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

## I-E-1 Nonadiabatic Transition and Chemical Dynamics: Multi-Dimensional Tunneling Theory and Applications of the Zhu-Nakamura Theory

**NAKAMURA, Hiroki**

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Tunneling and nonadiabatic transition are the most important quantum mechanical effects in chemical dynamics. They are important not only for understanding the dynamics properly, but also for controlling molecular functions. The Zhu-Nakamura (ZN) theory can be combined with the quasi-classical trajectory method and with the IVR (Initial Value Representation)-type semiclassical theory to deal with large chemical systems. Laser control of molecular processes and control of molecular functions can also be realized by properly controlling nonadibatic transitions. Furthermore, we have recently formulated an accurate theory for evaluating tunneling splitting and tunneling decay rate in multi-dimensional systems and also developed an efficient method to find caustics in multi-dimensional space. These methods combined with the ZN theory are expected to clarify various large scale chemical dynamics. This is a short review article on our recent activities mentioned above.

## I-E-2 Electron Transfer Rate to Cover the Whole Range from Adiabatic to Nonadiabatic Regime Based on the Zhu-Nakamura Theory

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A new formula for electron transfer is formulated to bridge the gap between the adiabatic and nonadiabatic limits. The key point is to reformulate the prefactor of the famous Marcus formula by using the Zhu-Nakamura theory of nonadiabatic transition. It is shown that the new formula gives an excellent agreement with the quantum mechanical numerical results and can explain well the experimental data of Nelsen *et al.*

## I-E-3 Semiclassical Theory of Electron Transfer Beyond the Perturbation Theory

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We consider a problem of evaluating electron transfer rate in the crossover region from nonadiabatic to adiabatic regime controlled by the electron coupling. Based on the generalized nonadiabatic transition state theory[1)] proposed to overcome the quantitative deficiencies of the conventional transition state theory, the rate applicable to multi-dimensional systems in the linear response limit is expressed as a product of the well-known Marcus formula and a coefficient which represents the correction with respect to nonadiabatic transition across the seam surface. In the case of general multi-dimensional systems the Monte Carlo approach can be utilized to evaluate the effective probability and the effective free energy for any general Hamiltonian system expressed in Cartesian coordinates with nonlinear reaction coordinates and the non-Condon effect taken into account. Numerical demonstration is made by using a model system with a collection of harmonic oscillators. The rate obtained shows a good agreement with that evaluated from the Fermi Gordon rule in the weak electronic coupling limit; while the latter theory fails in the strong electronic coupling regime as expected. Numerical tests also show that a matching technique from multi-mode to an effective one mode gives a very good result in wide range of electronic coupling strength and temperature except in the deep tunneling regime.

**Reference**

1) Y. Zhao, G.V. Mil'nikov and H. Nakamura, *J. Chem. Phys.* **121**, 8854 (2004).

## I-E-4 Generalized Trajectory Surface Hopping Approach

**OLOYEDE, Oluwaponmile[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki**
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The TSH method is generalized so as to be applicable to high dimensional systems with use of the Zhu-Nakamura formulas. Not only the classically allowed transitions but also the classically forbidden ones can be treated uniformly. Furthermore the transition direction can be determined from the Hessian of potential energy surfaces, even if the nonadiabatic coupling vector is not available.

## I-E-5 Semiclassical Theory of Thermal Rate Constant for Multi-Surface Processes

**CHIKAZUMI, Shinpei; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki**

A semiclassical theory is formulated with use of the Zhu-Nakamura theory by extending the trace formula devised by Miller and co-workers. The statistical Monte Carlo method makes it possible to apply this theory to multi-dimensional systems.

# I-F Theory of Nonadiabatic Transition

### I-F-1 Rabi Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

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[*Phys. Rev. A* **70**, 053611 (2004)]

The dynamics of coherent Rabi oscillations in coupled atomic and molecular Bose-Einstein condensates is considered taking into account the atom-atom, atom-molecule and molecule-molecule elastic interactions. The exact solution for the molecule formation probability is derived in terms of the elliptic functions. The two-dimensional space of the involved parameters (intensity and detuning) is analyzed and divided into two regions where the Rabi oscillations show different characteristics. A resonance curve is found, on which the molecular formation probability monotonically increases as a function of time. The maximum value of the final transition probability on this curve is 1/2 (*i.e.*, total transition to the molecular state) and it is achieved at high field intensities starting from a minimal threshold defined by the interspecies interaction scattering lengths. The explicit form of the resonance curve is determined, and it is shown that the resonance frequency position reveals a nonlinear dependence on the Rabi frequency of the applied field. A singular point is found on the resonance curve, where a power-law time evolution of the system is observed.

