I-C Theoretical Studies of Chemical Reaction Dynamics

I-C-1 Quantum Reaction Dynamics of O(^3P) + HCl on a New *ab initio* Potential Energy Surface

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[*J. Chem. Phys.* **113**, 1018 (2000)]

Quantum reaction dynamics of O(^3P) + HCl ↔ OH + Cl is studied by using a new *ab initio* potential energy surface calculated by Ramachandran *et al.* [*J. Chem. Phys.* **111**, 3862 (1999)] The hyperspherical elliptic coordinate approach is applied with an emphasis on elucidating reaction dynamics for J (total angular momentum quantum number) = 0. In terms of the previously established concept that reactive transitions are nothing but vibrationally nonadiabatic transitions at important avoided crossings, clear interpretations are given for the following dynamical features: (i) reactivity depending on potential energy surface topography, (ii) final rotational state distributions for specified initial rovibrational states, and (iii) resonance structures appearing in some reactions. Thermal rate constants are approximately estimated from the present $J = 0$ results by using the J-shift approximation. The present results are compared with our previous ones based on the different potential energy surface calculated by Koizumi-Schatz-Gordon (KSG). The calculated adiabatic potential energy curves of the present new surface have deep wells in the OH + Cl channel in contrast to the KSG potential energy surface. Consequently, the new surface leads to quite different dynamics from those on the KSG surface. Comparisons with the results obtained by quasiclassical trajectory calculations are also made.

I-C-2 Quantum-Classical Correspondence in the O(^3P) + HCl and Cl(^2P) + OH Reactions for Total Angular Momentum J = 0

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[*J. Chem. Phys.* **114**, 1549 (2001)]

A method for carrying out quasiclassical trajectory (QCT) calculations of A + BC(v,j) reactive collisions for the special case of the total angular momentum $J = 0$ is described. Since quantum reactive scattering calculations involving heavier atoms are not straightforward for the $J > 0$ case, this method is useful to establish the extent to which classical mechanics is applicable to a particular reaction. The method is tested by comparing the results of trajectory calculations for the $J = 0$ case with analogous quantum-mechanical (QM) calculations for the O(^3P) + HCl reaction and the reverse reaction Cl(^2P) + OH. The S4 potential surface, which is based on MRCI+Q/cc-pVTZ energies scaled by the scaled external correlation method [B. Ramachandran *et al.*, *J. Chem. Phys.* **111**, 3862 (1999)], is used for these calculations. The QCT and QM cumulative reaction probabilities are found to be in good agreement, especially for the Cl + OH reaction. The agreement between the two types of state-resolved reaction probabilities is less striking but improves considerably as the initial diatomic rotational quantum number j increases. A comparison is also made between the exact and J-shifted QCT thermal rate coefficients. These are found to be in excellent agreement, which is in keeping with similar agreement observed in the case of the quantum-mechanical exact and J-shifted thermal rate coefficients.

I-C-3 Cumulative Reaction Probability and Reaction Eigenprobabilities from Time-Independent Quantum Scattering Theory

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[*Phys. Rev. A* **63**, 042707 (2001)]

The cumulative reaction probability (CRP) is a gross characteristic of rearrangement collision processes defining the reaction rate constant. This paper presents a complete development of the approach to the theory of CRP that we have recently proposed [*Phys. Rev. Lett.* **80**, 41 (1998)]. In the core of this approach lies an alternative expression for CRP in terms of the outgoing wave Green's function which is formally equivalent to the Miller's definition of this quantity in terms of the scattering matrix [*J. Chem. Phys.* **62**, 1899 (1975)] and to the Miller-Schwartz-Tromp formula [*J. Chem. Phys.* **79**, 4889 (1983)], but is direct, in contrast to the former, and more suitable for practical calculations than the latter. Furthermore, our approach rests on solid grounds of time-independent quantum scattering theory and provides an appealing competitive alternative to the absorbing potential formulation given by Seideman and Miller [*J. Chem. Phys.* **96**, 4412 (1992); **97**, 2499 (1992)]. Ideologically, it is close to the approach considered earlier for a one-dimensional model by Manolopoulos and Light [*Chem. Phys. Lett.* **216**, 18 (1993)], but is formulated from scratch for realistic systems with many degrees of freedom. The strongest point of our approach is that its final working formulas are expressed in terms of the Wigner-Eisenbud matrix, so they can be easily implemented on the basis of many existing quantum scattering codes. All these features are discussed and illustrated by calculations of the CRP and reaction eigenprobabilities for two prototypical light atom transfer reactions in heavy-light-heavy triatomic systems in three dimensions for zero total angular momentum.

