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

I-D-1 Semiclassical Theory of Electronically Nonadiabatic Chemical Dynamics: Incorporation of the Zhu-Nakamura Theory into the Frozen Gaussian Propagation Method

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[*J. Chem. Phys.* **120**, 8937 (2004)]

The title theory is developed by combining the Herman-Kluk semiclassical 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: a one-dimensional problem of H_2^+ in a cw (continuous wave) laser field and a 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 energy range. Although the formulation is made for the case of laser induced nonadiabatic processes, it is straightforwardly applicable to ordinary electronically nonadiabatic chemical dynamics.

I-D-2 Semiclassical Frozen Gaussian Propagation Method for Electronically Nonadiabatic Chemical Dynamics: Møller Operator Formulation and Incorporation of the Zhu-Nakamura Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

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

The title theory is developed by combining the Herman-Kluk semiclassical theory for adiabatic propagation on single potential energy surface and the Zhu-Nakamura theory for nonadiabatic transition. A quite simple expression for the propagator based on classical trajectories is derived using the Møller operator formulation of scattering theory. The theory takes into account almost all quantum effects that occur during nonadiabatic transition, especially at low energies and is expected to be applicable to general chemical dynamics of high dimensions. Application to a two-dimensional model system shows that the theory works well for the propagation duration of several molecular vibrational periods and wide wave packet energy range.

I-D-3 Evaluation of Canonical and Microcanonical Nonadiabatic Reaction Rate Constants by Using the Zhu-Nakamura Formulas

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([1]IMS and Univ. Sci. Tech. China, China)

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

We consider a problem of calculating both thermal and microcanonical rate constant for nonadiabatic chemical reactions. Instead of using the conventional transition state theory (TST), we use a generalized seam surface and introduce a concept of a coordinate dependent effective nonadiabatic transition probability based on the Zhu-Nakamura (ZN) theory which can treat the nonadiabatic tunneling properly. The present approach can be combined with Monte Carlo method so as to be applicable to chemical reactions in complicated systems. The method is demonstrated to work well in wide energy and temperature range. Numerical tests also show that it is very essential for accurate evaluation of the thermal rate constant to use the generalized seam surface and take into account the nonadiabatic tunneling effect.

I-D-4 Trace Formula of Thermal Rate Constant for Multi-Surface Processes

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

The trace formula for thermal rate constant formulated by W. Miller and co-workers for electronically adiabatic reactions is extended so as to be applicable to multi-potential energy surface processes. A semiclassical theory is formulated with the Zhu-Nakamura theory incorporated to treat the electronically nonadiabatic transition. Adiabatic propagation on the single potential energy surface is treated by the Herman-Kluk type wave packet propagation.

I-D-5 Tragectory Surface Hopping Approach to Electronically Nonadiabatic Chemical Dynamics

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

With use of the Zhu-Nakamura formulas, the TSH method can be generalized so as to treat both classically allowed and forbidden transitions unformly. This new implementation is applicable to both crossing seam type and conical intersection type processes of high dimension.

I-E Theory of Nonadiabatic Transition

I-E-1 Analytic Solution to Wave Packet Dynamics in a Laser Field: The Case of Linear Chirp

NAKAMURA, Hiroki

[*Chem. Phys.* **295**, 269–273 (2003)]

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-2 Semiclassical Theory of Nonadiabatic Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir[1]**; USHAKOV, Vladimir**[1]**; NAKAMURA, Hiroki**
(*[1]Inst. Problems Chem. Phys., Russia)*

[*Russ. Chem. Phys.* **22**, 87 (2003)]

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. The result can be used in a more general problem involving the present type of asymptotic transitions.

I-E-3 Analytical Treatment of *S-P* Type Collisional Resonant Excitation Transfer

OSHEROV, Vladimir[1]**; USHAKOV, Vladimir**[1]**; NAKAMURA, Hiroki**
(*[1]Inst. Problems Chem. Phys., Russia)*

[*Russ. Chem. Phys.* **23**, 103 (2003)]

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-4 Rabi Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

ISHKHANYAN, Artur[1]**; CHERNIKOV, G. P.**[2]**; NAKAMURA, Hiroki**
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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 2-dimensional space of the involved parameters 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 transition probability on this curve is 1 (*i.e.*, total transition to the molecular state) and it is achieved at high field intensities starting from a minimal threshold determined by the inter-species 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 Quantum Dynamics of Chemical Reactions

I-F-1 Full Quantum Dynamics of Atom-Diatom Chemical Reactions in Hyperspherical Elliptic Coordinates

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

Explicit expressions of the full Hamiltonian of triatomic system in the hyperspherical elliptic (HSE) coordinates are derived. The derivation is made from the expressions in the Delves coordinates. A numerical algorithm is also presented to evaluate the surface eigenfunctions including all the effects of Coriolis coupling terms. The whole formalism is numerically tested by using the Cl + DH and O(^{1}D) + HCl reacton systems. The HSE coordinate system, which is well-known to be powerful to elucidate reaction mechanisms especially for heavy-light-heavy systems, is now ready to be applied for clarifying full quantum dynamics of such systems.

