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

I-B-1 Generalized Trajectory Surface Hopping Method Based on the Zhu-Nakamura Theory

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We present a generalized formulation of the trajectory surface hopping method applicable to a general multidimensional system. The method is based on the Zhu-Nakamura theory of a nonadiabatic transition and therefore includes the treatment of classically forbidden hops. The method uses a generalized recipe for the conservation of angular momentum after forbidden hops and an approximation for determining a nonadiabatic transition direction which is crucial when the coupling vector is unavailable. This method also eliminates the need for a rigorous location of the seam surface, thereby ensuring its applicability to a wide class of chemical systems. In a test calculation, we implement the method for the DH_2^+ system, and it shows a remarkable agreement with the previous results of C. Zhu, H. Kamisaka, and H. Nakamura, [*J. Chem. Phys.* **116**, 3234 (2002)]. We then apply it to a diatomic-in-molecule model system with a conical intersection, and the results compare well with exact quantum calculations. The successful application to the conical intersection system confirms the possibility of directly extending the present method to an arbitrary potential of general topology.

I-B-2 Semiclassical Treatment of Thermally Activated Electron Transfer in the Intermediate to Strong Electronic Coupling Regime under the Fast Dielectric Relaxation

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The generalized nonadiabatic transition-state theory (NA-TST) (Zhao, Y.; *et al. J. Chem. Phys.* **121**, 8854 (2004)) is used to study electron transfer with use of the Zhu-Nakamura (ZN) formulas of nonadiabatic transition is the case of fast dielectric relaxation. The rate constant is expressed as a product of the well-known Marcus formula and a coefficient which represents the correction due to the strong electronic coupling. In the case of general multidimensional systems, the Monte Carlo approach is utilized to evaluate the rate by taking into account the multidimensionality of the crossing seam surface. Numerical demonstration is made by using a model system of a collection of harmonic oscillators in the Marcus normal region. The results are naturally coincident with the perturbation theory in the weak electronic coupling limit; while in the intermediate to strong electronic coupling regime where the perturbation theory breaks down the present results are in the good agreement with those from the quantum mechanical flux-flux correlation function within the model of effective one-dimensional mode.

I-B-3 Electron Transfer Rate Uniformly Valid from Nonadiabatic to Adiabatic Regime Based on the Zhu-Nakamura Theory

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On the basis of the generalized nonadiabatic transition state theory recently introduced to remedy the crucial deficiencies of the conventional transition state theory, we have presented a new formula for electron transfer rate, which can cover the whole range from adiabatic to nonadiabatic regime in the absence of solvent dynamics control. The rate is expressed as a product of the well-known Marcus theory and a new coefficient that represents the effects of nonadiabatic transition at the crossing seam surface. The numerical comparisons are performed with different approaches and the present approach shows an excellent agreement with the quantum mechanical numerical solutions from weak to strong electronic coupling. The explanation of the experimental data of Nelson *et al.* manifests the potential applicability of the present theory.

I-B-4 Incorporation of Nonadiabatic Transition into Wave-Packet Dynamics

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Nonadiabatic wave-packet dynamics is factorized into purely adiabatic propagation and instantaneous localized non-adiabatic transition. A general formula is derived for the quantum-mechanical local nonadiabatic operator which is implemented within the framework of the R- matrix method. The operator can be used for incorporating the nonadiabatic transition in semclassical wave-packet dynamics.

I-B-5 Dynamics of Nonadiabatic Chemical Reactions

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New methods are proposed to treat nonadiabatic chemical dynamics in realistic large molecular systems

by using the Zhu-Nakamura (ZN) theory of curve-crossing problems. They include the incorporation of the ZN formulas into the Herman-Kluk type semiclassical wave packet propagation method and the trajectory surface hopping (TSH) method, formulation of the nonadiabatic transition state theory, and its application to the electron transfer problem. Since the nonadiabatic coupling is a vector in multi-dimensional space, the one-dimensional ZN theory works all right. Even the classically forbidden transitions can be correctly treated by the ZN formulas. In the case of electron transfer, a new formula which can improve the celebrated Marcus theory in the case of normal regime is obtained so that it

can work nicely in the intermediate and strong electronic coupling regimes. All these formulations mentioned above are demonstrated to work well in comparison with the exact quantum mechanical numerical solutions and are expected to be applicable to large systems which cannot be treated quantum mechanically numerically exactly. In order to take into account another quantum mechanical effect, namely, tunneling effect, an efficient method to detect caustics from which tunneling trajectories emanate is proposed. All the works reported here are the results of recent activities carried out in the author's research group. Finally, the whole set of ZN formulas is presented in Appendix.

I-C Theory of Multi-Dimensional Tunneling

I-C-1 Tunneling Splitting of Energy Levels and Rotational Constants in the Vinyl Radical C_2H_3

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The instanton theory newly implemented by two of the authors (G. V. M. and H. N.) is applied to hydrogen tunneling transfer in a vinyl radical. The converged instanton trajectory is found on the CCSD(T)/aug-cc-pVTZ level of an ab initio potential energy surface. The calculated ground-state energy splitting agrees with the recent high-resolution experimental data within 3% of discrepancy. The semiclassical wave function is used to estimate the splitting of the principal rotational constants of the radical.

I-D Laser Control of Molecular Processes and Development of Molecular Functions

I-D-1 Semiclassical Guided Optimal Control of Molecular Dynamics

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An efficient semiclassical optimal control theory applicable to multidimensional systems is formulated for controlling wave packet dynamics on a single adiabatic potential energy surface. The approach combines advantages of different formulations of optimal control theory: quantum and classical on one hand and global and local on the other. Numerical applications to the control of NCH-CNH isomerization demonstrate that this theory can provide an efficient tool to manipulate molecular dynamics of many degrees of freedom by laser pulses.

