I-D Applications of the Zhu-Nakamura Theory to Electronically Nonadiabatic Chemical Reactions

I-D-1 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.* **115**, 11036 (2001)]

By taking the three-dimensional $D^+ + H_2$ reaction system, the trajectory surface hopping method based on the Zhu-Nakamura theory is demonstrated to work much better than the 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-D-2 New Inplementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory. II. Application to the Charge Transfer Processes in the 3D DH_2^+ System

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

[*J. Chem. Phys.* **116**, 3234 (2002)]

The newly implemented trajectory surface hopping (TSH) method for the collinear system with use of the Zhu-Nakamura semiclassical theory of nonadiabatic transition [C. Zhu, K. Nobusada, and H. Nakamura, *J.Chem.Phys.* **115**, 3031 (2001)] is extended to treat 3D nonadiabatic reactions. Since the avoided crossing seam becomes a two-dimensional surface in the 3D system, the nonadiabaric transition region and the possibility of classically forbidden hops are enlarged very much in comparison with those in the collinear case. As a result, the contribution of the classically forbidden hops is quite a bit enhanced in the 3D system. Conservation of total angular momentum J is taken into account by slightly rotating the direction of momentum during the hop in the classically forbidden case. The method is tested by applying to the charge transfer processes in the 3D DH_2^+ system for $J = 0$. Numerical results clearly demonstrate that the new TSH method works very well at all energies and for all initial vibrational states considered compared to the old TSH method based on the Landau-Zener formula. The significant discrepancy between the two THS methods survives even at high collision energy and high vibrational states in contrast to the collinear case, indicating the importance of the classically forbidden hops in 3D systems. The new TSH method is considered to be a very promising method to deal with high dimensional nonadiabatic dynamics. It should also be noted that the new TSH method does not require any knowledge of nonadiabatic coupling and is based only on adiabatic potentials.

I-D-3 Elucidations of Nonadiabatic Tunneling Type and Conical Intersection Type Reactions with Use of the Zhu-Nakamura Theory

ZHU, Chaoyuan; MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

Based on the model 3D potential energy surfaces, electronically nonadiabatic chemical reaction dynamics are investigated with use of the Zhu-Nakamura theory. The trajectory surface hopping method and the IVR type semiclassical propagation method are employed. The dynamics are compared with the exact quantum computations and also with the usage of the Landau-Zener formula. It is aimed to develop a practically useful methodology applicable to multi-dimensional dynamics.

I-E Theory of Nonadiabatic Transitions

I-E-1 Nonadiabatic Transition: Concepts, Basic Theories and Applications

NAKAMURA, Hiroki

[*Nonadiabatic Transition: Concepts, Basic Theories and Applications* World Scientific / Imperial College Press; Singapore (2002)]

Chapter 1	Introduction: What is “Nonadiabatic Transition” ?
Chapter 2	Multi-Disciplinarity
Chapter 3	Historical Survey of Theoretical Studies
Chapter 4	Background Mathematics
Chapter 5	Basic Two-State Theory for Time-Independent Processes
Chapter 6	Basic Two-State Theory for Time-Dependent Processes
Chapter 7	Two-State Problems
Chapter 8	Effects of Dissipation and Fluctuation
Chapter 9	Multi-Channel Problems
Chapter 10	Multi-Dimensional Problems
Chapter 11	Complete Reflection and Bound States in the Continuum
Chapter 12	New Mechanism of Molecular Switching
Chapter 13	Control of Nonadiabatic Processes by an

External Field
Chapter 14 Conclusions: Future Perspectives
Appendix A Final Recommended Formulas for General Time-Independent Two-Channel Problem
Appendix B Time-Dependent Version of the Zhu-Nakamura Theory

I-E-2 Semiclassical Theory of Nonadiabatic Transition and Tunneling

ZHU, Chaoyuan; MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

[*Modern Trends in Chemical Reaction Dynamics* K. Liu and X. Yang, Eds., Advanced Series in Physical Chemistry, World Scientific (2003)]

1. Intruduction
2. Zhu-Nakamura Theory
   - 2.1 Summary of the theory
   - 2.2 Landau-Zener type
   - 2.3 Nonadiabatic tunneling type
   - 2.4 Time-dependent version
   - 2.5 Other types of nonadiabatic transitions
3. Applications to Multi-Channel Problems
   - 3.1 Various problems and numerical applications
   - 3.2 Control of molecular processes by external fields
4. Electronically Adiabatic Chemical Reactions
5. Electronically Nonadiabatic Chemical Reactions
   - 5.1 New implementation of the TSH method by the Zhu-Nakamura theory
   - 5.2 Charge transfer processes in the DH_2^+ system
6. Multi-Dimensional Tunneling
   - 6.1 Three types of problems and effects of multi-dimensionality
   - 6.2 Powerful theory for multi-dimensional tunneling
7. Future Perspectives

I-E-3 Analytical Solutions to Wave Packet Dynamics in a Laser Field

NAKAMURA, Hiroki

Analytical solutions are obtained for the nonadiabatic transition between two linear potentials in coordinate space coupled by a time-dependent laser field within the framework of the dressed-state (or Floquet) representation. This can provide a basis for the analysis of wave packet dynamics in a chirped laser field.

