimensional potential energy surfaces, where we consider fully the nuclear motions and nuclear spins.

Through the analysis of the rovibrational wavefunctions of these weakly bound complexes, we show that the dynamics of these complexes is closely connected to the shape of the intermolecular potentials. Close comparison to experiments is also done. For instance, we show that these weakly bound molecular systems are exhibiting complex spectral and dynamical features that cannot be accounted for using standard experimental and theoretical models. Especially, we show that the dynamics is governed by full quantum effects, including tunneling, large amplitude motions, anharmonic resonances and vibrational quantum localization. These findings can be generalized to molecular systems presenting plural potential wells separated by potential barriers. They are useful for understanding the complex quantum effects that may occur there.

Several examples will be presented: CO$_2$-N$_2$ [1,2], (CO$_2$)$_2$ [3], CO$_2$-CO [4], DABCO-Ar$_n$ [5-8].

References
Study of Reactive Angular distributions with the DCS_Regge Software Package

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State-to state-reactive angular distributions contain useful information about the reaction mechanism. This is particularly true at low energies, where the reaction may be influenced, or even dominated, by resonances. There are various approaches which help one extract this information. These include, for example, semiclassical methods [1], nearside-farside techniques [2,3], and the complex angular momentum approach (see, e.g., [4,5]). Recently, we combined some of these techniques in a software package, which we call DCS_Regge. The package compliments the previously published [6] ICS_Regge package, designed for analysing integral cross sections. In this talk, we apply the new code to the F+HD-> HF+D reaction, using the numerical scattering data. We will then go through each step of the analysis, in order to illustrate possible applications of the code.

Pronounced and hidden rainbows
in the angular scattering of chemical reactions

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Abstract

Rainbows are well known in the elastic and inelastic angular scattering of atoms and molecules. By a “rainbow,” we mean farside rainbows of the Airy (fold catastrophe) type. The question then arises if rainbows can occur in the angular scattering of state-to-state chemical reactions? The answer to this question is: Yes. In particular rainbows have been discovered and analyzed in the differential cross sections (DCSs) of the F + H$_2$ reaction [1, 2]. These rainbows have been described as “hidden” rainbows because their appearance in a DCS is quite different from the familiar rainbows of elastic scattering. Indeed it took 24 years before it was recognized that the angular scattering in the famous YT Lee molecular-beam experiments contain a rainbow.

The discovery of these hidden rainbows raises the question: Can a rainbow occur in a reactive DCS that is localized and pronounced, rather than being very broad and hidden? We have made a systematic study of this question using a simple, yet powerful, formalism based on Heisenberg’s S Matrix Principle [3, 4]. This formalism focusses on the properties of the S matrix. It does not use a pes. We have carried out partial wave computations, as well as uniform asymptotic (semiclassical) analyses, to prove that hidden and pronounced rainbows, including supernumerary rainbows, are a generic phenomenon in reactive DCSs.

Some recent relevant references


Rigid-bender close-coupling treatment of the inelastic collisions of H$_2$O with para-H$_2$

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H$_2$O is the third most abundant molecule in space after H$_2$ and CO. Because the density in molecular astronomical environments is very low ($n$(H$_2$) $\sim$ 10$^5$ – 10$^6$ cm$^{-3}$), the rovibrational populations are generally not at local thermodynamic equilibrium. Collisional rates with H$_2$ are thus needed to properly model the H$_2$O rovibrational excitation and line emission and more generally the local physical conditions in environments ranging from interstellar molecular clouds to stellar photospheres, circumstellar envelopes, and comets. We present a new method taking explicitly into account the coupling between rotation and bending of a non-linear triatomic molecule colliding with an atom. This approach based on a rigid-bender treatment of the triatomic molecule was originally developed for the case of triatomic molecule linear at equilibrium [1,2,3]. It is here extended to the case of a colliding bent triatomic molecule at equilibrium and applied to the case of the para-H$_2$+ H$_2$O inelastic collision [4] using a new adiabatically reduced 4D potential. The only studies related in spirit and available are the one of Dagdigian and Alexander in 2013 [5] which addresses the problem of the coupling between the rotation and the umbrella modes of CH$_3$ colliding with He and the one used by Loreau and Van der Avoird in 2015 [6] to treat the coupling between the rotation and umbrella modes of NH$_3$ in collisions with He. The results of the present method for purely rotational transitions are compared to those of rigid-rotor calculations while vibrational quenching rates of the first exited bending level are calculated for the first time at the close-coupling level.

References

Quantum dynamics studies of the F + H\textsubscript{2}O/CH\textsubscript{4} reactions

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Abstract
In this talk, I will present some of our recent works on quantum reactive scattering studies of the F + H\textsubscript{2}O/CH\textsubscript{4} reaction by using the time-dependent wave packet method. The potential energy surfaces used in these studies were recently constructed by using fundamental invariant neural network (FI-NN) fitting based on extensive coupled-cluster calculations by my group. Dynamical resonances, efficacy of initial vibrational excitation on the reactions will be discussed.
Kinetic Isotope Effects (KIE) can give insight in the specific details of reactions and elucidate, e.g., the deuterium fraction of molecules in the interstellar medium. Thermal rate constants and therefore also KIEs can be efficiently calculated employing the quantum transition state concept and utilizing the multiconfigurational time-dependent Hartree approach (MCTDH) for propagation of high-dimensional wave packets. In this talk, these approaches are reviewed and the thermal rate constants of the prototypical H$_2$+OH $\rightarrow$ H$_2$O+H and the H+CH$_4$ $\rightarrow$ H$_2$+CH$_3$ reaction as well as corresponding kinetic isotope effects will be discussed. If time permits, a novel approach to simulate reactive scattering by employing the ring polymer molecular dynamics (RPMD) approach will be discussed.
Several Levels of Theory for the Description of the Anomalous Isotope Effects in the Ozone Forming Reaction

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We developed a rigorous multi-level theoretical approach for the description of ozone forming reaction, with particular emphasis on identifying the molecular level mechanism of an intricate mass-independent isotope effect. At 0th level of theory the role of molecular symmetry is accurately outlined. This is not trivial, since large factors on the order of $\frac{1}{2}$ and 2 appear in seven (!) different places in the kinetics formalism. It is shown that this level of theory does not lead to any isotope effect. At the 1st level of theory, equivalent to the statistical description of the recombination process, the effect of atomic masses is taken into account to elucidate the roles of vibrational zero-point energies and rotational excitations. It is found that averaging over rotational distribution “smooths down” isotopic differences and leads to a relatively small effect, insufficient to explain experiments. At the 2nd level of theory the reaction is assumed to proceed through independent diabatic ro-vibrational channels, which permits to determine contribution of shape-type resonances, populated by tunnelling and trapped behind the centrifugal barrier. The absolute values of the rate coefficients obtained in this way are too small, and the resultant isotope effects do not look like experimental data. At the 3rd level of theory the role of Feshbach resonances is determined, by accurate close-coupling calculations using hyper-spherical coordinates, adaptive grids, sequential diagonalization truncation technique and complex absorbing potential. Comparison with available experimental data of Mauersberger group is presented.

Fig. 1: A map of pathways A, B and S (shown by green, red and blue arrows) for formation of singly substituted ozone. One contour line of the PES is given to show three entrance channels for $0 + QO$ and $Q + 0Q$ reagents, and three wells for symmetric $QQQO$ and asymmetric $QQ0Q$ products. Dashed line represents the reflection plane of symmetry.

References:
Calculation of quantum exact UV absorption cross-sections for interstellar and atmospheric chemistry

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Availability of accurate and high-resolution spectra for atmospheric and interstellar photochemistry modeling is a necessity when considering isotopic fractionation and shielding effects. There still are numerous diatomic compounds with missing UV absorption cross-sections that are very complicated to measure in laboratory setting. In this talk, we’ll be looking at SO[1] and S\(_2[2]\) as an important part of Archean sulfur cycle and possible source of sulfur mass-independent isotopic fractionation (S-MIF). Calculated absorption cross-sections and isotopic fractionation factors are discussed in detail.

New *ab-initio* potential energy curves were developed for both molecules and high resolution total absorption cross-sections for \(A^3\Pi \leftarrow X^3\Sigma^-\) transition, and two nonadiabatically coupled-potential (\([C^3\Pi - C^3\Pi] \leftarrow X^3\Sigma^-,\) and \([B^3\Sigma^- - 3^3\Sigma^-] \leftarrow X^3\Sigma^-\)) transitions in SO are calculated. For S\(_2\) the photoabsorption spectra were calculated for the transitions between ground state, \(X^3\Sigma^-\), and two excited states: \(B'^3\Pi_u\) and \(B^3\Sigma^-\).

The spectra were calculated using quantum-exact, time-independent R-matrix theory for one-dimensional systems. Using this method, we can obtain numerical solutions for the energies and wavefunctions of all discrete vibrational states on all electronic potential energy curves (PECs) by solving the following Schrödinger equation:

\[
\left( -\frac{1}{2\mu} \frac{d^2}{dr^2} + V(r) - EI - \frac{1}{\mu} M(r) \frac{d}{dr} + \frac{1}{\mu} \frac{d}{dr} M(r) \right) \psi_E(r) = 0,
\]

once the wavefunctions \(\psi_E\) are known, total absorption cross-sections can be calculated:

\[
\sigma_{\text{tot}}(\omega) = \frac{4}{3} \frac{\omega^3}{\hbar c} L_{a_0}(\omega, T) B_i(T) \left| \langle \psi_f | \mu | \psi_i \rangle \right|^2,
\]

where \(\omega\) is the excitation energy, \(L_{a_0}(\omega, T)\) is the Lorentzian broadening factor at energy \(\omega\), centered at discrete peak with energy \(a_0\), \(B_i(T)\) is the temperature-dependent boltzmann factor for the population of initial state \(i\), \(\psi_i\) and \(\psi_f\) are initial and final wavefunctions with electronic transition dipole moment \(\mu\).

References


Quantum Interference in the Predissociation of OH and SH

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As shown schematically in the figure, the A2Σ+ state of OH and SH are predissociated by crossings with three repulsive states (4Π, 4Σ−, and 2Σ−), which correlate at long range with the H+S(3Pj) [H+S(3Pj)] dissociation channel. Spin-orbit coupling allows pre-dissociation of the bound (A 2Σ+) state of SH (OH).