I-D-2 Selective Transition to the Closely-Lying States Cs($7D_{3/2}$) and Cs($7D_{5/2}$) by Femtosecond Laser Pulses

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A demonstration of coherent quantum control for ultrafast precise selection of closely-lying states is reported. A phase-locked pair of femtosecond laser pulses is generated through a pulse shaper to excite the ground-state cesium atom to the Cs($7D_{3/2}$) and Cs($7D_{5/2}$) states by two-photon absorption. The excited state population is measured by detecting fluorescence from each spin-orbit state. By controlling the phase-difference of the pulse pair, an ultrafast precise selection is accomplished. The contrast ratio of the maximal to minimal selection ratio exceeds 10^3 with the delay less than 400 fs.

I-D-3 Ab Initio Nonadiabatic Quantum Dynamics of Cyclohexadiene/Hexatriene Ultrafast Photoisomerization

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Reaction mechanisms of the ultrafast photoisomerization between cyclohexadiene and hexatriene have been elucidated by the quantum dynamics on the *ab initio* potential energy surfaces calculated by multi-reference configuration interaction method. In addition to the quantum wave-packet dynamics along the two-dimensional reaction coordinates, the semiclassical analyses have also been carried out to correctly estimate the nonadiabatic transition probabilities around conical intersections in the full-dimensional space. The reaction time durations of radiationless decays in the wave-packet dynamics are found to be generally consistent with the femtosecond time-resolution experimental observations. The nonadiabatic transition probabilities among the ground (S_0), first (S_1), and second (S_2) excited states have been estimated by using the semiclassical Zhu-Nakamura formula considering the full-dimensional wave-packet density distributions in the vicinity of conical intersections under the harmonic normal mode approximation. The cyclohexadiene (CHD) ring-opening process proceeds descending on the $S_1(1^1B)$ potential after the photoexcitation. The major part of the wave-packet decays from $S_1(1^1B)$ to $S_1(2^1A)$ by the first seam line crossing along the C_2-symmetry-breaking directions. The experimentally observed ultrafast S_1–S_0 decay can be explained by the dynamics through the S_1–S_0 conical intersection along the direction toward the five-membered ring. The CHD: hexatriene (HT) branching ratio is estimated to be approximately 5:5, which is in according with the experiment in solution. This branching ratio is found to be mainly governed by the location of the five-membered ring S_1–S_0 conical intersection along the ground state potential ridge between CHD and HT.

I-D-4 Atomic Hydrogen Transmission through Five-Membered Carbon Ring by the Mechanism of Non-Adiabatic Tunneling

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A novel usage of the non-adiabatic effects is proposed. In this proposal, atomic hydrogen penetrates through a five-membered carbon ring with the help of the non-adiabatic tunneling phenomenon. The cyclepentadienyl radical (C_5H_5) and pentaboron-substituted corannulenyl radical ($C_{15}H_{10}B_5$) are used to illustrate the mechanism. To demonstrate the proposal, first principles calculations are performed for the non-adiabatic dynamics on potential energy surfaces determined by multi-reference configuration interaction method. The results show that the non-adiabatic transitions between the ground and excited states essentially control the hydrogen atom transmission through the five-membered ring of a pentaboron-substituted corannulenyl radical. It is found that the transmission occurs more than once out of four incidences when an appropriate initial wave packet is chosen. The phenomenon can be interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transitions.

I-D-5 Laser Control of Reactions of Photoswitching Functional Molecules

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Laser control schemes of reactions of photoswitching functional molecules are proposed based on the quantum mechanical wave-packet dynamics and the design of laser parameters. The appropriately designed quadratically chirped laser pulses can achieve nearly complete transitions of wave packet among electronic states. The laser parameters can be optimized by using the Zhu-Nakamura theory of nonadiabatic transition. This method is effective not only for the initial photoexcitation process but also for the pump and dump scheme in the middle of the overall photoswitching process. The effects of momentum of the wave packet crossing a conical intersection on the branching ratio of products have also been clarified. These control schemes mentioned above are successfully applied to the cyclohexadiene/hexatriene photoisomerization (ring-opening) process which is the reaction center of practical photoswitching molecules such as diarylethenes. The overall efficiency of the ring opening can be appreciably increased by using the appropriately designed laser pulses compared to that of the natural photoisomerization without any control schemes.

I-D-6 Laser Control of Chemical Dynamics: Control of Electronic Transitions by Quadratic Chirping

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An effective scheme of the laser control of wave packet dynamics applicable to the systems of many degrees of freedom is discussed. It is demonstrated that by using specially designed quadratically chirped pulses fast and nearly complete excitation of wave packet can be achieved without significant distortion of its shape. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura (ZN) theory of nonadiabatic transition. The scheme is applicable to various processes such as simple electronic excitation,

pump-dump, and selective bond breaking, and it is actually numerically demonstrated to work well by taking diatomic and triatomic molecules as examples.

I-D-7 Laser Control of Chemical Dynamics: Control of Wave Packet Motion

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An efficient semiclassical optimal control theory for controlling wave packet dynamics on a single adiabatic potential energy surface applicable to the systems of many degrees of freedom is discussed with all the details. The approach combines advantages of different formulations of optimal control theory: quantum and classical on one hand and global and local on the other. The efficiency and reliability of the method is demonstrated by taking the systems of two and four dimensions as examples.