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

I-D-1 Trajectory Surface Hopping Approach to Conical Intersection System

MIL’NIKOV, Gennady V.; OLOYEDE, Ponmile[1]; NAKAMURA, Hiroki
([1]GUAS)

The Zhu-Nakamura theory was proved to work well within the TSH (trajectory surface hopping) scheme in the case of DH_2^+ which presents a typical example of crossing seam type chemical reactions. It was found that the classically forbidden nonadiabatic transitions which cannot be treated by the Landau-Zener theory play important roles. In the present work the similar kind of analysis is carried out for a triatomic model reaction system of conical intersection. By doing this we would like to establish a general TSH method applicable to high dimensional systems.

I-D-2 Incorporation of the Zhu-Nakamura Theory into the Frozen Gaussian Propagation Method

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

A new semiclassical theory is developed by combining the Herman-Kluk semicalassical theory for adiabatic propagation on single potential energy surface and the semiclassical Zhu-Nakamura theory for nonadiabatic transition. The formulation with use of natural mathematical principles leads to a quite simple expression for the propagator based on classical trajectories and simple formulas are derived for overall adiabatic and nonadiabatic processes. The theory is applied to electronically nonadiabatic photodissociation processes: one-dimensional problem of H_2^+ in a cw laser field and two-dimensional model problem of H_2O in a cw laser field. The theory is found to work well for the propagation duration of several molecular vibrational periods and wide wave packet energy range. Although the formulation is made for the case of laser induced nonadiabatic process, it is straghtforwardly applicable to ordinary electronically nonadiabatic chemical dynamics.

I-E Theory of Nonadiabatic Transitions

I-E-1 Semiclassical Theory of Nonadiabatic Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physics, Russia)

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

The semiclassical analysis is carried out for a two-state model potential system, in which two asymptotically degenerate Morse type 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. The result for non-crossing case provides the analytical expression of nonadiabatic transition matrix and can be used in a more general multichannel problem involving the present type of asymptotic transitions.

I-E-2 Analytical Treatment of S-P Type Collisional Resonant Excitation Transfer

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physics, Russia)

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

The analytical solution developed in the previous paper is applied to the S-P type collisional resonant excitation transfer between atoms. The corresponding cross-sections are calculated in the high energy approximation. Good agreement is obtained with the results calculated previously by Watanabe with use of the fully numerical integration of the time-dependent coupled differential equations. This indicates usefulness of the present analytical theory developed in our previous papers.

I-E-3 Analytic Solution to Wave Packet Dynamics in a Laser Field: The Case of Linear Chirp

NAKAMURA, Hiroki

[*Chem. Phys.* in press]

An analytical expression for the nonadiabatic transition probability is derived for the case that two linear potentials in coordinate space are coupled by a linearly chirped time-dependent laser field. This constitutes a solution to the wave packet dynamics in the high energy approximation. Numerical calculations are carried out to demonstrate the applicability of the formula.

I-E-4 Nonadiabatic Transition—An Origin of Mutability of This World

NAKAMURA, Hiroki

(In "Nonadiabatic Transitions in Quantum Systems," Russian Academic Publishing House, to be published)

A brief review of the Zhu-Nakamura theory and a brief explanation how to use the theory are presented together with some numerical applications. Recent theoretical developments on the other types of nonadiabatic transitions such as non-crossing case, exponential potential model and transitions among asymptotically degenerate states are also briefly described. Further discussions are made on laser control of molecular processes, intriguing phenomenon of complete reflection, and its applications such as molecular switching and bound states in the continuum.

I-E-5 Semiclassical Theory for Quantum Defect Function of Diatomic Molecules

SOLOVEV, Evgeni A.[1]; NAKAMURA, Hiroki
([1]IMS and Macedonian Acad. Sci. and Arts, Macedonia)

[*J. Phys. B* **36**, 3697 (2003)]

The simple analytical expression for the quantum defect function $\Delta_{lm}(R)$ of diatomic molecule is derived with use of the uniform semiclassical approach including the effects of hidden-crossing. $\Delta_{lm}(R)$ is a function of the internuclear distance R and the effective charge at each nucleus which is again a function of R. Thus, in the case of homonuclear molecule this expression gives universal dependence on R. The derived expression is applied to H_2 molecule. The quantum defects are found to be in good agreement with the *ab initio* numerical data by Wolniewicz and Dressler (*J.Chem.Phys.* **100**, 444).