There have been numerous experimental studies of the lifetimes of the A 2Σ+ vibration-rotation levels.1 Most theoretical studies of this process have used the Fermi Golden Rule to predict these lifetimes based on high quality ab initio calculations of the potential curves, and of the underlying spin-orbit couplings.

Of particular interest is the branching between the three accessible spin-orbit states of the S(3Pj=0,1,2) [O(3Pj=0,1,2)]. These ratios will reflect the relative strength of the three spin-orbit couplings at the crossings, weighted by the vibrational wavefunctions of the SH(A, v,j) levels, and quantum interference as the products recede. A complexity is the transformation between the spin-coupled basis (in which the states are labelled in the figure) and the atom-coupled basis |Ja⟩|sj⟩ in which the asymptotic states are defined.

To obtain predissociation rates and branching ratios, we use the driven-equations formulation of Freed and co-workers,2 as implemented by Manolopoulos and Alexander,3 specifically for the direct photodissociation of HCl.4 Our quantum scattering calculations are based on our MRCI potential curves and couplings. As implemented in our Hibridon scattering code, we can simultaneously determine the distribution of the current density between the adiabatic electronic states, giving a time-independent, energetically monochromatic picture of the non-adiabatic dynamics as the H–S products recede.

We will compare our results with the predictions of Parlant and Yarkony5 (OH) and those of Lee, Freed, and co-workers6 (SH) and with the experimental branching ratio determinations by Zhang and co-workers.7

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Recent progress in the theory of chemical reactions; From a perspective of nonadiabatic electron dynamics

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We review and discuss our recent progress in nonadiabatic electron dynamics, which we term as Time-Domain Quantum Chemistry. We are particularly interested in chemical phenomena and concepts arising from entanglement between electronic and nuclear dynamics, most of which are characterized by the bifurcation of electronic and/or nuclear wave packets. Characteristic phenomena emerging from nonadiabatic dynamics in radiation fields are also our concern.

In this talk, specific subjects are selected from the following items we have been studying:

1) Theoretical framework
   a) Nonadiabatic electron wave packets in path-branching representation [1]
   b) Time-dependent variational principle; quantum and semiclassical dynamics (including natural path branching) in mapped spaces
   c) Relativistic theory for nonadiabatic electron wave packet dynamics in radiation fields

2) Symmetry breaking due to nonadiabatic dynamics
   a) Direct observation and control of quantum wave packets passing across a symmetry-allowed conical intersection
   b) Control of symmetry-allowed conical intersections by chemical substitution
   c) Jahn-Teller effects from the view point of molecular force
   d) The Lorentz-force-like molecular force arising from the genuine multi-dimensional effect of nonadiabatic interactions; breaking optical symmetry; electromagnetic vector field vs. nonadiabatic field

3) Chemical principles behind water splitting
   a) Proton transfer versus hydrogen migration in excited states
   b) Coupled proton electron-wavepacket transfer (CPEWT) and inverse CPEWT as a universal mechanism of charge separation in organic and biological molecular systems
   c) Efficient separation of protons and electrons; inhibition of charge recombination and Y-shape acceptors
   d) The role of ground state conical intersection; photoemission of firefly vs. charge separation
   e) Chemical mechanisms of unidirectional transfers of protons and electrons

4) Electron dynamics in highly quasi-degenerate electronic-state manifold (Chemistry beyond the notion of potential energy surface)
   a) Highly excited states of boron clusters
   b) Reconnection of “dynamical chemical bonds”; Hyper-resonance

5) Characteristic electron flux induced by entanglement between electrons and nuclei
   a) Flux analyses of nonadiabatic chemical dynamics
   b) Anomalous photon emission due to the coupling of nonadiabatic intramolecular electron transfer and laser fields applied
   c) Optical confinement of an excited state wave packet without dissociation

6) Miscellaneous
   a) Dynamics of ultrafast photoionization and Auger decay in molecules
   b) Nonadiabatic electron wave packet dynamics in statistical environments like solvents
   c) Classical nonadiabatic dynamics; sudden transitions resisting the “slaving principle”.

Beyond Born-Oppenheimer Theories on Multi-State Spectra and Scattering Processes

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First principle based beyond Born-Oppenheimer (BBO) theory is presented for the construction of highly accurate diabatic potential energy matrix to explore multi-mode multi-surface photoelectron spectra [1-5] and reactive collision processes. [6-9] While calculating those diabatic surfaces, \textit{ab initio} adiabatic potential energy surfaces (PESs) and nonadiabatic coupling terms (NACTs) are employed. [1-9] The workability of BBO theory for excited state processes is demonstrated by computing the photodetachment spectra of NO$_2^-$, NO$_3^-$ and C$_6$H$_6$ in comparison with experimental ones. [1,3,5] Semi-circular conical intersection (CI) seam rather than a point between ground (1$^1$A') and first excited (2$^1$A') states of H$_3^+$ are new interesting observations. [6] The reactive scattering dynamics has been carried out on diabatic surfaces of H$_3^+$ system [7] in hyperspherical coordinates for total angular momentum zero and non-zero situations to calculate cross sections for reactive non-charge transfer, reactive charge transfer and non-reactive charge transfer processes, and compared with experimentally measured ones. In addition, we have constructed \textit{ab initio} based accurate diabatic PESs of F+H$_2$ system with the aim of computing various experimentally observable quantities. [8,9] Jahn-Teller and Renner-Teller types of CIs along with Pseudo Jahn-Teller couplings are also discussed.

References:
In order to investigate theoretically the time-dependent dynamics of molecules irradiated with intense laser fields, we have to solve the time-dependent Schrödinger equation (TDSE). The standard method for solving the TDSE is based on the Born-Huang expansion of the molecular wave function, and this method has been known to work well as long as the number of electronically excited states prepared by the irradiation of the laser field is not more than a few. However, in an intense laser field, electronic excitation proceeds excessively, leading to the formation of electronically highly excited states such as doubly excited states and Rydberg states and to the multiple ionization. Furthermore, associated with the electronic excitations chemical bond breaking and vibrational excitations can also proceed.

In this talk, we introduce an alternative method called the extended multiconfiguration time-dependent Hartree-Fock (Ex-MCTDHF) method [1] to solve the TDSE for molecules in intense laser fields more efficiently than the Born-Huang expansion approach. In the Ex-MCTDHF method, which is an extension of the multiconfiguration time-dependent Hartree-Fock method [2, 3], we include the protonic degrees of freedom on the same footing as the electronic degrees of freedom. The total molecular wave function is written as

\[
\Psi(r_e, r_p, R, t) = \sum_{ij} C_{ij}(R,t) \Phi_i(r_e, t) \Lambda_j(r_p, t),
\]

where \(r_e\) is the coordinates of the electrons, \(r_p\) is the coordinates of the protons, \(R\) is the coordinates of the heavy nuclei other than protons, \(C_{ij}(R,t)\) is an \(R\)-dependent expansion coefficient, and \(\Phi_i(r_e, t)\) and \(\Lambda_j(r_p, t)\) are time-dependent Slater determinants, which are constructed from time-dependent spin-orbitals. Because both \(\Phi_i(r_e, t)\) and \(\Lambda_j(r_p, t)\) depend on time, we can treat efficiently both electronic excitation and vibrational excitation. In the Ex-MCTDHF method, we do not use potential energy surfaces because the electronic Slater determinants \(\Phi_i(r_e, t)\) do not depend on the nuclear coordinates \(R\) and \(r_p\).

We have carried out a proof-of-principle application of the Ex-MCTDHF method to the simplest molecular system, \(H_2^+\), being exposed to an intense laser field [4, 5]. By comparing the results obtained by the Ex-MCTDHF method and the results obtained with a numerically exact method, we show that not only the vibrational and electronic excitations but also the dissociation and ionization can be described well by the Ex-MCTDHF method when the number of terms included in the sum in Eq. (1) is sufficiently large.

References
A diagrammatic approach to understanding complicated nonadiabatic chemical reaction dynamics

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Nonadiabatic chemical reaction dynamics are complex and difficult to understand with simple examination of the simulated dynamics, as shown in Fig. 1(b). This is because the wavepackets repeatedly bifurcate, merge, and interfere with each other due to nonadiabatic transitions. Thus, we developed an alternative approach to understanding the complicated nonadiabatic dynamics. This alternative approach is based on the diagrams shown in Figs. 1(d) and (e). These diagrams visualize the structure of the complicated nonadiabatic dynamics as occurrence patterns of dynamical events, such as wavepacket bifurcation, turning, and dissociation. [1]

We applied this diagrammatic method to the elucidation of the mechanism of power-law decay in the nonadiabatic photodissociation dynamics of alkali halides shown in Fig. 1(c). We derived an analytical formula for the power-law decay based on the diagrams and showed that the power-law decay is due to the structure of the diagram in Fig. 1(e) and quantum wavepacket interference. [1]

In this presentation, I will talk about the details of the formulation of the diagrams and the application mentioned above.

Reference
New time-dependent wave functions methods: 
Second Quantization based Time-dependent Hartree and Multi-Configurational 
extensions and Time-dependent Vibrational Coupled Cluster

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In this theoretical focused talk I will describe second quantization based formulation of

I will describe our work on re-parameterization of the classic time-dependent Hartree (TDH) approach (time-dependent self-consistent field) in terms of second-quantization based exponential parameterization.[1] Although the derivation of the exponential parameterized TDH (X-TDH) is more complicated than for the corresponding linear parameterized TDH (L-TDH), X-TDH can be implemented in a highly efficient manner applicable to thousands of degrees of freedom. I will briefly describe our initial attempts to generalize our formulation to the case of the well-known[2] Multi-configurational Time-Dependent Hartree approach.

In the second part of the talk I will describe the theory and implementation of a time-dependent vibrational coupled cluster methodology. In analogy to our time-independent vibrational coupled cluster method, we propose an exponential cluster parameterization of the time-dependent wave function. I will discuss some of the issues and peculiarities arising from employing a non-variational wave function approach, and how working equations can be obtained. Initial results will be presented at the two-mode coupling level, TD-VCC[2], which has also applicability to large molecular systems.

Implementation of the methods in our generally available MidasCpp code (midascpp.gitlab.io) is described.