I-F Quantum Dynamics of Chemical Reactions

I-F-1 Accurate Quantum Dynamics of Electronically Nonadiabatic Chemical Reaction in the DH_2^+ System

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

[*J. Chem. Phys.* **116**, 654 (2002)]

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 nonreactive 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 behavior and some interesting dynamical features are found.

I-F-2 Chemical Reactions in the O(^1D) + HCl System I. Ab Initio Global Potential Energy Surfaces for the $1^1A'$, $2^1A'$, and $1^1A''$ States

NANBU, Shinkoh; KAMISAKA, Hideyuki[1]; BIAN, Wensheng; AOYAGI, Mutsumi[2]; TANAKA, Kiyoshi[3]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and Kyushu Univ.; [3]Hokkaido Univ.)

[*J. Theor. Comp. Chem.* in press]

New global *ab initio* potential energy surfaces (PES) are presented for the low-lying $1^1A'$, $1^1A''$ and $2^1A'$ electronic states which are correlated to O(^1D) + HCl. These potential energy surfaces are computed by using the multi-reference configuration interaction method with the Davidson correction (MRCI+Q). The reference functions are constructed by the complete active space self-consistent field (CASSCF) calculations using the quadruple zeta + polarization basis set augmented with diffuse functions. The computations are carried out at about 5000 molecular conformations on each three-dimentional potential energy surface. The high accuracy of the computations is confirmed by a comparison with the available most accurate data for the ground state $1^1A'$; thus the present work is the first report of the accurate potential energy surfaces for the two excited states. Three low-lying transition states on the excited surfaces, two (TS2 and TS4) on $1^1A''$ and one (TS3) on $2^1A'$, are found. Since TS2 and TS3 are as low as 0.07 eV and 0.28 eV, respectively, and correlate to the OH($^2\Pi$) + Cl(^2P) product, these excited surfaces are expected to play quite important roles in the reaction dynamics. Possible effects of nonadiabatic couplings among the three PESs are also briefy discussed, although the nonadiabatic couplings have not yet been estimated. The quantum reaction dynamics on these three PESs are discussed in the second accompanying paper.

I-F-3 Chemical Reactions in the O(^1D) + HCl System II. Dynamics on the Ground $1^1A'$ State and Contributions of the Excited ($1^1A''$ and $2^1A'$) States

KAMISAKA, Hideyuki; NANBU, Shinkoh; BIAN, Wensheng; AOYAGI, Mutsumi[1]; TANAKA, Kiyoshi[2]; NAKAMURA, Hiroki
([1]IMS and Kyushu Univ.; [2]Hokkaido Univ.)

[*J. Theor. Comp. Chem.* in press]

Using the accurate global potential energy surfaces for the $1^1A'$, $1^1A''$, and $2^1A'$ states reported in the previous sister paper I, detailed quantum dynamics calculations are performed for these three adiabatic surfaces separately for $J = 0$ (J: total angular momentum quantum number). Overall reaction probabilities for O + HCl → OH + Cl and H + ClO, the branching ratio between the two reactions, effects of the initial rovibrational excitation, and product rovibrational distributions are evaluated in the total energy region $E_{tot} \leq 0.9$ eV. Significant contributions to the overall reaction dynamics are found from the two excited $1^1A''$ and $2^1A'$ potential energy surfaces, clearly indicating the insufficiency of the dynamics only on the found $1^1A'$ surface. The detailed dynamics on the excited surfaces are reported in the third paper of this series.

I-F-4 Chemical Reactions in the O(^1D) + HCl System III. Quantum Dynamics on the Excited ($1^1A''$ and $2^1A'$) Potential Energy Surfaces

KAMISAKA, Hideyuki; NANBU, Shinkoh; BIAN, Wensheng; AOYAGI, Mutsumi[1]; TANAKA, Kiyoshi[2]; NAKAMURA, Hiroki
([1]IMS and Kyushu Univ.; [2]Hokkaido Univ.)

