I-F Theory of Nonadiabatic Transition

I-F-1 Non-Adiabatic Transitions in a Two-State Exponential Potential Model

PICHL, Lukas[1]; OSHEROV, Vladimir I.[2]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and Inst. Chem. Phys., Russia)

[*J. Phys. A: Math. Gen.* **33**, 3361 (2000)]

A general two-state exponential potential model is investigated and the corresponding two-channel scattering problem is solved by means of semiclassical theory. The analytical expression for the non-adiabatic transition matrix yields a unified expression in the repulsive and previously studied attractive case. The final formulae are expressed in terms of model-independent quantities, *i.e.* the contour integrals of adiabatic local momenta. Oscillations of the overall transition probability below the crossing of diabatic potentials are observed in the case of strong coupling. The theory is demonstrated to work very well even at energies lower than the diabatic crossing region. Based on our results the unified theory of non-adiabatic transitions, covering the Landau-Zener-Stueckelberg and Rozen-Zener-Demkov models in such an energy range, is possible.

I-F-2 Complete Solutions of the Landau-Zener-Stueckelberg Curve Crossing Problems, and Their Generalizations and Applications

NAKAMURA, Hiroki

[*The Physics of Electronic and Atomic Collisions*, Y. Itikawa *et al.* Eds., Am. Inst. Phys., 495 (2000)]

The compact analytical complete solutions recently obtained for the two-state Landau-Zener-Stueckelberg problems are reviewed and explained. The theory covers both Landau-Zener (LZ) type in which the two diabatic potential curves cross with the same sign of slopes and the nonadiabatic tunneling (NT) type in which the potentials cross with different signs of slopes. The theory is applicable virtually in the whole range of energy and coupling strength and is convenient for practical use. The new theory for time-dependent nonadiabatic transition can be formulated from the time-independent theory of the LZ-type. The utilizability of the theory to various multi-channel problems and also to multi-dimesional problems is demonstrated and explained. The intriguing phenomenon of complete reflection which appears in the NT-case is explicitly utilized to propose a new type of molecular switching and to control molecular processes such as molecular photodissociation. Also proposed is a new way of controlling molecular processes by using time-dependent external fields. Finally, a trial to formulate a unified analytical theory to cover both Landau-Zener-Stueckelberg and Rosen-Zener-Demkov types of nonadiabatic transitions is briefly touched upon.

I-F-3 Complete Reflection in Two-State Crossing and Noncrossing Potential Systems

PICHL, Lukas[1]; NAKAMURA, Hiroki; HORACEK, Jiri[2]
([1]GUAS; [2]IMS and Charles Univ.)

[*J. Chem. Phys.* **113**, 906 (2000)]

A semiclassical study is made for the complete transmission and the complete reflection phenomena in two coupled molecular potential systems. The conditions for these phenomena to occur are expressed analytically in terms of nonadiabatic transition probabilities and phase integrals, which can be provided by the semiclassical theory. We also introduce an exactly solvable analytical model of diabatically avoided crossing, in which two diabatic potentials coupled by a constant coupling are close together in a certain spatial region. These models and phenomena may be useful in controlling various molecular processes in laser fields, since in the dressed or Floquet state formalism molecular potentials can be shifted up and down and are made to cross or avoid crossing with other potentials.

I-F-4 Nonadiabatic Transitions due to Curve Crossings: Complete Solutions of the Landau-Zener-Stueckelberg Problems and Their Applications

ZHU, Chaoyuan; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Phys. Chem. Res.)

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

I. Introduction
II. Physical Significance of Level Crossing
III. Complete Solutions of the Two-State Landau-Zener-Stueckdberg Problems
    A. Brief Historical Survey
    B. Complete Solutions
        (1) Landau-Zener Case
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IV. How to Deal with Multi-Channel and Multi-Dimensional Problems
    A. Multi-Channel Processes
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        (2) Numerical Applications
    B. Multi-Dimensional Problems
V. Other Models
    A. Exponential Potential Model
    B. Rosen-Zencr-Demkov Model
    C. Special Cases of Exponential Potential Model
    D. Remarks
VI. Time-Dependent Level Crossings
    A. Complete Solutions of the Quadratic Model
    B. Generalizations and Applications
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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

I-F-5 New Type of Nonadiabatic Dynamics: Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Chem. Phys., Russia)

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

I-G Theoretical Studies of Chemical Reaction Dynamics

I-G-1 Electronically Adiabatic Chemical Reactions Analyzed by the Semiclassical Theory of Nonadiabatic Transition

ZHU, Chaoyuan; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[1]
([1]Hokkaido Univ.)