### I-F-2 A Basic Two-State Model for Bosonic Field Theories with a Cubic Nonlinearity

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[*J. Phys. A: Math. Gen.* **38**, 3505–3516 (2005)]

A basic nonlinear two-state model generic in classical and bosonic field theories with a cubic nonlinearity is considered. 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 semiclassical atom-molecule amplitudes to a nonlinear Volterra integral equation for the molecular probability. A uniformly convergent series solution to the problem is constructed for the weak interaction limit. The Landau-Zener model is considered as a specific example. The first approximation term is derived and an asymptotic expression for the nonlinear transition probability is established in the weak interaction regime.

### I-F-3 Incorporation of Nonadiabatic Transition into Wave Packet Dynamics

**MIL'NIKOV, Gennady V.; ZOU, Shiyang[1]; NAKAMURA, Hiroki**
*([1]IMS and Univ. Bristol, U.K.)*

Non-adiabatic 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 non-adiabatic operator which is implemented within the framework of R-matrix method. The operator can be used for incorporating the nonadiabatic transition in semclassical wave packets dynamics.

# I-G Theory of Multi-Dimensional Tunneling

### I-G-1 Instanton Theory for the Tunneling Splitting of Low Vibrationally Excited States

**MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki**

[*J. Chem. Phys.* **122**, 124311 (2005)]

We develop the instanton theory for calculating the tunneling splitting of excited states. For the case of low vibrational quantum states we derive a canonically invariant formula which is applicable to a multidimensional system of arbitrary Riemannian metric. The effect of multidimensionality in relation to the vibrational excitation is explained in terms of the effective frequencies along the instanton trajectory. The theory is demonstrated to work well by taking $HO_2$ molecule as an example.

### I-G-2 Effect of Out-Of Plane Vibration on the Hydrogen Atom Transfer Reaction in Malonaldehyde

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[*Chem. Phys. Lett.* **397**, 435–440 (2004)]

Tunneling splitting of the vibrational ground state is calculated for a planar model of malonaldehyde by the instanton method of Mil'nikov and Nakamura with use of *ab initio* potential energy surface. The planar model gives much larger tunneling splitting than the previous full dimensional calculations, indicating a strong effect

of the anharmonic coupling between the in-plane and out-of-plane modes. The anharmonicity is related to the Coriolis coupling between the OH stretching vibration and the pseudo-rotation of the hindered rotor. The present results suggest that the multidimensional effects should be carefully taken into account in the tunneling dynamics of polyatomic molecules.

### I-G-3 Ground State and Vibrationally Assisted Tunneling in the Formic Acid Dimer

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[*J. Chem. Phys.* **123**, 074308 (2005)]

The previously developed instanton theory[1)] is applied to the calculation of vibrationally assisted tunneling splitting of the deuterated formic acid dimer $(DCOOH)_2$ with all the degrees of freedom taken into account. The ground state tunnel splitting is determined by the density functional theory combined with coupled cluster level of quantum chemistry to be 0.0038 $cm^{-1}$ which is comparable to the experimental value 0.0029 $cm^{-1}$. Further, the tunnel splittings of fundamental excitations are estimated for frequencies below 300 $cm^{-1}$. In this energy range it is found that the excitation modes may either enhance or suppress tunneling as compared to the ground state. For the higher frequency modes a rapid growth of the tunnel splitting is observed. At frequencies above 1000 $cm^{-1}$ the semiclassical solution becomes unstable and no reliable tunneling splittings can be obtained. This is in vast contrast to the adiabatic approximation to the instanton theory in which the tunnel splittings can be retrieved up to 3000 $cm^{-1}$. We discuss this disparity from the viewpoint of the multidimensional character of tunneling in hydrogen bonds and the adiabatic approximation is concluded to be inaccurate.