I-E-6 Non-Linear Landau-Zener Model for Photoassociation of Cold Atoms

ISHKANYAN, Artur[1]; NAKAMURA, Hiroki
([1]IMS and Engineering Cent. Armenian Natl. Acad. Sci., Armenia)

A basic nonlinear model of the two state problem generic in classical and bosonic field theories with a cubic nonlinearity is considered taking the photoassociation of an atomic Bose-Einstein condensate as a specific example. For the class of models with constant external field amplitude a general strategy for attacking the problem is developed based on the reduction of the initial system of equations for the semi-classical atom-molecule amplitudes to a nonlinear Volterra integral equation for the molecular probability. The first approximation term of a uniformly convergent series solution to the Landau-Zener problem is derived and an asymptotic expression for the nonlinear transition probability to the molecular state is established for the weak interaction regime.

I-E-7 Nonadiabatic Transitions Induced by a Laser Field

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physic, Russia)

The analytical study is carried out for a basic non-adiabatic atomic collision problem of two quantum states coupled by a laser field. The exact semiclassical solution has been found for the resonant type transitions and in the low frequency laser field limit. The high frequency field limit has also been considered in pseudoenergy ridge approach by a matching method.

I-F Quantum Dynamics of Chemical Reactions

I-F-1 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; AOYAGI, Mutsumi; KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki; BIAN, Wensheng[2]; TANAKA, Kiyoshi[3]
([1]GUAS; [2]IMS and Shandong Univ., China; [3]Hokkaido Univ.)

[*J. Theor. Comput. Chem.* **1**, 263 (2002)]

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-dimensional 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 briefly discussed, although the nonadiabatic couplings have not yet been estimated. The quantum reaction dynamics in these three PESs are discussed in the second accompanying paper, Paper II.

I-F-2 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[1]; NAKAMURA, Hiroki; NANBU, Shinkoh; AOYAGI, Mutsumi; BIAN, Wensheng[2]; TANAKA, Kiyoshi[3]
([1]GUAS; [2]IMS and Shandong Univ., China; [3]Hokkaido Univ.)

[*J. Theor. Comput. Chem.* **1**, 275 (2002)]

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 $E_{\mathrm{tot}} \leq 0.9$ 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 ground 1^1A' surface. The detailed dynamics on the excited surfaces are reported in the third paper of this series.

I-F-3 Chemical Reactions in the O(^1D) + HCl System III. Quantum Dynamics on the Excited (1^1A'' and 2^1A') Potential Energy Surfaces

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

[*J. Theor. Comput. Chem.* **1**, 285 (2002)]

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 this 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-4 Quantum Reaction Dynamics of Triatomic Systems in the Hyperspherical Elliptic Coordinates

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

The Hamiltonian expression for the case of general nonzero total angular momentum J is derived in the hyperspherical *elliptic* coordinates which present a powerful tool for analyzing heavy-light-heavy reactions. Implementation of scattering calculations is also discussed. Numerical demonstrations are made by taking the Cl + HD reaction as an example.

I-G Theory of Multi-Dimensional Tunneling

I-G-1 Practical Implementation of the Instanton Theory. II. Decay of Metastable State Through Tunneling

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

[*J. Chem. Phys.* **117**, 10081 (2002)]

A new instanton theory for decay rate problem at zero temperature is presented. The canonically invariant expression for the lifetime of metastable state is derived. The theory is fully implemented by an effective numerical recipe to find the instanton trajectory and is applicable to any high dimensional systems.