[*Phys. Chem. Phys.* **2**, 557 (2000)]

The previously proposed qualitative conceptualization of heavy-light-heavy (HLH) chemical reactions on a single potential energy surface (PES) as vibrationally nonadiabatic transitions at avoided crossings along the potential ridge lines is confirmed and further extended. An analytical as well as quantitative analysis of three-dimensional HLH reactions is carried out by applying the new semiclassical theory of nonadiabatic transition established by Zhu and Nakamura. About one thousand avoided crossings which appear in the sea of adiabatic potential curves obtained in the hyperspherical coordinate approach are classified into relevant and irrelevant ones for reactive transitions by introducing a certain diabatic decoupling procedure based on the dimensionless parameter of the new semiclassical theory. Thus about one hundred of three kinds of avoided crossings relevant for reactive transitions are specified and treated analytically. The cumulative reaction probabilities can be quite nicely reproduced quantitatively. This indicates that the clarification and conceptualization of reaction mechanisms can be done even analytically. State-to-state reaction processes can be qualitatively nicely comprehended as before, but cannot be quantitatively well reproduced, simply because inelastic transitions are not necessarily localized and cannot be well comprehended in terms of nonadiabatic transitions due to avoided crossings. An interesting series of avoided crossings responsible for rotationally inelastic transitions are found at energy lower than the threshold of reaction in the case of exo- or endoergic reaction.

I-G-2 Quantum Reaction Dynamics of O(^{3}P) + HCl on a New Ab Initio Potential Energy Surface

NOBUSADA, Katsuyuki[1]; NAKAMURA, Hiroki; LIN, Yongjing[2]; RAMACHANDRAN, B.[2]
([1]Hokkaido Univ.; [2]Louisiana Tech. Univ.)

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

Quantum reaction dynamics of O(^{3}P) + 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-Cordon (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-G-3 Quantum-Classical Correspondence in the O(^{3}P) + HCl and Cl(^{2}P) + OH Reactions for Total Angular Momentum $J = 0$

LIN, Yongjing[1]; RAMACHANDRAN, B.[1]; NOBUSADA, Katsuyuki[2]; NAKAMURA, Hiroki
([1]Lousiana Tech. Univ.; [2]Hokkaido Univ.)

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, E. A. Schrader III, J. Senekowitsch and R. E. Wyatt, *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-G-4 New Implementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory

ZHU, Chaoyuan; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[1]
([1]Hokkaido Univ.)

The Zhu-Nakamura theory, the complete set of analytical solutions of the Landau-Zener-Stueckelberg curve crossing problems, can be applied to multi-dimensional reaction dynamics involving electronically nonadiabatic transitions due to potential energy surface crossings. The theory can be incorporated into various types of semiclassical propagation methods such as the trajectory surface hopping method, the semiclassical method with use of the initial value representation and the cellular frozen Gaussian propagation method. Even the phases due to nonadiabatic transition are provided by the Zhu-Nakamura theory and can be taken into account. The simplest application of the theory is the usage of nonadiabatic transition probability in the trajectory surface hopping method. Even the classically forbidden transitions can be properly treated. First application is made to the collinear H_3^+ reaction system and shows very encouraging good agreement with the quantum mechanical results.

I-G-5 Diabatic Slow Variable Discretization Approach in Time-Independent Reactive Scattering Calculations

MIL'NIKOV, Gennady V.[1]**; NAKAMURA, Hiroki**
([1]IMS and Inst. Struct. macrokinetics, Russia)

We propose a new recipe for the R matrix propagation which combines advantages of the slow Variable Discretization (SVD) and the diabatic-by-sector approach. Within the framework of the hyperspherical coordinate approach this novel scheme allows us to avoid calculations of surface functions for most of the DVR (discrete variable representation) radial points, which significantly reduces the computational time and required memory with the simplicity and the accuracy of the SVD preserved. The properties of the R-matrix propagation as a variational procedure are discussed to justify a proper choice of numerical parameters. This 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-6 Quantum Dynamics in the DH_2^+ Reaction System

KAMISAKA, Hideyuki[1]**; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki**[2]
([1]GUAS; [2]Hokkaido Univ.)

As one of the typical electronically nonadiabatic chemical reactions, we have carried out quantum mechanically accurate calculations of the title system. The potential energy surface used is an analytical fit of the new ab initio calculations done by Ichihara *et al*. For the quantum dynamics the hyperspherical elliptic coordinate system is employed. At low energies where only the electronically adiabatic processes occur, the overall feature can be explained by the statistics basically because of the deep potential well in the ground electronic potential surface. There appears, however, an interesting deviation from the statistics in the case of electronically nonadiabatic reactions.