References


A matrix product state formulation of the multiconfiguration time-dependent Hartree (MPS-MCTDH) theory will be presented. The Hilbert space that is spanned by the direct products of the phonon degree of freedoms, which is linearly parameterized in the MCTDH ansatz and thus results in an exponential increase of the computational cost, is parametrized by the MPS form. Equations of motion based on the Dirac-Frenkel time-dependent variational principle is derived by using the tangent space projection and the projector-splitting technique for the MPS, which have been recently developed. The mean-field operators, which appear in the equation of motion of the MCTDH single particle functions (SPF), are written in terms of the MPS form and efficiently evaluated by a sweep algorithm that is similar to the DMRG sweep. The efficiency and convergence of the MPS approximation to the MCTDH are demonstrated by quantum dynamics simulations of extended excitonic molecular systems.

References:
Using Gaussian basis functions without equations of motion

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The use of Gaussian basis functions (GBFs) within quantum dynamics simulations offers several benefits, and several methods have been developed to take advantage of these. Usually the benefits come coupled with several drawbacks, one of the most notable being the question of how the basis set should be adapted to the changing wave function. Indeed, most GBF methods (e.g. vMCG, AIMS, G-MCTDH, CCS, aTG, MP-SOFT, etc.) differ primarily in how they allow basis functions to move as the simulation proceeds. In most cases the movement of the basis functions depends on some equations of motion, which vary from fully quantum mechanically variational through to purely classical.

Over the past few years we have developed a method specifically designed to avoid the problems associated with selecting and implementing GBF equations of motion, the Basis Expansion Leaping multiconfiguration Gaussian (BEL MCG) method. In this method we use the variational flexibility afforded by the non-orthogonal nature of GBFs to propagate for short periods in a set of stationary GBFs. Critically, we then use a novel algorithm to reexpress the wave packet in a set of new GBFs, appropriate for the time-evolved state. This process is repeated as the wave packet evolves in time. In this talk I will describe the BEL MCG method and illustrate some of its features with recent applications.

References

Automatic spatial extension of a time-dependent wavefunction expanded in terms of Gaussians

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Gaussian functions have been used as the most successful basis set for quantum chemistry electronic structure calculations. Many attempts [1-3] were also made to apply Gaussian basis sets to study ultrafast reaction (nuclear) or electronic dynamics of molecules. The localized nature of Gaussians significantly reduces the number of positions at which one should compute the potential energy. However, numerous time-dependent moving Gaussians may approach one another in the configuration (coordinate) or phase space. The nonorthogonality and overcompleteness of Gaussian basis sets trigger severe numerical instabilities when many Gaussians are required for expansion.

In this talk, we present a simple time-evolution method for molecular quantum dynamics, in which the wavefunction is expanded in terms of time-independent Gaussians placed at von Neumann unit cells [4] in the phase space, with a threshold parameter $\epsilon$ to determine the expansion accuracy. The wavepacket is propagated by solving the equations of motion for expansion coefficients only. Re-expansion is made when the change in wavefunction exceeds another threshold parameter $\delta$ ($>\epsilon$). Gaussians necessary for representing the wavefunction are automatically selected merely by adding new Gaussians to or subtracting Gaussians from the basis set.

The present method has been applied to model tunneling systems in one to three dimensions [5]. Figure 1 shows a two-dimensional quadruple-well potential in which the wells A and D are 2.4 cm$^{-1}$ lower than B and C because of the $x$-$y$ coupling. The mass of the particle is the proton mass and the initial wavefunction is a Gaussian localized in the well A. As the wavepacket is transferred to the other wells by tunneling, reselection of Gaussian basis functions is repeated 12 times up to $t \sim 4.5$ ps and 358 Gaussians are then distributed to cover the whole range of the four wells. The wavepacket returns to the well A at $t \sim 49$ ps and its behavior agrees well with the exact one obtained by the split-operator method. This Gaussian expansion method is able to accurately evaluate the tunneling time and direction in multidimensional systems.

We will also discuss the results of on-the-fly quantum dynamics simulations of small molecules obtained by combining our method with electronic structure calculations.

References


Fig. 1 Wavepacket propagation (solid line: our method, dotted line: split-operator method), the number of Gaussians used for expansion, $N$, and their central positions.
Molecular dynamics simulations of ultrafast electronic relaxation dynamics in an iron(II) complex

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The ultrafast electronic relaxation processes of transition metal complexes have been attracted much interest because of the importance in potential applications such as data storage and dye-sensitized solar cells. Accordingly, for example, ultrafast electronic relaxation from photoexcited metal-to-ligand charge transfer (MLCT) states in a prototypical iron(II) complex, [Fe(bpy)₃]²⁺ (bpy=bipyridine), has been investigated by time-resolved spectroscopies [1]. However, because multiple excited states including both d-d and MLCT excited states with different spin multiplicities could be involved in the ultrafast processes, the underlying mechanism has not been well clarified in detail.

To clarify such processes, dynamics simulations considering electronic transitions would be useful. However, it is well known that high-level electronic structure theories are usually required for the description of excited states of transition metal complexes due to strong electron correlation effects. As a result, dynamics simulations using quantum chemical calculations with reasonable accuracy are computationally very demanding for systems including transition metal complex, and thus dynamics simulations on full dimensional potential energy surfaces have been still limited.

Considering these, we have been developing a model electronic Hamiltonian which can compute multiple d-d excited states of [Fe(bpy)₃]²⁺ in a computationally cheap fashion. We have been applying this model Hamiltonian to molecular dynamics (MD) simulations for obtaining insight into the excited state dynamics [2–4]. The model Hamiltonian is composed of several metal-ligand interaction terms modeled by reasonably simple functions, and the potential energies of d-d excited states are obtained by diagonalizing the model Hamiltonian. The spin-orbit and non-adiabatic coupling elements can be analytically evaluated within the framework of the model Hamiltonian. Recently, we have been extending this model Hamiltonian to deal with MLCT excited states simultaneously.

In this talk, the basic strategy to construct the model electronic Hamiltonian, applications of the model Hamiltonian to MD simulations, and the current progress will be presented.

References
Solvation of sodium clusters and polyaromatic hydrocarbons into helium droplets: exotic and metastable phases

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Abstract

Helium is considered as an ideal cryogenic medium to study, at high resolution, the properties of molecular dopants under conditions that are similar to isolated or very dilute environment such as interstellar media. Most molecular dopants bind strongly enough to be fully solvated and lie near the droplet center, helium atoms in the immediate vicinity of the dopant gaining the ability to localize or even freeze into so-called Atkins' snowballs. In this contribution we explore by means of path-integral molecular dynamics simulations the stepwise solvation of cationic polyaromatic hydrocarbons by helium atoms. We show how the anisotropic character of these molecules gives rise to an equally anisotropic localization behavior near the aromatic planes or at their periphery [1,2]. In particular, we predict that oligomers of such large, planar dopants could be trapped into metastable configurations sandwiched by a helium frozen layer in typical pick-up experiments [3].

Occasionally, the dopant could bind helium even more weakly than to helium itself. This notably occurs for small alkali clusters, owing to the strong Pauli repulsion between the valence shells of the alkali and the helium atoms. However, as the size of the metal cluster increases the van der Waals interaction also increases and eventually triggers solvation of the cluster. Again, path-integral molecular dynamics simulations were performed to investigate the size range at which this solvation takes place [4].

References

We report theoretical investigations on the dynamics of doped He nanodroplets in real-time. He nanodroplets are intriguing, quantum fluid objects of finite size. Doping them with atoms or molecules makes them a particularly interesting model to study the fate of an excited system in or on them. The doping process itself is still not fully understood, in particular in the presence of quantum vortices. Helium density functional theory (He-DFT) approach and its time-dependent version (He-TDDFT) are the best compromise between accuracy and feasibility to study the stability and real time dynamics of doped helium droplets with a size comparable to experiments.[1] Comparing with highly detailed recent experiments such as those combining pump-probe spectroscopy with velocity map imaging allows to shed light on the importance of energy transfers between the excited atomic or molecular system and this unusual quantum solvent.

In this presentation, the recent work conducted in collaboration between the Barcelona and the Toulouse teams on $^4$He nanodroplets will be reviewed. The following processes will be presented, depending on time:

• doping [2], possibly with quantum vortices [3]
• real time dynamics of photo-excited alkalis on the droplet surface [4]
• electronic relaxation induced by the helium environment [5, 6]

References

Dynamics and mechanisms of complex chemical reactions on \textit{ab initio} analytical potential energy surfaces

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We investigate the dynamics and mechanisms of chemical reactions using analytical \textit{ab initio} potential energy surfaces (PESs) and quasi-classical trajectory and/or quantum methods. After many successful applications for atom + methane reactions, we have recently initiated an \textit{ab initio} analytical PES-based approach for studying the dynamics of bimolecular nucleophilic substitution (Sn2) reactions. Millions of trajectories obtained on the analytical PESs revealed a novel double-inversion mechanism for Sn2 reactions,\textsuperscript{1} unexpected leaving-group effects,\textsuperscript{2} non-traditional front-side complex formation,\textsuperscript{3} and unprecedented agreement with experiments.\textsuperscript{2,4} In the present talk I will focus on our most recent results on (a) the effect of the level of electronic structure theory on the dynamics of the F\textsuperscript{-} + CH\textsubscript{3}I reaction,\textsuperscript{5} (b) joint theoretical–experimental study of the mode-specific dynamics of the F\textsuperscript{-} + CH\textsubscript{3}I Sn2 and proton-transfer reactions,\textsuperscript{6} (c) uncovering the role of the stationary points in reaction dynamics,\textsuperscript{6} (d) ROBOSURFER – an automatic PES developer program package, and (e) analytical \textit{ab initio} PESs and dynamics for the F\textsuperscript{-} + CH\textsubscript{3}Br, F/Cl + C\textsubscript{2}H\textsubscript{6},\textsuperscript{7} OH\textsuperscript{-} + CH\textsubscript{3}I,\textsuperscript{8} and F\textsuperscript{-} + CH\textsubscript{3}CH\textsubscript{2}Cl\textsuperscript{9} reactions.