I-C-4 Photo-Dynamics and Reaction Dynamics of Molecules (Satellite of ICPEC XXI)

MITSUKE, Koichiro; NAKAMURA, Hiroki

[*Comments Atom. Mol. Phys.* **2**, D75 (2000)]

The above-named satellite meeting was held in Okazaki on July 31st to August 2nd, 1999. The scientific program consisted of 21 invited lectures and 32 contributed papers covering various topics of molecular photoionization, photodissociation and chemical reaction dynamics. Several invited papers at this meeting are briefly summarized.

I-C-5 New Implementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory

ZHU, Chaoyuan; NOBUSADA, Katsuyuki[1]; NAKAMURA, Hiroki
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[*J. Chem. Phys.* **115**, 3031 (2001)]

A new implementation of the trajectory surface hopping (TSH) method is proposed to treat multi-dimensional nonadiabatic dynamics by incorporating the analytical Zhu-Nakamura semiclassical theory of nonadiabatic transition. The problem of classically forbidden hops in the TSH method can now be solved and dealt with just as easily as the classically allowed hops by introducing nonvertical hopping techniques. This is made possible, because the theory can treat both classically allowed and forbidden hops accurately in a unified way. The Zhu-Nakamura theory also enables us to predetermine important regions of potential energy surface (PES) before carrying out any dynamics calculations, and thus to save a lot of computational efforts. The charge transfer processes in the collinear H_3^+ system are studied numerically to test the new TSH method. Comparing the new and old versions of TSH with exact quantum calculations, the new method shows much better agreement with the exact calculations. It also works well when all transitions are classically forbidden and the old method fails completely.

I-C-6 Significant Improvement of the Trajectory Surface Hopping Method by the Zhu-Nakamura Theory

ZHU, Chaoyuan; KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki
([1]GUAS)

[*J. Chem. Phys.* in press]

By taking the 3D $D^+ + H_2$ reaction system, the trajectory surface hopping method based on the Zhu-Nakamura theory is demonstrated to work much better than old one and to be very promising to treat high-dimensional electronically nonadiabatic processes. The difference between the new and old survives even at high initial vibrational states and high energies.

I-C-7 Accurate Quantum Dynamics of Electronically Nonadiabatic Chemical Reactions in the DH_2^+ System

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[*J. Chem. Phys.* in press]

Three-dimensional accurate quantum dynamics calculations are carried out for the DH_2^+ system for $J = 0$ (J: total angular momentum quantum number) by the hyperspherical coordinate approach with use of the new potential energy surfaces constructed based on the recent *ab initio* quantum chemical calculations. Not only electronically nonadiabatic reactions, *i.e.* reactive charge transfer processes, but also electronically adiabatic reactions and electronically nonadiabatic non-reactive processes are investigated. Because of the deep well on the electronically adiabatic ground surface, there appear a large number of resonances and the electronically adiabatic reactions are mostly statistical. Nonadiabatic transitions along the potential crossing seam cause deviations from the statistical behaviour and some interesting dynamical features are found.

I-D Theory of Nonadiabatic Transitions

I-D-1 Nonadiabatic Dynamics: Transitions Between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; NAKAMURA, Hiroki
([1]IMS and Russian Acad. Sci.)

[*Phys. Rev. A* **63**, 052710 (2001)]

Nonadiabatic transitions between asymptotically degenerate potential curves are discussed. Both crossing and noncrossing two-coupled-Morse-potential systems are studied semiclassically as well as quantum mechanically. Conditions for the appearance of a nonadiabatic transition are clarified. The case of inverse power potentials at infinity is also analyzed. Expressions of nonadiabatic transition probability are obtained.