I-H New Way of Controlling Molelular Processes

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

NAGAYA, Kuninobu[1]**; TERANISHI, Yoshiaki**[2]**; NAKAMURA, Hiroki**
([1]GUAS; [2]Inst. Phys. Chem. Res.)

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

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 ω we create two nonadiabatic tunneling (NT) type curve crossings between the ground electronic bound state shifted up by one photon energy ħω 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-H-2 New Way of Controlling Molecular Processes by Lasers

TERANISHI, Yoshiaki[1]; NAGAYA, Kuninobu[2]; NAKAMURA, Hiroki
([1]Inst. Phys. Chem. Res.; [2]GUAS)

[*Quantum Control of Molecular Reaction Dynamics*, R. J. Gordon and Y. Fujimura Ed., World Scientific, in press]

Control of molecular processes by lasers has attracted much attention recently, and several schemes have been proposed such as coherent control, pump-dump method, pulse-shape driven method, adiabatic rapid passage with linear chirp, and π-pulse. Considering the importance of nonadiabatic transitions due to curve crossing not only in ordinary molecular processes but also in molecular processes induced by lasers, we have proposed a new way of controlling nonadiabatic transitions by sweeping laser frequency and/or intensity at curve crossings among the dressed (or Floquet) states. By using the newly developed time-dependent theory of nonadiabatic transitions, we can analytically formulate appropriate control conditions. On the other hand, the intriguing phenomenon of complete reflection in the nonadiabatic tunneling (NT) type transition in the time-independent framework has been utilized to propose a new mechanism of molecular switching and a new possibility of controlling molecular photodissociation. These new ideas are briefly reviewed in this report.

I-I New Methods to Treat Scattering Problems

I-I-1 Analytical Treatment of Singular Equations in Dissociative Recombination

PICHL, Lukas[1]; NAKAMURA, Hiroki; HORACEK, Jiri[2]
([1]GUAS; [2]Charles Univ.)

[*Comput. Phys. Commun.* **124**, 1 (2000)]

The Lippmann-Schwinger type singular integral equation, which arises in the multi-channel quantum defect theory of dissociative recombination process, is investigated. The singularity of its kernel is treated analytically by introducing an energy dependent quadrature. In many cases of physical interest the energy-dependent coupling potential, which gives the integral kernel of the equation, is quasi-separable in a way that allows to write down an analytical solution. The analytical treatment as well as the new solution are illustrated by taking the H_2^+ as an example. Our method is demonstrated to be much better than the conventional ones, such as the first order perturbation theory and the grid method.

I-I-2 Stable and Efficient Evaluation of Green's Function in Scattering Problem

MIL'NIKOV, Gennady V.[1]; NAKAMURA, Hiroki; HORACEK, Jiri[2]
([1]IMS and Inst. Struct. macrokinetics, Russia; [2]IMS and Charles Univ.)

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-J Theoretical Study of Multi-Dimensional Tunneling

I-J-1 Theoretical Study of Multidimensional Proton Tunneling in the Excited State of Tropolone

WOJCIK, Marek J.[1]; NAKAMURA, Hiroki; IWATA, Suehiro; TATARA, Wiktor[1]
([1]Jagiellonian Univ.)

[*J. Chem. Phys.* **112**, 6322 (2000)]

Ab initio CIS/6-3lG** and CIS/6-3l ++G** calculations have been carried out in the $\tilde{A}$-state of tropolone for the stable and saddle point structures. The calculated energies and geometries have been compared with the previous results of Vener *et al.* The energy barrier for the proton tunneling amounts to 12.0 kcal/mol from the CIS/6-31G** calculations, and l3.0 kcal/mol from the CIS/6-31++G** calculations. The normal mode frequencies have been computed including modes coupled to the proton tunneling mode. Two-dimensional and three-dimensional model potentials, formed from symmetric mode coupling potential and squeezed double well potential, have been fitted to the calculated energy barrier, geometries, and frequencies, and used to analyze proton dynamics. The calculated energy splittings for different vibrationally excited states have been compared with the available experimental data. The CIS/6-3l ++G** calculation gives good estimation of the tunneling energy splitting in the vibrationally ground state of tropolone. The model PES explain monotonic decrease in tunneling splittings with the excitation of the out-of-plane modes, however underestimate the actual splittings. The increase of the tunneling splitting with the excitation of the v_{13} and v_{14} modes is qualitatively correct.