I-G-2 Tunneling Splitting in Polyatomic Molecules: Application to Malonaldehyde

MIL'NIKOV, Gennady V.; YAGI, Kiyoshi[1]; TAKETSUGU, Tetsuya[2]; NAKAMURA, Hiroki; HIRAO, Kimihiko[1]
([1]Univ. Tokyo; [2]Ochanomizu Univ.)

[*J. Chem. Phys.* **119**, 10 (2003)]

We report an accurate and efficient full dimensional semiclassical *ab initio* method for calculation of energy level splitting due to tunneling in polyatomic system. The method is applied to 21-dimensional 9-atomic malonaldehyde molecule. The tunneling splittings obtained are $\Delta E(\mathrm{H}) = 21.2$ cm^{-1} for hydrogen atom transfer and $\Delta E(\mathrm{D}) = 3.0$ cm^{-1} for deuterium atom transfer, which are in excellent agreement with the experimental values of 21.6 cm^{-1} and, 2.9 cm^{-1} respectively. We believe that the present analysis gives the final solution to the longstanding problem.

I-G-3 Semiclassical Theory of Tunneling Splitting for Vibrationally Excited States

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The theory developed before for ground state tunneling splitting is extended to excited state. Both longitudinal and transverse excitation are considered and canonically in variant formulas of energy splitting are derived for the low-lying excited states. The multi-dimensional effect of oscillation of tunneling splitting against vibrational excitation can be nicely interpreted in terms of the local frequency.

I-G-4 A Novel Method to Determine Caustics on a Family of Classical Trajectories

OLOYEDE, Ponmile[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]GUAS)

A new method to find caustics in multi-dimensional space is proposed. This is composed of the solution of the first order differential equations satisfied by $A_{ij} = \delta p_i/\delta q_j$ and the canonical transformation to avoid the divergence of this quantity. The repetitive use of this transformation enables us to detect closely-lying caustics. This method is useful in semiclassical treatment of chemical dynamics, since we can take into account the tunneling effects by restarting tunneling trajectories from caustics.

I-H Laser Control of Molecular Processes

I-H-1 Control of Molecular Processes by a Sequence of Linearly Chirped Pulses

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]GUAS; [2]Adv. Photon Res. Cent.)

[*J. Chem. Phys.* **117**, 9588 (2002)]

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 multilevel 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-H-2 Control of Photodissociation Branching Using the Complete Reflection Phenomenon: Application to HI Molecule

FUJISAKI, Hiroshi; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki
([1]Adv. Photon Res. Cent.)

[*J. Theor. Comput. Chem.* **1**, 245 (2002)]

The laser control of photodissociation branching in a diatomic molecules 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 $I(^2P_{3/2})(HI \rightarrow H + I)$ and $I^*(^2P_{1/2})$-$(HI \rightarrow H + I^*)$ 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-H-3 Photodissociation of H_2^+ and HD^+ in an Intense Laser Field

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

[*Phys. Rev. A* **66**, 05412 (2002)]

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 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. Photodissociation 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-4 Control of Photodissociation by Using a Sequence of Chirped Pulses and Nonadiabatic Transitions

ZOU, Shiyang; KONDORSKIY, Alexey[1]; NAKAMURA, Hiroki
([1]IMS and Levedev Physical Inst., Russia)

Laser control of photodissociation is decomposed into two processes: (1) to shift an initial wave packet to an appropriate position on the ground potential curve, and (2) to let that packet transit to upper dissociative potential curve. The first step can be realized by using a sequence of chirped pulses and the second step is made possible by controlling the nonadiabatic transition between the dressed states.

I-I New Method of Scattering Calculation

I-I-1 Calculation of Resonances in a *dtμ* Molecule by the R-Matrix Method

MIL’NIKOV, Gennady V.; NAKAMURA, Hiroki

[*Phys. Rev. A* **67**, 034501 (2003)]

Using the spectral representation of Green’s function, we calculate the density of states and extract parameters of resonances in the scattering system. The method is implemented for the resonances in the *dtμ* molecule below the *tμ* ($n = 2$) threshold.