References

Automated Generation and Analysis of Reaction Path Networks for Systematic Understanding of Reactivity in Complex Systems

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Paths of chemical reactions are studied theoretically by exploring the quantum chemical potential energy surface (PES) while performing quantum chemical calculations. Local minima and first-order saddle points on the PES are computed as equilibrium (EQ) structures of molecules and transition state (TS) structures of chemical reactions. Therefore, it is an important subject to develop a method for finding EQs and TSs systematically on the PES.

We have developed an automated reaction path search method called an artificial force induced reaction (AFIR) method [1]. It has been applied to elucidate mechanisms of various chemical reactions [2]. The AFIR method has been implemented in the global reaction route mapping (GRRM) program, where the AFIR method implemented for molecular systems is available in GRRM17 [3]. The AFIR method can generate the reaction path network which is a network of EQs via reaction paths linking them. A resultant reaction path network contains hundreds or more EQs and thus are highly complicated. We therefore have developed a new kinetic approach called a rate constant matrix contraction (RCMC) method which is applicable to huge reaction path networks [4]. Furthermore, by combining the AFIR method with the RCMC method, we have established an approach by which, starting from a set of reactants and catalysts, the product and all byproducts, their generation ratio, as well as their generation mechanisms under a given experimental condition can be elucidated automatically [5]. This approach enabled systematic prediction of chemical reactions.

In the presentation, applicability of AFIR and RCMC methods will be discussed with some examples. The AFIR method is applicable to chemical reactions of various types such as photoreactions, enzyme reactions, reactions on metal surfaces, phase transitions, and so forth. Application examples to these reactions will also be presented.

References


Theoretical analysis on reactions of carbon cluster chain ions $C_n^\pm + H_2$ ($n=2-8$)

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Due to the flexible balance of s and p orbitals, carbon species are found in many different geometrical forms: linear chains, planar graphene, and three dimensional fullerenes. Furthermore, in the astrophysics and combustion communities, many studies have been performed on carbon clusters with a focus on the effect of geometric structure towards the reactivity. Although there have been a lot of studies on these clusters, an understanding of their fairly complex electronic states as well as the reaction dynamics is still lacking. Here we will present theoretical results, based on CCSD(T) and B3LYP with cc-pVTZ basis set, concerning the size and charge dependent reactivity of linear carbon ions $C_n^\pm$ ($n = 2-8$) and $H_2$. For the cation reaction, we present results showing that the difference in ground electronic state affects the odd-even variation in reactivity. A barrierless radical abstraction forming $C_nH^+$ occurs through a direct head on approach for the $^2\Sigma$ ground electronic state for odd $n C_n^+$. In contrast, a carbene-like insertion forming $C_nH_2^+$ occurs through a sideways approach for the $^2\Pi_{g/u}$ ground electronic state for even $n C_n^+$. On the other hand, for the anions, both the even and odd linear chain have the $^2\Pi_{g/u}$ ground electronic state. In addition, we found that for both even and odd $n$, the bimolecular reaction along the minimum energy pass produces the $C_nH_2^-$ adduct with a large exothermicity. However, when dynamical effects were included in the simulation, while we observed only the $C_nH_2^-$ product for odd chains, a complex product branching forming $C_nH_2^-$, $C_nH^- + H$, and $HCnH^-$ was seen for the even chains. To the best of our knowledge, this is the first time a roaming like reaction was seen for bimolecular reactions of carbon chain clusters. The fact that we can observe many products though dynamics effect highlights the flexibility in the molecular orbital of the carbon cluster to adapt to the different position of the roaming hydrogen atom.

References

EXCITATION AND DESTRUCTION OF THE OH$^+$ and OD$^+$ IONS by H ATOMS

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In space, deuterated species are surprisingly highly abundant. Following the recent discovery of OH$^+$, we are studying the possible formation of the OD$^+$ molecule in the interstellar medium. New quantum reactive scattering calculations for the O$^+$ + HD and OD$^+$ + H collisions have been carried out to obtain state-to-state cross sections and rate constants by means of an accurate wave packet approach [1-3] using the doublet and quartet ground H$_2$O$^+$ electronic potential energy surfaces correlating to the open shell reactants. Calculations were performed for collision energies in the range of 1 meV to 0.7 eV and for different initial rotational excitation of the reagent molecules. These calculations provide us detailed information about the possible detection of OD$^+$ in space. A review will be presented for ion-molecule collision processes that occur in the evolving chemistry of astronomical environments.

References:

Mode-selective chemistry in the reactions of CH$_4$ and CHD$_3$ with hydrogen

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The present talk focuses on the mode-selective chemistry of methane and its isotopomers. Reactions of atoms with methane are prototypical examples of polyatomic reaction processes which are intensively studied by experiment and theory. Combining the quantum transition state concept and the numerically efficient (multi-layer) multi-configurational time-dependent Hartree (MCTDH) approach, rigorous full-dimensional quantum dynamics calculations can study these six atom reactions in detail and obtain fully quantum state resolved reaction probabilities.

Accurate results for the H + CHD$_3$ → H$_2$ + CD$_3$ and H + CH$_4$ → H$_2$ + CH$_3$ reactions will be presented and discussed. The ro-vibrational control of the chemical reactivity of CHD$_3$ and CH$_4$ mostly follows intuitive patterns and can be qualitatively understood employing generalized Polanyi rules and the sudden approximation. However, interesting deviations from the expected behavior are found for the H + CHD$_3$ → H$_2$ + CD$_3$ reaction. Here a surprisingly large reactivity of triply umbrella excited CHD$_3$ reactants is found which results from Fermi resonance-type state mixing. The effect is called "reactivity borrowing" and can be interpreted as the reaction dynamics analog of the well-known "intensity borrowing" in spectroscopy. Furthermore, the correlation between the quantum states of the reactants and products is analyzed. While for the H + CH$_4$ → H$_2$ + CH$_3$ reaction the "loss of memory" phenomenon, which is a consequence of the bottleneck function of the transition state, results in product state distributions almost independent of the initial vibrational excitation of the methane reactant, a more complex pattern is observed for the H + CHD$_3$ → H$_2$ + CD$_3$ reaction.
Investigation of quantum branching dynamics involved with photoexcited electrons in molecular aggregates

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The branching dynamics of quantum wave packets in a single electronic state as well as the coupled multiple electronic states determine the time dependent populations of molecular species and the energy distribution for electrons and ions in molecular systems. Recent advances in microscopic and ultrafast science have encouraged researchers to obtain an ultimate picture about chemical reaction dynamics. With this background, one of the important issues is to elucidate the entangled dynamics of excited electrons and molecular states which are created under the effect of light-matter, non-adiabatic and spin-orbit couplings. Electron dynamics are directly related to a light-energy conversion process, such as, (a) an exciton diffusion and charge separation, (b) a photosynthesis including light harvesting and (c) a reorganization of molecular quantum state via an excited electronic state manifold. The present talk includes the following works.

(1) Quantum dynamics study on the isomerization effect on multi-channel unimolecular dissociation

The unimolecular dissociation of formaldehyde at the energy near the barrier threshold in the ground electronic state has multi-reaction channels including isomerization. The competition between isomerization, hydrogen molecule detachment and atom ejection channels changes with the increase of total energy affected by a wave packet bifurcation and quantum hydrogen tunneling. That was analyzed with use of quantum wave packet dynamics calculation on the developed potential energy surface without the roaming channel.

(2) Nonadiabatic electron dynamics with wave packet bifurcation and path representation

I introduce the study of nonadiabatic electron dynamics in complicated fluctuate excited states as well as a practical scheme for describing electron dynamics along nonadiabatic paths with phase space averaging as a reduction from the full description of non-Born-Oppenheimer chemical theory by Takatsuka.

The topics are (i) nonadiabatic wave packet in a co-existence of laser and nonadiabatic kinematic coupling (ii) quantum interference around conical intersection and decoherence (iii) reduction of the evaluation cost associated with path branching for complex multiple nonadiabatic transitions (iv) nonadiabatic electron dynamics involved with quasi-degenerate excited states and laser field.

(3) Migration dynamics of excited electrons in molecular aggregates

Recently we introduced a practical calculation scheme for the description of excited electron dynamics in molecular aggregates within a group diabatic Fock representation. This scheme makes it easy to analyze the interacting time-dependent excitation of local sites in complex systems involved with light-electron couplings. The present scheme is intended for investigations on the migration dynamics of excited electrons in light-induced energy transfer systems. Through local group analysis of the dynamical electrons, we can obtain an intuitive understanding of the electron transfers between the monomers. This method was implemented in the real time chemical dynamics program suite, RTChem, developed by the author. For the ab initio electronic structure calculation, we used NTCIChem.

References

Formation of small molecules in interstellar space

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The roles of gas-phase and gas-grain processes in the interstellar medium (ISM) are important to know for understanding the chemical evolution of the ISM. In this work we investigate the formation of small molecules through radiative association. In radiative association two species collide and during the collision a photon is emitted, which carries away enough energy that the fragments stick together and end up in a bound state of the forming molecule. The emission of the photon is an improbable event giving small cross sections for molecule formation through radiative association. However, since the ISM is so dilute, energy loss by three-body collisions are even less likely. Thus radiative association can still be an important process for forming new molecules, particularly in dust poor regions.

Successful experimental measurements of radiative association rate constants for small molecules are very few due to the very small cross sections. It is thus of interest to make theoretical calculations to estimate these rate constants. Here we perform quantum dynamical calculations of cross sections and rate constants for the formation of CO [1,2] and HCO [3] through radiative association.

CO and HCO may be important species in the formation of complex organic molecules in space. It has for instance been proposed that a possible route for methanol formation could be [4]

\[ \text{CO} \rightarrow \text{HCO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{H}_3\text{CO} \rightarrow \text{H}_3\text{COH} \]

To investigate the CO → HCO step in this mechanism we employ a recent 3D potential energy surface for HCO which is based on high level ab initio calculations and we perform new ab initio calculations to obtain the 3D dipole moment surfaces that we require. We then perform quantum dynamics calculations for several values of the total angular momentum, but a J-shifting procedure is used to obtain reaction probabilities for additional J-values allowing us to obtain the cross sections and rate constants.

The thermal rate constants that we calculate are so small that the gas-phase H+CO radiative association in a cold interstellar medium cannot be the process in the first step of the sequence shown above leading to the formation of methanol.