I-D-2 Nonadiabatic Transitions due to Curve Crossings: Complete Solutions of the Landau-Zener-Stueckelburg Problems and Their Applications

ZHU, Chaoyuan; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki

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[*Adv. Chem. Phys.* **117**, 127 (2001)]

I. Introduction
II. Physical Significance of Level Crossing
III. Complete Solutions of the Two-State Landau-Zener-Stueckelberg Problems
  A. Brief Historical Survey
  B. Complete Solutions
    1. Landau-Zener Case
    2. Nonadiabatic Tunneling Case
IV. How to Deal with Multichannel and Multidimensional Problems
  A. Multichannel Processes
    1. General Framework
    2. Numerical Applications
  B. Multidimensional Problems
V. Other Models
  A. Exponential Potential Model
  B. Rosen-Zener-Demkov Model ($\beta_1 = \beta_2 = 0$)
  C. Special Cases of Exponential Potential Model ($\beta_1 = (1/\beta_2)$)
  D. Remarks
VI. Time-Dependent Level Crossings
  A. Complete Solutions of the Quadratic Model
  B. Generalizations and Applications
  C. Other Models
VII. New Way of Controlling Molecular Processes by Time-Dependent External Fields
  A. Basic Theory
  B. Control by Laser Field
    1. Landau-Zener Type of Nonadiabatic Transition
    2. Rosen-Zener Type of Nonadiabatic Transition
    3. Exponential Type of Nonadiabatic Transition
VIII. Future Perspectives
  Acknowledgments
  References

I-D-3 New Type of Nonadiabatic Dynamics: Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
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The WKB-type semiclassical analysis is carried out for a two-state model potential system, in whitch two asymptotically degenerate Morse potentials are coupled by an exponential diabatic coupling. Both crossing and non-crossing cases are treated and explicit analytical expressions for the full scattering matrix are obtained. A numerical test demonstrates the accuracy of the theory.

I-E Laser Control of Molecular Processes

I-E-1 Laser Control of Molecular Photodissociation with Use of the Complete Reflection Phenomenon

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[*J. Chem. Phys.* **113**, 6197 (2000)]

A new idea of controlling molecular photodissociation branching by a stationary laser field is proposed by utilizing the unusual intriguing quantum-mechanical phenomenon of complete reflection. By introducing the Floquet (or dressed) state formalism, we can artificially create potential curve crossings, which can be used to control molecular processes. Our control scheme presented here is summarized as follows. First, we prepare an appropriate vibrationally excited state in the ground electronic state, and at the same time by applying a stationary laser field of the frequency we create two nonadiabatic tunneling (NT) type curve crossings between the ground electronic bound state shifted up by one photon energy and the excited electronic state with two dissociative channels. In the NT-type of curve crossing where the two diabatic potential curves cross with opposite signs of slopes, it is known that the complete reflection phenomenon occurs at certain discrete energies. By adjusting the laser frequency to satisfy the complete reflection condition at the NT type curve crossing in one channel, the complete dissociation into the other channel can be realized. By taking one- and two-dimensional models which mimic the HOD molecule and using a wave packet propagation method, it is numerically demonstrated that a molecule can be dissociated into any desired channel selectively. Selective dissociation can be realized even into such a channel that cannot be achieved in the ordinary photodissociation because of a potential barrier in the excited electronic state.

I-E-2 New Way of Controlling Molecular Processes by Lasers

TERANISHI, Yoshiaki[1]; NAGAYA, Kuninobu[2]; NAKAMURA, Hiroki
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[*Adv. in Multi-Photon Processes and Spectroscopy* **14**, R. J. Gordon and Y. Fujimura, Eds., World Scientific, pp. 215–227 (2000)]

Two new ways of controlling molecular processes are proposed. One is to weep laser frequency and/or intensity at avoided crossings among dressed states to control nonadiabatic transitions there. The second is to use the intriguing phenomenon of complete reflection in the nonadiabatic tunneling type transition in the time-independent framework. The newly completed semiclassical theory of nonadiabatic transitions can give a nice analytical formulation for these.