I-F-2 Quantum Dynamics of O(^{1}D) + HCl Reactions

ZHAO, Yi[1]; NANBU, Shinkoh; NAKAMURA, Hiroki
([1]IMS and Univ. Sci. Tech. China, China)

Quantum dynamics calculations of O(^{1}D) + HCl are carried out with the three potential energy surfaces (1^1A’, 2^1A’, 1^1A”) taken into account. The three accurate potential energy surfaces are already available (*J. Theor. Comput. Chem.* **1**, 263, 275, 285 (2002)).

I-G Theory of Multi-Dimensional Tunneling

I-G-1 On the Determination of Caustics

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

[*J. Theor. Comput. Chem.* **3**, 91 (2004)]

This paper presents a numerical method which locates caustics of classical trajectories on-the-fly. The method is conceptually simple and is applicable to a system of arbitrary dimensions. The efficiency of the method is demonstrated by determining caustics of trajectories in the 2-D Henon-Heiles potential and of trajectories used to simulate a triatomic reaction process for J (total angular momentum) = 0.

I-G-2 Simple and Accurate Method to Evaluate Tunneling Splitting in Polyatomic Molecules

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

[*J. Chem. Phys.* **120**, 5036 (2004)]

A practical and accurate semiclassical method for calculating the tunneling slpitting of the ground state in polyatomic molecules is presented based on a recent version of the instanton theory [*J. Chem. Phys.* **115**, 6881 (2001)]. The method uses *ab initio* quantum chemical data for the potential energy surface without any concominant extrapolation and requires only a small number of *ab initio* data points to get convergence even for large molecules. This enables one to use an advanced level of electronic structure theory and achieve a high accuracy of the result. The method is applied to the 9-atomic malonaldehyde molecule by making use of the potential energy surface at the level of CCSD(T) with the hybrid basis set of aug-cc-pVTZ (for oxygen atoms and the transferred hydrogen atom) and cc-pVTZ (for other atoms).

I-G-3 Effect of Out-Of Plane Vibration on the Hydrogen Atom Transfer Reaction in Malonaldehyde

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

Tunneling splitting of the ground vibrational state is calculated for the 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 of the hydrogen atom. 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-4 Tunneling Splitting in Vinyl Radical C_2H_3

MIL’NIKOV, Gennady V.; ISHIDA, Toshimasa[1]; NANBU, Shinkoh; NAKAMURA, Hiroki
([1]Shizuoka Univ.)

Tunneling splitting of the ground vibrational state in vinyl radical is calculated with use of our theory developed before (*J. Chem. Phys.* **117**, 9588 (2002)). The potential energy surface is calculated accurately by the CCSD(T)/(aug-)cc-pvTZ method. The splitting obtained (= 0.53 cm^{-1}) is in very good agreement with the recent experiment (= 0.54 cm^{-1}) (*J. Chem. Phys.* **120**, 3604 (2004)).

I-G-5 Semiclassical Theory of Tunneling Splitting of Vibrationally Excited State

MIL’NIKOV, Gennady V.; NAKAMURA, Hiroki

The practical implementation of the instanton theory (*J. Chem. Phys.* **117**, 9588 (2002)) is extended so as to be applicable to vibrationally excited states. The effect of multi-dimensionality found before (*J. Chem. Phys.* **102**, 3977 (1995)) can now be nicely interpreted by the analytical expression.

I-H Laser Control of Molecular Processes

I-H-1 Semiclassical Formulation of Optimal Control Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

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

In the present paper semiclassical formulation of optimal control theory is made by combining the conjugate gradient search method with new approximate semiclassical expressions for correlation function. Two expressions for correlation function are derived. The simpler one requires calculations of coordinates and momenta of classical trajectories only. The second one requires extra calculation of common semiclassical quantities; as a result additional quantum effects can be taken into account. The efficiency of the method is demonstrated by controlling nuclear wave packet motion in a two-dimensional model system.

I-H-2 Control of Electronic Transitions of Wave Packet by Using Quadratically Chirped Pulses

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

We consider an effective scheme for the laser control of the nonadiabatic wave packet dynamics. It is shown that by using specially designed quadratically chirped pulse one can achieve fast and complete excitation of the wave packet without distortion of its shape. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura (ZN) theory regardless of the dimensionality of the system. The efficiency of the laser control scheme is demonstrated by several examples: complete $\mathrm{B}^1\mathrm{II} \leftarrow \mathrm{X}^1\Sigma^+$ excitation in LiH, control of the wave packet dynamics in Nak by using pump-dump mechanism and the bond selective photodissociation of H_2O.

I-H-3 Selective Excitation to Closely-Lying Cs ($7D_{3/2}$) and Cs ($7D_{5/2}$) by Femtosecond Laser Pulses

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([1]JARI.; [2]Kyoto Univ.; [3]Japan Atomic Energy Res. Inst.)