The formation of CO by radiative association was calculated both for forming $^{12}\text{CO}$ and $^{13}\text{CO}$. Surprisingly large isotope effects were obtained, which will be mentioned and discussed.

Time permitting I will also bring up recent results on radiative association to form CO$^+$ and (NaH$_2$)$^+$. References

Dynamics of complex-forming bimolecular reactions

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Radical-molecule reactions in which the two reactants can form a van der Waals complex often occur in atmospheric and combustion chemistry. The theoretical description of such reactions is generally based on some version of statistical rate theories, which assume complete randomization of energy within the complex. Dynamical methods can provide more detailed information by revealing what actually happens in the reacting system. Our ultimate goal is to understand the connection between the shape of the potential energy surface and the dynamics of the reaction. We have studied the reactions

\[
\begin{align*}
  \text{CH}_3 + \text{HBr} & \rightarrow \text{CH}_4 + \text{Br} \quad (R1) \\
  \text{OH} + \text{HBr} & \rightarrow \text{H}_2\text{O} + \text{Br} \quad (R2) \\
  \text{OH} + \text{HI} & \rightarrow \text{H}_2\text{O} + \text{I} \quad (R3)
\end{align*}
\]

using the quasiclassical trajectory method. The potential surfaces used are: for reaction R1 the extended version of the potential surface generated by Czakó; for reaction R2 the PES published by Bowman’s group; for reaction R3 a potential surface we calculated using 80,000 ab initio points calculated with the CCSD(T)/R12-aug-ccpVTZ method, including spin-orbit corrections.

In the talk we present the PES for reaction R3 as well as state-resolved excitation functions and rate coefficients for all three reactions. In addition, mass effects will be used to demonstrate the important factors determining the dynamics of these reactions.

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Abstracts of
Short Orals & Posters
Charge and spin collisional dynamics in cold ion-atom systems

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Hybrid systems of laser-cooled trapped ions and ultracold atoms combined in a single experimental setup have recently emerged as a new platform for fundamental research in quantum physics and chemistry [1]. Reaching ultracold s-wave quantum regime is one of the most important challenges in this field at the moment. Unfortunately, the lowest attainable temperatures in experiments using the Paul ion trap are limited by the rf-field-induced heating related to the micromotion [2]. A possible solution to this problem is the use of ion-atom mixtures with the large ion-to-atom mass ratio [2]. The Yb⁺/Li combination is the best candidate among mixtures which allows for straightforward laser cooling of both ions and atoms.

I will present how ab initio quantum chemistry calculations support and guide quantum physics experiments in our experimental-theoretical collaboration with the group of Prof. Rene Gerritsma at the University of Amsterdam. The radiative charger transfer and association losses theoretically predicted for the Yb⁺/Li system to be small [3] were recently experimentally confirmed [4] opening the way for sympathetic cooling and application in quantum simulation [5]. Additionally, we showed and explained that the charge transfer rate constants for ions in excited electronic states are three orders of magnitude larger [4]. Next, we investigated the spin dynamics of single trapped Yb⁺ ions in a cold, spin-polarized bath of ⁶Li atoms [6]. We combined ab initio quantum scattering calculations with the measured spin dynamics and found that even in the mK temperature regime the spin-exchange rate constants still depend strongly on the difference between assumed singlet and triplet scattering lengths. Our results indicated a large difference between the singlet and triplet scattering lengths in Yb⁺/⁶Li, which would be beneficial for the observation of Feshbach resonances [6]. Finally, the first results towards reaching quantum regime of ion-atom collisions and observing collision resonances have recently been obtained.

References

Radiative emission of neutrino pair from atoms and molecules: theoretical estimation of emission spectra
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Neutrinos are the most common particles, next to 3K photons, in the present universe, however some of their properties, including their absolute masses and mass type (Majorana or Dirac), have not yet determined experimentally, because these neutrinos are neutral and interact with the other particles only through the weak interaction. Although the conventional target for exploration of neutrino properties has been nuclei, it has recently been discussed that atoms and molecules may become good targets for determining neutrino parameters such as the neutrino mass type (Majorana or Dirac), and the CP violating phases including Majorana phases [1-3]. Most of these observables are difficult to measure in neutrino oscillation experiments. In this work, we consider deexcitation of atoms or molecules in a metastable level $|e\rangle$ emitting a neutrino pair and a photon; $|e\rangle \rightarrow |g\rangle + \gamma + \nu_i \nu_j$ where $\nu_i$'s are neutrino mass eigenstates. This process exists as a combined effect of second order in the electromagnetic interaction and the weak interaction of the standard electroweak theory, as schematically shown in the figure below. The shape of photon spectra from this process reflect the properties of neutrinos, namely unknown neutrino parameters. In this work, we compute the photon spectra arising from the radiative neutrino pair emission processes of metastable excited states of I$_2$ molecule [4] and Au atom, and will discuss how the spectra shape depend on the neutrino parameters [5].

![Diagram of neutrino emission process](image)

References
[5] This presentation is based on works performed with M. Yoshimura, N. Sasao, M. Ebara, B. Das and other co-workers.
Visualization technique of dynamical reaction pathways: application to non-IRC pathways of SN2 reaction

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[Introduction] The intrinsic reaction coordinate (IRC) is defined as a minimum energy pathway connecting two minimum structures (MINS) via a transition state structure (TS) on the potential energy surface (PES) and gives an intuitive picture of chemical reaction. Recently, the global reaction route mapping (GRRM) strategy has been proposed, which enables us to construct a global reaction route network by exploring the IRC pathways systematically.¹ The global reaction route network for a given molecular system is a useful tool to predict unknown chemical reactions, but there was no attempt to visualize the network into 2- or 3-dimensional coordinate space. Very recently, we employed a classical multidimensional scaling (MDS) method to embed multidimensional data into the lower-dimensional space with preserving their mutual distances as much as possible. The results revealed that classical MDS finds significant principal coordinates which describe structural transformations well without background knowledge.²

In the reaction dynamics fields, ab initio molecular dynamics (AIMD) method without potential functions has been carried out. By following the structural changes along the AIMD trajectories, the dynamical reaction processes can be obtained, but it is not an easy task to grasp an intuitive picture from complicated massive time-series data. In this study, we project the dynamical reaction pathways of AIMD trajectories into 2-dimensional principal coordinate space determined by classical MDS to elucidate the dynamics effects on reaction path picture. The target is the SN2 reaction of OH⁻ + CH₃F → [CH₃OH…F]⁻ for which the previous study shows that 90% of AIMD trajectories starting from TS did not follow the IRC pathway.³ By applying classical MDS to the single IRC pathway, AIMD trajectories are projected into the reaction route map spanned by the 2-dimensional principal coordinates.

[Computational details and results] We calculated the IRC pathway at MP2/6-31+G* level and carried out our AIMD simulations with 50 trajectories from TS to the product region at the same computational level. Fig. 1 shows that 101 structures along the IRC pathway are embedded in 2-dimensional principal coordinate space. By mapping 50 trajectories into this 2-dimensional coordinate space, we can show that 43 trajectories are assigned as direct dissociation pathways, which deviate from the IRC pathway at a large curvature region due to dynamics effects. In this presentation, the details of methodologies and dynamical reaction pathways of trajectories will be presented.

References
Generation of Anharmonic Potential Energy Surface Using SINDO

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We have developed a suite of programs, SINDO, which generates the potential energy surface (PES) of polyatomic molecules based on normal coordinates and solves the vibrational Schrödinger equation with the PES. In this presentation, I will introduce latest updates in the PES generator of SINDO, which has the following features:

2. Generation of a grid PES based on harmonic oscillator DVR. [2]
3. A combination of QFF and grid PES based on a multiresolution method. [3]
5. A portable interface with GAUSSIAN and other ab initio programs to obtain the energy and gradients.
6. Parallel calculations over grid points.

I will show recent applications to vibrational calculations of a protonated water tetramer, H+(H2O)4 [4], and a solute/solvent system and biomolecules based on a PES derived from the QM/MM calculations [5].

References

P 1

Visualization technique of dynamical reaction pathways: application to non-IRC pathways of SN2 reaction

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References

Fig. 1. The IRC pathway of SN2 reaction spanned by two principal coordinates.
Energetics and control of ultracold isotope-exchange reactions between heteronuclear dimers in external fields

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We show that isotope-exchange reactions between ground-state alkali-metal, alkaline-earth-metal, and lanthanide heteronuclear dimers consisting of two isotopes of the same atom are exothermic with an energy change in the range of 1–8000 MHz, thus resulting in cold or ultracold products [1]. For these chemical reactions, there are only one rovibrational and at most several hyperfine possible product states. The number and energetics of open and closed reactive channels can be controlled by the laser and magnetic fields. We suggest a laser-induced isotope- and state-selective Stark shift control to tune the exothermic isotope-exchange reactions to become endothermic, thus providing the ground for testing models of the chemical reactivity (Fig. 1). The present proposal opens the way for studying the state-to-state dynamics of ultracold chemical reactions beyond the universal limit with a meaningful control over the quantum states of both reactants and products.

Fig. 1. (a) Scheme of the state-selective AC Stark shift control. Different levels corresponds to different isotope mixtures (energies are not in scale). (b) The AC Stark shift for different laser detunings vs. the laser field Rabi frequency $\Omega$. (c) Zeeman levels of $^{87}$Rb$_2$ vs. the magnetic field.

References
Study of the HF + C\(^+\) reaction under conditions of astrophysical interest

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The recent detections of CF\(^+\) in galactic and extragalactic regions [1-2] have increased the interest in the fluorine chemistry in the interstellar medium. The CF\(^+\) molecule is formed by the reaction of HF with C\(^+\) [3]. The study of this reaction is the focus of this work. In a first step, a large grid of \textit{ab initio} energies at the MRCI-F12/cc-pVQZ-F12 level of theory was computed. Then, the reactive potential energy surface was fitted using a reproducing kernel Hilbert space based method. Finally, quasi-classical trajectories were employed for determining the reactive rate coefficients from 50 K to 2000 K [4]. The formation of CF\(^+\) in excited vibrational states is also discussed. Furthermore, our results are compared with those reported in the literature.