**Reference**

1) *J. Chem. Phys.* **122**, 124311 (2005).

# I-H Laser Control of Molecular Processes

### I-H-1 Laser Control of Electronic Transitions of Wave Packet by Using Quadratically Chirped Pulses

**ZOU, Shiyang[1]; KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki**
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[*J. Chem. Phys.* **122**, 084112 (2005)]

An effective scheme is proposed for the laser control of wave packet dynamics. 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 sharpe. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura theory of nonadiabatic transition. If the wave packet is not too narrow or not too broad, then the scheme is expected to be utilizable for multidimensional systems. 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 (LiH, NaK, $H_2O$) as examples.

### I-H-2 Semiclassical Guided Optimal Control of Molecular Dynamics

**KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki**

An efficient semiclassical optimal control theory applicable to multi-dimensional 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: quatntum and classical on one hand and global and local on the other. Numerical applications to the control of NCH-HNC isomerization demonstrate that this theory can provide an efficient tool to manipulate molecular dynamics of many degrees of freedom by laser pulses.

# I-I Development of New Molecular Functions

## I-I-1 A Theoretical Study of Cyclohexadiene/Hexatriene Photochemical Interconversion: Miltireference Configuration Interaction Potential Energy Surfaces and Transition Probabilities for the Radiationless Decays

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[*Chem. Phys. Lett.* **401**, 487–491 (2005)]

The overall energetics and the feature of reactive potential energy surfaces for the photochemical interconversion between cyclohaxadiene (CHD) and all-*cis*-hexatriene (cZc-HT) have been investigated using the multireference configuration interaction (MRCI) calculations. The adiabatic and the diabatic potential energy surfaces of the ground and the excited states have been calculated along the Jacobi coordinates. The conical intersections among the states are estimated and the corresponding non-adiabatic transition probabilities are calculated using the semiclassical Zhu-Nakamura formula. The $1^1B$-$2^1$-A decay occurs by $C_2$-symmetry-breaking motion around the conical intersection. The non-adiabatic transition to $1^1A$ occurs by the motion toward the 5-menbered ring.

## I-I-2 Reaction Dynamics of Cyclohexadiene/Hexatriene Ultrafast Photoisomerization through Conical Intersections

**TAMURA, Hiroyuki; NANBU, Shinkoh[1]; ISHIDA, Toshimasa[2]; NAKAMURA, Hiroki**
*([1]IMS and Kyushu Univ.; [2]IMS and Kyoto Univ.)*

Fundamental mechanisms of photochromism applicable to molecular switches and memories are clarified using quantum mechanical wave-packet dynamics on the accurate *ab initio* potential energy surfaces. Cyclohexadiene/hexatriene ultrafast photoisomerization has been considered as a model system. The results are in agreement with the femtosecond time-resolution experiments. The overall reaction dynamics is revealed from photoexcitation to the ground state products *via* non-adiabatic transitions through conical intersections governing the excited state lifetime and the reaction yield. It is also found that the second excited state plays an important role in the dynamics and the efficiency of photochromism.

## I-I-3 Encapsulation of Hydrogen Atoms by Fullerenes and Carbon Nanotubes with the Use of Nonadiabatic Transition

**NANBU, Shinkoh[1]; ISHIDA, Toshimasa[2]; NAKAMURA, Hiroki**
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A probable mechanism is proposed to encapsulate hydrogen atoms into carbon nanotubes (CNTs) as well as fullerenes. In this mechanism, a non-adiabatic effect on nuclear dynamics, specifically the non-adiabatic tunneling effect, enables transmission of hydrogen atoms. A cap of CNTs or a pentagonal moiety (five-membered rings) of fullerenes is mimicked by corannulene molecule ($C_{20}H_{10}$). The three-dimensional quantum mechanical wave packet dynamics calculations are carried out on the accurate ab initio potential energy surfaces of the ground and excited states. It is shown that a hydrogen atom can transmit through the five-membered ring of corannulene more than once out of four incidences when five carbon atoms in the second layer are replaced by borons. The result is interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transition.