Ultrafast selection of closely lying excited states with a broadband light source is reported for a demonstration of precise coherent quantum control based on pulse shaping technique. Transform-limited pulses emitted from a Ti:Sapphire oscillator were shaped to phase-locked pulse pairs by an acousto-optic programmable dispersive filter and focused into cesium vapor to excite the atoms in the ground state to the Cs($7D_{3/2}$) and Cs($7D_{5/2}$) states *via* two-photon absorption. The relative excitation probability to each spin-orbit state was measured through the fluorescence to the Cs($6P_{1/2}$) and Cs($6P_{3/2}$) states, and was found to exhibit complete modulation with a period of π as a function of the phase-difference between two pulses. At the destructive phase, the fluorescence vanished below the detection limit. The best contrast of the selection ratio exceeded a thousand within 400-fs delay.

I-I Development of New Molecular Functions

I-I-1 Conversion between Cyclohexadiene and Hexatriene as a Model of Photochromism

TAMURA, Hiroyuki; NANBU, Shinkoh; ISHIDA, Toshimasa[1]; NAKAMURA, Hiroki
([1]Shizuoka Univ.)

High level of quantum chemical calculations of potential energy surfaces of the title molecules have been carried out. The conical intersection between 2'A and 1'A states, which is expected to play an important role for the photo conversion, has been found and the previously reported results are found to be not necessarily accurate. The corresponding dynamics calculations will be carried out.

I-I-2 Transmission of Atoms through Ring Molecules as a Model of Encapsulation by Carbon Nanotubes

NANBU, Shinkoh; ISHIDA, Toshimasa[1];
NAKAMURA, Hiroki
([1]Shizuoka Univ.)

The systems composed of ring molecules such as $C_{20}H_{10}$ and atoms such as H, Na, and Li have been studied quantum chemically and dynamically. It is found that in the case that five carbon atoms are replaced by borons nonadiabatic transitions between ground and first excited adiabatic states play a crucial role and hydrogen atom can transmit the ring with high efficiency by appropriately adjusting its translational energy.

I-J Theoretical Studies of Electron Dynamics in Molecular Systems

Electron dynamics in molecular systems is an intrinsic process in a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

I-J-1 High-Order Harmonic Generation from Silver Clusters: Laser-Frequency Dependence and the Screening Effect of *d* Electrons

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([1]Univ. Tsukuba)

[*Phys. Rev. A* **70**, 043411 (7 pages) (2004)]

We present time-dependent density functional studies of harmonic generation from Ag_2 and Ag_8 in pulsed laser fields. The harmonic generation is strongly dependent on the laser frequency. The harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. Such resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence *s*-electrons are shaken effectively at the tuned laser frequency and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have found that the polarizable core *d*-electrons significantly screen the valence *s*-electrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The screening effect of the *d* electrons becomes more important in the system of Ag_8 than Ag_2.

I-J-2 Multiple Ionization of a Silver Diatomic Molecule in an Intense Laser Field

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([1]Hokkaido Univ.; [2]Univ. Tsukuba)

[*Chem. Phys. Lett.* to be submitted]

Time-dependent density functional studies of multiple ionization of Ag_2 in an intense laser field 10^{14} W/cm^2 are presented. Special emphasis is placed on elucidating frequency dependence and an effect of the *d* electrons on the ionization processes. The multiple ionization occurs depending non-monotonically on the laser frequency. The valence *s* electrons are earlier emitted from the molecules, especially when the applied laser field is in tune with the dipole resonance frequency of the system, and then the *d*-electron emission occurs. Differently from the valence *s*-electrons, the *d* electrons are emitted more efficiently with increasing the laser frequency. We have computationally demonstrated that the *s* and *d* electrons move reciprocally toward the opposite directions such that the *s*-electron density induced in the laser field is cancelled out. This screening effect of the *d* electrons suppresses the multiple ionization in comparison with molecular systems without inner-shell electrons such as alkali metal clusters.

I-K Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide significantly different physicochemical properties such as optical response, catalysis, and reactivity from corresponding bare metal clusters or bulk metals. We have investigated electronic structures and photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-K-1 Electronic Structure and Photochemical Properties of a Monolayer-Protected Gold Cluster

NOBUSADA, Katsuyuki

[*J. Phys. Chem. B* **108**, 11904–11908 (2004)]

The electronic structure of a monolayer-protected gold cluster, $[Au_{13}(SCH_3)_8]^{3+}$, has been investigated by performing density functional calculations. The cluster has a characteristic structure with O_h molecular symmetry and eight (111) facets of a centered cuboctahedral Au_{13} core cluster are fully passivated by eight methanethiolates. The bond distance between two neighboring gold atoms (= 3.673 Å) is much larger than that of the bare Au_{13} cluster (= 2.929 Å), whereas the Au–S bond distance is 2.403 Å. These atomic rearrangement means that the methanethiolates stabilize the enlarged bare Au_{13} cluster by bonding to the (111) hollow sites of the bare cluster. The absorption spectrum of the $[Au_{13}(SCH_3)_8]^{3+}$ cluster is simulated within time-dependent density functional theory. The spectrum shows clear absorption peaks and each peak is assigned to specific excitation processes.