References


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We present the chaotic dynamics model (CDM) which we have developed recently to go beyond the standard statistical approach for complex-forming atom-diatom reactions. We highlight that the quenching of interferences is less efficient than intuitively expected, leading to asymmetries in state-to-state differential cross sections and marked oscillations in J-resolved reaction probabilities as a function of collision energy.
Theoretical study of the $\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$ reaction.

Potential energy surface, kinetics and dynamics.

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Within the Born-Oppenheimer approximation, to describe the nuclei motion, i.e., stretching, bending, out-of-plane and torsion about the C-C bond, we have developed a full-dimensional analytical potential energy surface for the gas-phase hydrogen abstraction reaction of ethane by hydrogen atom, named PES-2018.\textsuperscript{1} It is a valence-bond/molecular-mechanics surface, with 60 adjustable parameters which are fitted to high-level ab initio calculations of CCSD(T)/aug-cc-pVTZ level and higher. This surface provides the energy of the system and also numerical gradients, i.e., numerical first energy derivatives, it is continuous and leads smoothly from reactants to products by using switching functions, based on hyperbolic tangents. PES-2018 presents a barrier height of 11.62 kcal mol\textsuperscript{-1} and it is practically thermoneutral, -0.18 kcal mol\textsuperscript{-1}, reproducing the ab initio information used as input.

This surface has been used in kinetics and dynamics studies of the title reaction.\textsuperscript{2} Kinetically, using the variational transition-state theory with multidimensional tunnelling corrections, the rate constants obtained reproduce the experimental evidence at high temperatures, with differences of ~25\%, while at low temperatures, where experimental information is not available, tunnelling is responsible of 99\% of reactivity. Dynamically, the excitation function presents the typical behaviour of reactions with barrier and the theoretical results, obtained by using quasi-classical trajectory calculations, simulate the experimental evidence in the energy collision range 10-50 kcal mol\textsuperscript{-1}.

References:


Acknowledgements

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On-the-fly molecular dynamics simulations of the excited-state branching reaction of stilbene derivatives

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Conical intersection (CI) of the potential energy surfaces (PESs) of the adiabatic electronic states plays a significant role in photoreactions. Recent progress in theoretical chemistry has made it feasible to elucidate the mechanism and dynamics of photoreactions involving a nonradiative decay through CIs by the highly sophisticated quantum chemical approaches, ab initio surface hopping molecular dynamics with the nonadiabatic coupling terms [1]. Stilbene (SB) is a typical molecule that shows cis–trans photoisomerisation about the central C=C bond on the $\pi\pi^*$ excitation, and the photoisomerisation process of SB has been investigated by many experimental and theoretical studies. $\pi\pi^*$-excited cis-SB exhibits ultrafast decay to the ground state with a lifetime of around 1.0 ps via the CI points of the singlet excited-state (S1) and ground-state (S0) PESs in the twist region where the central C=C bond is twisted; this is known as the phantom state (P*). Theoretical studies on the decay mechanism of the $\pi\pi^*$-excited cis-SB have confirmed the twisting motion of the central C=C bond in the S1 state, and this motion is known as the "hula-twist". Femtosecond Raman spectroscopy with quantum chemical calculations has clarified the initial nuclear dynamics of the $\pi\pi^*$-excited cis-SB based on the transit change of the vibrational spectra [2]. It is known that $\pi\pi^*$-excited cis-SB has a by-product, 4a,4b-dihydrophenanthrene (DHP). The branching ratio of the products from $\pi\pi^*$-excited cis-SB has been reported to be cis:trans:DHP = 55:35:10. We carried out reaction-path calculations on the S1-PES and on-the-fly molecular dynamics (MD) simulations for the $\pi\pi^*$-excited cis-SB at the spin-flip (SF)-TDDFT level of theory and discussed the reaction mechanism and dynamics [3]. Along the steepest descent pathway starting from the Franck–Condon cis-structure, the two H atoms bound to the central C=C first move quickly so that each C-H-C-H2 fragment in SB becomes planar and the S1-PES becomes very flat; then, the pathway becomes sharply curved toward the DHP-form. It was found that the pathway shows a bifurcation in a very flat region of the S1-PES: one direction is toward the DHP region as the pathway itself indicates, whereas the other is toward the twist region with a very small activation barrier. The branching ratio from the on-the-fly MD simulations on the $\pi\pi^*$-excited cis-SB indicated that the dominant product is trans-SB (trans:DHP = 35:13), which is consistent with the experimental data. This result suggests the importance of dynamics in the photoreaction. In this talk, I introduce our recent theoretical studies on 1,1'-dimethyl-stilbene [4] and $\alpha$-methyl-stilbene [5], and discuss the difference in reaction pathways and dynamics among stilbene and stilbene derivatives.

References
Automated Error Control and Static Electron Correlation Treatment in Divide-and-Conquer Method

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For reducing the computational efforts for quantum chemical calculations of large systems, there have been proposed many fragmentation-based approaches, one of which is the divide-and-conquer (DC) method [1]. In the DC method, each subsystem consists of the disjoint central region and its neighboring region called the buffer region. The energy error introduced by the DC approximation can be systematically decreased by increasing the size of the buffer region. However, the preliminary assessment is required because the appropriate size of the buffer region depends on the system. In this presentation, we will report our recent attempts to automatically determine the buffer region for the self-consistent field (SCF) [2] and second-order Møller–Plesset perturbation (MP2) calculations with controlling the energy error introduced by the DC approximation.

The fragmentation-based linear-scaling methods, including the DC method, have been mainly applied to the SCF and dynamical electron correlation theories. The static electron correlation plays an essential role for modelling bond-dissociation processes, biradicals, and chemical bonds involving transition metal atoms. However, there have been reported only a few attempts to combine the fragmentation-based method with the static correlation theories other than the layered (or embedding) schemes [3]. To enable the static correlation calculations of large systems, we have combined the DC method with the Hartree–Fock–Bogoliubov (HFB) theory [4], which can effectively describe the static correlation within the HF-like protocol [5]. In the presentation, we will also report the energy gradient calculation scheme for the DC-HFB calculations.

References

Theoretical study of static and dynamic reaction pathways on collision reaction of CF$_3^+$ and CO

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【Introduction】 The intrinsic reaction coordinate (IRC) [1] has been widely employed to understand an elementary reaction process in theoretical studies. The IRC is defined as a mass-weighted steepest descent pathway which connects reactant and product minima (MINs) via a transition structure (TS), corresponding to a first order saddle point. For a reaction without TS, such as a dissociation reaction, meta-IRC (defined as a mass-weighted steepest descent pathway from a non-TS geometry) is used as a reaction path. The IRC and meta-IRC are static reaction pathways on the potential energy surface, and the molecular system sometimes deviates from these paths due to its kinetic energy. If the static reaction pathway has a valley-ridge inflection point (which possibly invokes a bifurcation of dynamical trajectory) or a large curvature region on the way, the dynamical effect becomes essential [2]. Since 2004, anharmonic downward distortion following (ADDF) method, one of the automated reaction path search methods, has been developed and extended to various types of chemical reactions [3]. ADDF method can automatically find TSs and dissociation channels (DCs) starting from one MIN structure. By combining ADDF and IRC computations, we can get a global static reaction path network on the PES for a target molecular system. As an experimental approach, a guided ion beam (GIB) study of ion-molecule collision reaction also gives information of the barrier heights of the entire reactions. As to the CF$_3^+$ + CO collision reaction, we found that the GIB experimental result is inconsistent with the calculated global static reaction path network. To clarify the reason for this inconsistency, we investigate the static reaction pathways of the collision reaction of CF$_3^+$ and CO in detail, and also carry out ab initio molecular dynamics (AIMD) simulations to examine dynamic reaction pathways.

【Results and Discussion】 As to the F$_2$CCFO$^+$ isomerization, where the picture of reaction from the IRC was thought to break down, the IRC had some large curvature regions before the TS (Fig. 1.), indicating that the molecular system possibly deviated from the IRC before reaching the TS. AIMD simulations indicated that the molecular system could not go through the large curvature region and turned around. It was shown that most of the AIMD trajectories followed the competing DC. Analyses of the AIMD trajectories based on static reaction pathways [4] were applied to this molecular system to intuitively understand the dynamic reaction pathways and the results will be discussed during the presentation.

【References】

![Fig. 1. Change of reaction path curvature and potential energy of the F$_2$CCFO$^+$ isomerization](image-url)
Understanding the Broadening of the H$_9$O$_4^+$ Infra-Red Spectrum Through Clustering of Path Integral Molecular Dynamics Trajectories

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Developments in infra-red (IR) spectroscopy allow for highly resolved spectra of small protonated water clusters such as H$_9$O$_4^+$ and (H$_2$O)$_{21}$H$^+$. By assigning these spectra using theoretical anharmonic methods further understanding into how the free proton behaves in solution can be gained. Previously we calculated to anharmonic spectrum of the protonated water cluster H$_9$O$_4^+$ [2], shown in the figure 1. While accurate, there are some discrepancies between the broadening profiles. These might be caused by the omission of nine low lying cluster relaxation modes, which are hard to model using rectilinear normal coordinates as were done in the study.

![Fig. 1. The experimental [1] and calculated spectrum of H$_9$O$_4^+$ [2]. The orange labels correspond to motions observed from the H$_3$O$^+$ core of the cluster, while the green are motions of the surrounding waters. The purple labels mark bands which are caused by couplings to low lying cluster relaxation modes. In the current study we aim to model the broadening of the strong feature around 2600-2800 cm$^{-1}$, as well as the broad feature between 1700-1800 cm$^{-1}$ using the Weight Averaged Approach [3] to model the effects of cluster relaxation motions. We use a path integral molecular dynamics trajectory to accurately include the quantum effects of those 9 motions and their correlations with other motions of the cluster. The trajectory is then clustered according to molecular geometry parameters, and the spectrum is calculated for a select number of geometries which are weighted by their occurrence in the trajectory.