[*J. Theor. Comp. Chem.* in press]

Using the accurate global potential energy surfaces for the $1^1A''$ and $2^1A'$ states reported in the previous sister paper I, detailed quantum dynamics calculations are performed for these adiabatic surfaces separately for $J = 0$ (J: total angular momentum quantum number). In addition to the significant overall contributions of these states to the title reactions reported in the second paper II of these series, quantum dynamics on these excited potential energy surfaces (PES) are clarified in terms of the PES topographies, which are quite different from that of the ground PES. The reaction mechanisms are found to be strongly selective and nicely explained as vibrationally nonadiabatic transitions in the vicinity of potential ridge.

I-F-5 Use of Diabatic Basis in the Adiabatic-by-Sector R-Matrix Propagation Method in Time-Independent Reactive Scattering Calculations

MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

[*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 → 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 Laser Control of Molecular Processes

I-G-1 Control of Photodissociation Branching Using the Complete Reflection Phenomenon: Application to HI Molecule

FUJISAKI, Hiroshi; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki
([1]IMS and JAERI)

[*J. Theor. Comp. Chem.* in press]

The laser control of photodissociation branching in a diatomic molecule is demonstrated to be effectively achieved with use of the complete reflection phenomenon. The phenomenon and the control condition can be nicely formulated by the semiclassical (Zhu-Nakamura) theory. The method is applied to the branching between I($^2P_{3/2}$) (HI → H + I) and I*($^2P_{1/2}$) (HI → H + I*) formation, and nearly complete control is shown to be possible by appropriately choosing an initial vibrational state and laser frequency in spite of the fact that there are three electronically excited states involved. Numerical calculations of the corresponding wavepacket dynamics confirm the results.

I-G-2 Control of Molecular Processes by a Sequence of Linearly Chirped Pulses

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2];

NAKAMURA, Hiroki
([1]IMS and Univ. Sherbrooke; [2]IMS and JAERI)

A new scheme of controlling molecular processes by a sequence of linearly chirped pulses is proposed and is applied to selective excitation of an energy level among closely lying ones and to complete electronic excitation of a diatomic molecule. The basic idea is quite different from the conventional ones utilizing chirped pulses in the sense that the present one does not rely on the idea of adiabatic rapid passage at all, but tries to control basic nonadiabatic transitions explicitly. Control of molecular processes can be achieved by controlling nonadiabatic transitions among Floquet (or dressed) states with use of the interference effects. The scheme can be formulated with use of the analytical theories of nonadiabatic transitions, and the proper control parameters can be estimated theoretically. Numerical demonstrations are provided to confirm the robustness of the method in comparison with the other conventional ones. Namely, the present scheme is shown to be stable against the variation of pulse area, complete and selective in population transfer, and fast to accomplish the transition. It is expected that the method can be applied to general multi-level systems and various types of wave packet dynamics. Its experimental realizability can also be expected, since linear chirping can now be relatively easily realized and manipulated.

I-G-3 Selective Excitation among Closely Lying Multi-Levels

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]IMS and Univ. Sherbrooke; [2]IMS and JAERI)

[*Laser Control and Manipulation of Molecules* A. Bandrauk, R. J. Gordon and Y. Fujimura, Eds., ACS Symposium Series 821, American Chemical Society (2002)]

A new idea is proposed to accomplish selective and complete excitation to any specified state among closely lying multi-levels. 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-G-4 Photodissociation of H_2^+ and HD^+ in an Intense Laser Field

KONDORSKIY, Alexey[1]; NAKAMURA, Hiroki
([1]IMS and Lebedev Phys. Inst., Russia)

The photodissociation of H_2^+ and HD^+ by an intense laser pulse is investigated by solving the close-coupling equations without discretization. For the case of H_2^+ the photodissociation spectra are calculated under the condition mimicking the experimental one and a fairly good agreement with the experiment is obtained. The uncertainty in the relative phases of initial states is found to lead to somewhat of smoothing of the spectra, depending on the pulse length. It is also found that Raman type transitions via intermediate dissociation continuum play an important role in determining the photodissociation spectra. This leads to a population increase of lower vibrational states and deforms the spectral profile. Dissociation from the lower vibrational states due to the bond softening is not strong enough.

Photodissocitaion spectra and angular distribution are calculated also for HD^+ under the same conditions as in the H_2^+ case. The dipole transitions lead to additional structures in the energy spectra and angular distribution. There is a noticeable difference in the peak positions of dissociation spectrum for particles dissociated by the direct electronic dipole transition and by the transitions *via* intermediate bound states.

The photodissociation dynamics is further clarified by using the three-dimensional plots of the spectra as a function of the field intensity and frequency.