I-E-3 Selective Excitation Among Closely Lying Multi-Levels

NAGAYA, Kuninobu[1]; **TERANISHI, Yoshiaki**[2]; **NAKAMURA, Hiroki**
([1]GUAS; [2]IMS and RIKEN)

[*Laser Control and Manipulation of Molecules*, Amer. Chem. Soc., in press]

A new idea is proposed to accomplish selective and complete excitation to any specified state among closely lying multilevels. The basic idea is to control nonadiabatic transitions among dressed states by sweeping the laser frequency periodically. Both three- and four-level models are treated by the semiclassical theory of nonadiabatic transition and conditions of complete excitation are formulated. Numerical demonstrations are presented in comparison with the π-pulse and adiabatic rapid passage.

I-E-4 Control of Molecular Processes by a Train of Linearly Chirped Pulses: Selective and Complete Excitation

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A new scheme of controlling molecular processes is proposed. The scheme is to manipulate nonadiabatic transitions among Floquet states and can be formulated analytically. Complete selective excitation among closely lying levels and complete electronic excitation of a diatomic molecule are numerically demonstrated. This is proved to be better and more robust compared to the other methods such as the phase-lock and the adiabatic rapid passage. Experimental realizability can also be expected, since linear chirping can be now relatively easily manipulated.

I-F Theory of Multi-Dimensional Tunneling

I-F-1 Practical Implementation of the Instanton Theory for the Ground State Tunneling Splitting

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[*J. Chem. Phys.* **115**, 6881 (2001)]

The instanton theory is reformulated with use of the path integral approach and the WKB approximation to the Schrödinger equation. Both approaches are shown to provide the same results. A new practically useful semiclassical formula is derived for the tunneling splitting of the ground state, which can be implemented for high-dimensional systems. The theory is applicable to systems of arbitrary Riemannian metric and is also supplemented by a practical numerical recipe to evaluate the instanton trajectory, *i.e.* periodic orbit, in multidimensional space. Numerical examples are presented for 3D and 21D systems of HO_2 and malonaldehyde, respectively.

I-G New Methods for Scattering Calculation

I-G-1 Stable and Efficient Evaluation of Green’s Function in Scattering Problem

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[*Comput. Phys. Commun.* **135**, 278 (2001)]

A new methodology similar to the R-matrix propagation technique is invoked to propose the practical recipe for efficiently calculating the Green's function in scattering problem. High accuracy of the proposed approach is demonstrated by taking examples of very deep tunneling and complex-valued nonlocal potential which describes low-energy dissociative attachment process between electron and molecules.

I-G-2 Use of Diabatic Basis in the Adiabatic-By-Sector R-Matrix Propagation Method in Time-Independent Reactive Scattering Calculations

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[*Comput. Phys. Commun.* **140**, 381 (2001)]

We propose a new recipe for the *R*-matrix propagation which combines the ideas of the adiabatic-by-sector (ABS) method and the sequential diagonalization/truncation technique. The *R*-matrix is determined in the adiabatic representation but the method does not require calculations of adiabatic channel functions at radial points inside the sector of propagation. This is a modification of the previously proposed ABS approach and can significantly reduce the computational time and memory in the energy independent part of scattering calculations. The code is checked by a test calculation of the reaction $O(^3P) + HCl \rightarrow OH + Cl$ using a LEPS potential energy surface (PES). The applicability of the method is further demonstrated by accurate quantum calculations of the endoergic reaction $H(^2S) + O_2(^3\Sigma_g^-) \rightarrow OH(^2\Pi) + O(^3P)$.

I-G-3 Regularization of Scattering Calculations at R-Matrix Poles

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Physical quantities of scattering expressed in terms of R-matrix are not well defined at *R*-matrix poles. It is shown that these unphysical singularities can be removed and the regularized expressions are obtained. The method is straightforwardly applicable to various quantities of scattering theory such as reactance matrix, Green’s functions, cumulative reaction probability and density of resonance states.

I-H Theoretical Study of Dissociative Attachment

I-H-1 Study of Dissociative Electron Attachment to HI Molecule by Using R-Matrix Representation for Green’s Function

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The new method of the calculation of scattering Green’s function recently proposed by the authors is applied to the process of dessociative attachment of low-energy electrons to HI molecule previously considered by Horáček, Domcke and Nakamura. The calculation is extended to vibrationally and rotationally excited target gas molecules. The temperature dependence of the dissociative attachment cross section is studied in details.