References
**Benchmark ab initio study of the X + C\textsubscript{2}H\textsubscript{6} [X = F, Cl, Br, I] systems, dynamics of the X + C\textsubscript{2}H\textsubscript{6} [X = F, Cl] reactions, and PESs for spectroscopy**

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We investigate the thermochemistry of the X + C\textsubscript{2}H\textsubscript{6} [X = F, Cl, Br, I] reactions using high-level *ab initio* methods, *i.e.* augmenting the CCSD(T)-F12b/aug-cc-pVQZ energies by core-correlation, post-CCSD(T) and spin–orbit corrections, focusing on three different reaction pathways: H-abstraction, methyl-substitution, and H-substitution, with the latter two proceeding via either Walden-inversion or front-side-attack mechanisms.\(^1\) On the basis of this study we develop global analytical *ab initio* spin-orbit-corrected potential energy surfaces (PESs) for the Cl and F + C\textsubscript{2}H\textsubscript{6} reactions using the permutationally invariant monomial symmetrization approach (MSA) and an in-house automatic-PES-developer program, called ROBOSURFER. With the analytical PESs at hand we also investigate the dynamics of these two 9-atomic reactive systems using the quasi-classical trajectory (QCT) method. Besides studying the halogen atom + ethane reactions, we also develop analytical *ab initio* PESs for the CH\textsubscript{4}·Ar\textsuperscript{2} and the CH\textsubscript{4}·F\textsuperscript{−} weakly-bound complexes, which PESs are subjects of spectroscopic investigations.

![Diagram](image)

**References**


Algebraic geometric analysis of ADDF paths around one equilibrium

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Chemical reaction is assumed to proceed along some energetically favourable pathway from an equilibrium structure (EQ) to another one. The most famous definition of such pathway is the intrinsic reaction coordinate (IRC)[¹]. The IRC is defined as the steepest descent path from a transition state (TS) to two distinct EQs in mass-weighted coordinates. While it is not the sole possible definition of static reaction path, it has described various chemical reaction processes successfully. However, the understanding of chemical reaction path or the IRC still remains not enough. As mentioned in the beginning, chemical reaction is assumed to proceed from an EQ. So, it is desirable to understand the behaviour of reaction paths starting from an EQ via the properties of the EQ. Unfortunately, the IRC is not suitable for this purpose because its definition depends on not EQ but TS. In order to reveal the relation between EQ’s properties and the behaviour of reaction paths, another definition of reaction pathway is necessary.

One possible candidate of such definition is ADDF path, which is used in the ADDF (Anharmonic Downward Distortion Following) method[²]. ADDF path is the curve given by connecting anharmonic downward distortion (ADD) maxima on contours of the harmonic potential around an EQ. The ADDF method explores TSs and dissociation pathways around an EQ. Since ADDF path is energetically favourable pathway and goes through near the TS[³], it has the potential to describe chemical reaction processes. And most importantly, the direction of ADDF paths around an EQ can be calculated by algebraic method non-iteratively with only the properties of the EQ. We applied this algebraic method to H₂O and showed that ADDF path can be treated as an affine variety in the neighbourhood of an EQ.

Fig.3 shows the ADD maxima on a sphere centred at the EQ with radius 0.3 hartree¹/², which is a contour of harmonic potential in the scaled normal coordinates. These ADD maxima were calculated simultaneously by the algebraic method. Also, we compared the ADDF paths computed algebraically and the actual ADDF paths and confirmed that they almost coincide in the neighbourhood of the EQ.

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Ultracold collisions of alkali-metal and alkaline-earth-metal ions with spin-polarized metastable helium atoms
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Ion-atom mixtures with the large ion-to-atom mass ratio are the most promising systems to reach the quantum regime of ion-atom collisions in experiments using hybrid traps [1]. The helium is one of the lightest atoms. From this perspective, helium in the metastable $^3S$ electronic state is an appealing component of such mixtures. Additionally, the Bose-Einstein condensate of $^4$He$^*$ and Fermi gas of $^3$He$^*$ were obtained. The metastable helium possesses high internal energy leading to it high reactivity, which can be a source of significant trap losses.

In this work, we investigated cold interactions and collisions of He$^*$ with the following ions: Li$^+$, Na$^+$, K$^+$, Rb$^+$, Be$^+$, Mg$^+$, Ca$^+$, Sr$^+$. The closer inspection of possible reaction channels showed that during a collision between lighter ions (Li$^+$, Na$^+$, Be$^+$, Mg$^+$) and He$^*$ the charge transfer process leading to He$^+$($^2S$) and neutral metal atom is energetically possible even assuming spin polarization of the system. Alkaline-earth-metal ions (Be$^+$, Mg$^+$, Ca$^+$, Sr$^+$) are subject to Penning ionization leading to the formation of He ($^1S$) and doubly ionized alkaline-earth metal. Obviously, all systems studied here can be a subject to spin relaxation. In order to evaluate the rate constants of charge transfer collisions, we studied transition dipole moments between relevant electronic states. We also proposed and analyzed prospects for using magnetically tunable Feshbach resonances to control charge transfer and Penning ionization processes.

References

**The effect of phonon modes and electron-hole pair couplings on molecule-surface scattering processes**

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The effect of phonon modes and electron-hole pair (elhp) couplings at different surface temperature for H\textsubscript{2}/D\textsubscript{2} scattering on Cu(111)/Ni(100) surfaces have been explored by assuming weakly correlated interactions between molecular DOFs with surface modes and elhp excitations through a Hartree product type wavefunction, where the initial state distributions for the phonon modes and the elhp couplings are incorporated by using Bose-Einstein and Fermi-Dirac probability factors, respectively. We have carried out four (4Dx2D) and six (6D) dimensional quantum dynamics [1, 2, 3] on such an effective Hamiltonian, and depict the calculated sticking/transition probabilities and energy transfer from molecule to the surface. The phonon modes change the chemisorption process, whereas both phonon and elhp interactions show physically meaningful trend both for reaction as well as transition probabilities with respect to experimental [4, 5] and other theoretical [6] results. We have also performed 6D quantum dynamics on H\textsubscript{2}/D\textsubscript{2}-Cu(111) systems with a chemically accurate potential energy surface build by Static Corrugation Model (SCM) [7], where the normal mode frequency and transformation matrix are calculated either from VASP-SRP48, FBD and EDIM metal-metal potential. The calculated reaction probabilities for H\textsubscript{2}/D\textsubscript{2}-Cu(111) systems are very close with the experimental [4] results.

**References**

Theoretical studies of chemical reactions for biomolecules induced by positron attachment

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Positrons is an antiparticle with mass of an electron but with positive charge. When a positron collides with an electron, pair-annihilation occurs and gamma-rays are emitted. This unique nature has been applied to positron emission tomography (PET) which can probe cancer cells in human bodies. In this application, high energy positrons produced from beta decays are used. Recently collision experiments of low-energy positrons with molecules have been performed due to advances in a positron beam technique. The results of those experiments revealed the existence of resonances associated with vibrationally excited state of positron-attached molecules. However, the dynamics of molecules in an atomic level are poorly elucidated.

In this work, we focus on dynamical mechanisms induced by positron attachment from computational viewpoints. We discuss proline which is one of amino acids shown in Fig.1. We have performed time-dependent quantum wave packet calculations within local complex potential theory to obtain annihilation spectra. Since it is not feasible to perform full-dimensional quantum dynamics calculations, only two nuclear degrees of freedom were considered. Positronic potential energy surface was calculated using multi-component molecular orbital (MC_MO) theory[1].

In fig.2, we displayed the calculated spectrum. In the spectrum, we found several peaks, which are corresponding to the resonance states associated with vibrational excited states in positron-attached proline[2].

Fig.1 Proline molecule

Fig.2 Annihilation spectrum

References
Theoretical Investigation of Spin-Forbidden Mechanism in Simple Chemical Reactions.

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Chemical reaction containing heavy element has generally low-lying electronic states with different spin multiplicities due to higher-order angular momentum orbitals. In this case, spin-inversion (spin-forbidden transition) frequently occurs, where the energies of the two potential energy surfaces with different spin states are close. Thus, the understanding of the mechanism and dynamics of spin-inversion processes is very important in chemistry of heavy elements [1].

It is intuitively difficult to understand the molecular structure at the spin-inversion point. We have recently developed an automated computational algorithm to find the spin-inversion point and applied to the Nb(6D,4F,2G) + C_2H_4 reaction [2]. Fig. 1 shows the potential energy pathway leading to the most stable ^4NbC_2H_2 + H_2 products. Three spin-inversion points have been found, which are mostly associated with hydrogen atom transfer. This suggests that the spin-inversion processes are playing important roles in C–H activation of C_2H_4 by Nb atom.

We have also started a research project on the photodetachment spectrum of GeH_2^- anion (^2B_1) for understanding of spin-inversion between the ^1A_1 and ^3B_1 states of neutral GeH_2. This system is simple, so it is easy to perform full-dimensional nonadiabatic wave packet calculations including spin-orbit coupling.

References
Non-adiabatic ab initio Molecular Dynamics on Ultra-violet Photodissociation of Methylamine

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Methylamine (CH₃NH₂) is a derivative of ammonia (NH₃) and is considered to have the electronic structure similar to NH₃. Ultra-violet photodissociation process of the N-H bond of NH₃ is characterized by non-adiabatic transition which occurs near the conical intersection where the potential energy surfaces of the singlet excited state (S₁) and the singlet ground state (S₀) get close to each other along the reaction path associated with umbrella motion. For CH₃NH₂, C-H bonds, C-N bond and N-H bonds are assumed to be dissociated by ultraviolet light like NH₃, but the detailed dissociation mechanism is still unknown. Reaction yield and branching ratio of products etc. are discussed in experimental research by Reed et al. [1] and Onitsuka et al. [2] On the other hand, in the theoretical study by Morokuma et al. [3], although multiple reaction paths have been proposed by determining the energy correlation diagrams concerning the S₁ and T₁ states, the reaction yield and the branching ratio of products have not been confirmed yet. In this study, we elucidate its reaction mechanism by conducting a theoretical simulation based on non-adiabatic ab initio molecular dynamics for the photodissociation reaction of isolated CH₃NH₂ molecules so as to correspond to the experimental evidence in gas phase.

The ab initio MD simulation incorporating the Zhu-Nakamura TSH method after vertical excitation to the S₁ state was carried out by velocity Verlet method. The quantum chemical calculations were treated at MS-MR-CASPT2 level for 8 electrons in 10 orbitals with the aug-cc-pVDZ basis set. The time step was 1.00 fs, and the maximum time-evolution was 400 fs. The initial condition was determined by random number generation subject to the Wigner distribution. All ab initio calculations were carried out using the electronic structure program Molpro 2012.1.