I-H Theory of Multi-Dimensional Tunneling

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

MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

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

The instanton theory is reformulated with use of the path integral approach and the Wentzel-Kramers-Brillouin 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 three-dimensional (3D) and 21D systems of HO_2 and malonaldehyde, respectively.

I-H-2 Instanton Theory for Multi-Dimension Decay through Tunneling

MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

In our recent publication, we have formulated a practically efficient theory for the tunneling splitting of the ground state. The final result is applicable to large dimensional systems with an arbitrary metric system. The idea can be generalized to be applied to decay of a metastable state through tunneling. An efficient method to find an instanton path and a canonically invariant expression of the decay rate can be formulated. The final result can be applied virtually to any high dimensional systems.

I-I New Methods for Scattering Calculations

I-I-1 Regularization of Scattering Calculations at *R*-Matrix Poles

MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

[*J. Phys. B: At,. Mol. Opt. Phys.* **34**, 791 (2001)]

Physical quantities of scattering expressed in terms of the *R*-matrix are not well defined *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 scattering theory quantities such as the reactance matrix, the Green function, the cumulative reaction probability and the density of resonance states.

I-I-2 Calculation of Resonances *via* the *R*-Matrix Method

MIL'NIKOV, G. V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia)

Using the new spectral representation of Green's function previously proposed by us [*Comput. Phys. Commun.* **135**, 278 (2001)], we calculate the density of states and extract parameters of resonances in scattering system. The method is implemented for the resonances in $dt\mu$ molecule below $t\mu(n = 2)$ threshold.

I-J Theoretical Studies of Dissociative Attachment and Dissociative Recombination

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

KOLORENČ, P.[1]; ČÍŽEK, M.[1]; HORÁČEK, J.[1]; MIL'NIKOV, G. V.[2]; NAKAMURA, Hiroki
([1]Charles Univ., Czech Republic; [2]IMS and Inst. Struct. Macrokinetics, Russia)

[*Physica Scripta.* **65**, 328 (2002)]

The new method of calculation of scattering Green's function recently proposed by the authors (G. V. Mil'nikov, H. Nakamura and J. Horáček, *Comput. Phys. Commun.* **135**, 278 (2001)) is applied to the process of dissociative attachment of low-energy electrons to HI molecule previously considered by Horáček, Domcke and Nakamura (*Z. Phys. D* **42**, 181(1997)). The calculation is extended to vibrationally and rotationally excited targets gas molecules. The temperature dependence of the dissociative attachment cross section is determined.

I-J-2 Analytical Treatment of the *K*-Matrix Integral Equation in the Dynamics of Superexcited Molecules

PICHL, Lukas[1]; HIYAMA, Miyabi[2]; NAKAMURA, Hiroki
([1]Aizu Univ.; [2]Univ. Tokyo)

Superexcited states (SES) constitute one peculiar class of electronically highly excited states of molecules whose internal energies exceed the corresponding lowest ionization potentials. They play important roles in various fields of chemistry and physics as intermediate states of dynamic processes. It is crucial to understand the characteristics of the central SES in order to systematically comprehend the various dynamic processes. Dissociative recombination represents one of good typical examples. According to the difference in the autoionization mechanisms the SESs are classified into the following two kinds:(i) multiply or inner-shell excited state, which is called "SES of the first kind," and (ii) rovibrationally excited Rydberg state, which is called "SES of the second kind." The dynamics of SES are governed by the two basic interactions: the electronic coupling $V(R, \epsilon)$ between the first kind of SES and the electronic continuum, and the quantum defect function $\mu(R)$, where R is the internuclear distance and ϵ is the electron energy. If these two quantities are available together with the potential curves $E_d(R)$ of the first kind of SES, then the MQDT (multi-channel quantum defect theory) presents a very powerful tool to investigate the various dynamics. These quantities should be basically evaluated by quantum chemical electronic structure theory, but it is not easy generally to obtain accurate absolute values, unfortunately, especially in the case of $V(R, \epsilon)$. It is crucial to use spectroscopic experiments to improve the information. In this sense the interplay among quantum chemistry, dynamics theory, and experiment is very important. There is still one theoretical obstacle in this procedure. That is the solution of the K-matrix singular integral equation. The first order perturbation theory or the grid method is usually employed; but they are not accurate enough or not efficient enough. Here we present a new method which enables us to deal with the equation even analytically. Finally, when non-adiabatic transitions at potential curve crossings are to be analyzed, for instance in order to find out the final state branching in dissociative recombination, the compact and accurate Zhu-Nakamura theory can be used instead of the Landau-Zener formula.