For temporal evolution of 99 classical trajectories, three types of bond dissociation process appeared, the dissociation of N-H bond, C-H bond, and C-N bond, together with no bond dissociation up to 400 fs. Figure 1 shows the time evolution of potential energies and each bond length. N-H bond dissociation is the most frequent, accounting for 80 % of total; this result agrees well with the experimental data (75 %) by Reed et al [1]. The relaxation lifetime from the S₁ state and the latency time in N-H bond dissociation was calculated to be 119.29 fs and 7 fs, respectively.

References


Figure 1. Time variation of potential energy and bond-length.
Development of efficient time-evolution method based on operator transformation: three-term recurrence-relation method

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Electron dynamics, an ultrafast phenomenon occurring in attoseconds, was recently observed by experiments and has attracted much attention. Real-time propagation (RT) of time-dependent theories have been applied to theoretically describing electron dynamics, such as time-dependent Hartree-Fock (TDHF) method and time-dependent density functional theory (TDDFT) [e.g., 1-5]. However, RT-TDHF/TDDFT calculations are computationally demanding, because time-evolution operator should be evaluated thousands of times by numerical integration such as the Runge-Kutta method. In this study, we developed an efficient time-evolution method based on operator transformation, which is called three-term recurrence-relation (3TRR) method [6]. Simple 3TRR describing time evolution was derived by using operator-transformation with arcsine function, being inspired by the real-wave-packet method [7] for nuclear wave packet dynamics with time-dependent Schrödinger equation. In 3TRR method, it was found that energy and time are also transformed along with the operator transformation. Therefore, back-transformation equations for energy and time were derived to obtain original energy and time. In addition, it was verified that time evolution of 3TRR method has unitarity. We applied 3TRR method to equation of motion for density matrix in RT-THDF/TDDFT. Table 1 shows computational cost of RT-TDHF calculation of small molecules. 3TRR method achieved about four times faster RT-TDHF calculation than conventional fourth-order Runge-Kutta (RK4) method.

Table 1. Computational cost of RT-TDHF/MCP-dzp calculations with 3TRR and RK4 methods.

<table>
<thead>
<tr>
<th>System</th>
<th>Elapsed time [sec]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RK4⁴</td>
<td>3TRR⁵</td>
</tr>
<tr>
<td>H₂</td>
<td>12.6</td>
<td>4.2</td>
</tr>
<tr>
<td>H₂O</td>
<td>63.2</td>
<td>16.9</td>
</tr>
<tr>
<td>CH₂O</td>
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</tr>
<tr>
<td>C₆H₆</td>
<td>24041.7</td>
<td>6087.2</td>
</tr>
<tr>
<td>C₆H₅OH</td>
<td>70845.9</td>
<td>17935.7</td>
</tr>
<tr>
<td>NO₂-C₆H₄-NH₂</td>
<td>414341.7</td>
<td>104221.2</td>
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</tbody>
</table>

⁴Xeon E5-2680 (2.70GHz), 1 core.

References

Ab initio molecular dynamics study of excited-state intramolecular proton transfer and the dissociation of ortho-nitrophenol

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[Introduction] It is known that the ortho-nitrophenol (o-NP) excited to the first excited singlet state (S1) shows excited-state intramolecular proton transfer (ESIPT) from the hydroxyl to the nitro group, and then relaxes into the ground state (S0), by the time-resolved photoemission spectroscopy study combined with quantum chemical calculations [1]. It is also known that o-NP releases OH radical or nitrous acid (HONO) by photoexcitation in the gas phase. Figure 1 shows a scheme of the reaction. Quantum yields of OH and HONO from photolysis of o-NP were measured as OH : HONO = 0.69 : 0.34 at 308 nm and 0.70 : 0.39 at 351 nm [2]. Zhu et al. investigated ESIPT and the subsequent relaxation process to the So state by ab initio molecular dynamics (AIMD) simulations with the global switching algorithm based on the Zhu-Nakamura theory [3]. They concluded that ESIPT takes place in the triplet state through an intersystem crossing from singlet to triplet state. However, the mechanism of the dissociation process including ESIPT is not clear yet. In this study, we aim to elucidate the mechanism of ESIPT and the following dissociation of OH or HONO by AIMD simulation based on multi-configurational wavefunction and multi-reference perturbation theory.

[Results and discussion] To examine the photo-dissociation process of o-NP, the low-lying three singlet and three triplet states were computed at the SA-CASSCF and CASPT2 levels with Sapporo-DZP-2012 basis sets, using Molpro2012. We examined characters of the excited states at the ground state equilibrium structure, using active spaces of n electrons in n orbitals (n = 4, 6, 8, 10). The S1 state is ππ* state for n = 4, 6, 8, while ππ* state for n = 10 at the SA-CASSCF level, but the S1 state is ππ* state for all n at the CASPT2 level. Thus, we concluded that the S1 state of o-NP is ππ* state. AIMD trajectory calculations were started from the Franck-Condon region in the S1 state, with the initial conditions determined by normal mode sampling in the ground state with a temperature of 300 K and with the velocity-Verlet algorithm using SPPR program [4]. In the AIMD simulations, ESIPT was observed in the S1 state in all trajectories with an average time of 39.0 fs after photoexcitation, followed by activations of several vibrational modes. The detailed results of the dissociation process will be discussed in the presentation.

[References]
Quantum molecular dynamics simulations of pure and Ne-doped helium clusters
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Large helium clusters are often used as cryogenic matrix in spectroscopy because they have unique properties such as large zero-point amplitude and bosonic superfluidity. [1–3] Many experimental and theoretical studies have been performed for pure or impurity-doped helium clusters. However, the early stage of ionization dynamics has not understood well. Thus, we performed quantum molecular dynamics for pure and Ne-doped helium clusters (Heₙ, NeHeₙ, n = 40, 100). We used path-integral and ring-polymer molecular dynamics (PIMD and RPMD) because they can efficiently describe nuclear quantum effects of helium motions.

Figure 1 shows the ionization spectra of Heₙ and NeHeₙ (n = 40–100) calculated by the PIMD method. In the energy ranges of 20.5–21.5 eV and 24.0–25.0 eV, Ne and He ionization peaks appeared, respectively. We found that the ionization spectra of NeHeₙ were very similar to those of Heₙ in the energy ranges of 24.0–25.0 eV. The RPMD simulations have also been performed to understand the initial nuclear dynamics through the instantaneous ionization of NeHe₁₀₀.

![Figure 1](image)

Figure 1. Ionization spectra as a function of the binding energy for He₄₀, He₁₀₀ (black line) and NeHe₄₀, NeHe₁₀₀ (blue line).

References
Nonadiabatic ab initio molecular dynamics simulations in solution

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Coulombic interaction energy is inversely proportional to the distance between two charged particles and converges to zero very slowly; a quite large cutoff-radius distance is required to treat molecular dynamics in solution. One of theoretical approaches to solve this problem is the Ewald summation method, which is well-known as a method to divide Coulombic interaction into two series which rapidly converge. One of further developments, the particle-mesh Ewald (PME) summation method, accelerates the original approach by Ewald summation method and is quite popular for MD simulations.

In the present work, the PME summation method was applied to the ONIOM (our Own N-layered Integrated molecular Orbitals and molecular Mechanics, [1]) scheme (PME-ONIOM) for validating the Coulombic interaction in solution. The two different photochemical reactions were actually performed as nonadiabatic ab initio molecular dynamics (MD) simulations with the Zhu-Nakamura trajectory surface hopping (ZN-TSH) method, (i) the photoisomerization of a (Z)-penta-2,4-dieniminium cation (protonated Schiff base, PSB3) in methanol solution, and (ii) the photochromic reaction between 1,3-Cyclohexadiene (CHD) and 1,3,5-cis-Hexatriene (HT) in both hexane and ethanol solvents.

The two different $S_1$ lifetimes of PSB3 were found to be 3.483 ps and 82 fs, which were consistent with the experimental trend [2, 3], moreover the mystery of the product branching ratio could be solved. On the other hand, the high nonpolar-nonpolar affinity between CHD and the solvent was observed in hexane solvent, which definitely affected the $S_1$ lifetimes, the product branching ratio of CHD:HT, and solute (CHD) dynamics. In ethanol solvent, however, the CHD solute was isomerized in the solvent cage caused by the first solvation shell. The photochemical dynamics in ethanol solvent results in the similar property to the process appeared in vacuo (isolated CHD dynamics) [4, 5].

References
Chemical Kinetics under extreme environments: latest news and preview

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Recently experimental and theoretical progress in chemical kinetics are documenting an ample spectrum of phenomena on reactions occurring under conditions has shown that when extended to low temperatures, deviations are observed even with no apparent changes in the chemical mechanism or in the physical nature of the moieties¹. Here, we present and apply a set of exact, phenomenological and first-principles tools to describe temperature dependence of rate constants under extreme conditions. The deviations from linearity in Arrhenius plot leads to distinct regimes, denoted sub-Arrhenius, super-Arrhenius and anti-Arrhenius²: the first two case correspond, respectively, to higher or lower reactivity as temperature decreases, and therefore to a decrease or increase of the apparent activation energy, $E_a$; the last and extreme case arises when the activation energy has negative value. Recent systematic investigations lead to a simple formulation in terms of a single deformation parameter, $d$, denominated as deformed-Arrhenius ($d$- Arrhenius) which is inspired by Tsallis non-extensive statistical mechanics and exploits Euler’s expression of the exponential function as the limit of a succession. We are mainly concerned with illustrating case studies on (i) super-Arrhenius kinetics, including treatment of diffusion and viscosity in supercooling and glass material; temperature dependence of biological rate processes and plasma catalysis³ (ii) sub-Arrhenius kinetics, regarding quantum mechanics proton or atomic hydrogen transfer in chemical reactions of interest in astrochemistry⁴,⁵, astrobiology, and also in atmospheric and industrial applications; and (iii) anti-Arrhenius kinetics, where processes with no energetic obstacles are rate-limited by molecular reorientation requirements, such as documented for OH + HX (X= I and Br)⁶ and in F + HD elementary chemical reactions.

References