I-F Theoretical Studies of Chemical Reaction Dynamics

I-F-1 Quantum Reaction Dynamics of Heavy-Light-Heavy Systems: Reduction of the Number of Potential Curves and Transitions at Avoided Crossings

NOBUSADA, Katsuyuki[1]; TOLSTIKHIN, Oleg I.[2]; NAKAMURA, Hiroki
([1]Hokkaido Univ.; [2]IMS and Lebedev Phys. Inst.)

[*J. Phys. Chem. A* **102**, 9445 (1998)]

Two decoupling procedures are proposed within the framework of the hyperspherical coordinate approach in order to reduce the number of states in the close-coupling calculations and to clarify the reaction mechanisms. Sharply avoided adiabatic states are diabatically connected and relabeled without any diabatic coupling there. This is named diabatic decoupling and is useful for decoupling two manifolds of states belonging to different categories. Furthermore, the number of states is reduced in such a way that only a limited number of adjacent adiabatic states are taken into account in the close-coupling calculations for each relevant state. This is called adiabatic decoupling scheme. These reductions of the number of states enable us to analyze reactions in terms of nonadiabatic transitions at avoided crossings among the small number of adiabatic potential curves. The method is applied to O(^{3}P) + HCl → OH + Cl and Cl + HCl → HCl + Cl. The idea of vibrationally nonadiabatic transitions at avoided crossings together with the concept of potential ridge introduced in our previous paper can untangle the congested potential curves and clarify reaction mechanisms.

I-F-2 Quantum Reaction Dynamics of Cl + HCl → HCl + Cl: Vibrationally Nonadiabatic Reactions

NOBUSADA, Katsuyuki[1]; TOLSTIKHIN, Oleg I.[2]; NAKAMURA, Hiroki
([1]Hokkaido Univ.; [2]IMS and Lebedev Phys. Inst.)

[*J. Mol. Struct. (THEOCHEM)* **461-462**, 137 (1999)]

Quantum reaction dynamics of Cl + HCl → HCl + Cl for J (total angular momentum) = 0 is studied with use of the hyperspherical *elliptic* coordinate approach recently proposed by the authors. Thanks to the numerical efficiency of this approach, the reactions involving vibrational quantum jumps up to three are calculated accurately. Actually, all transitions among the states up to $v = 3$ and $j = 15$, in other words up to the total energy $E = 1.3$ eV, are covered, where v and J represent vibrational and rotational quantum numbers, respectively. Because of the symmetry of the system, the vibrationally adiabatic reactions are generally more probable than the nonadiabatic ones. However, some specific vibrationally nonadiabatic reactions even with two or three vibrational quantum jumps are found to occur efficiently. The concepts of potential ridge and non-adiabatic transitions at avoided crossings near the ridge lines enable us to comprehend the reaction mechanisms nicely.

I-F-3 Quantum Reaction Dynamics of an Asymmetric Exoergic Heavy-Light-Heavy System: Cl + HBr → HCl + Br

MIL'NIKOV, Gennady V.[1]; TOLSTIKHIN, Oleg I.[2]; NOBUSADA, Katsuyuki[3]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia; [2]IMS and Lebedev Phys. Inst.; [3]Hokkaido Univ)

[*Phys. Chem. Chem. Phys.* **1**, 1159 (1999)]

Quantum dynamics calculations for HBr + Cl → Br + HCl are carried out using the hyperspherical elliptic coordinates. The concepts of potential ridge and nonadiabatic transitions at avoided crossings introduced previously for isoergic and symmetric three-dimensional heavy-light-heavy reactions are confirmed to be useful to clarify the mechanisms of vibrationally non-adiabatic reactions in this exo-(or endo-)ergic system. The role of important avoided crossings which dominate the reaction dynamics is illustrated.

I-F-4 On the *J*-Shift Approximation in Quantum Reaction Dynamics

NOBUSADA, Katsuyuki[1]; NAKAMURA, Hiroki
([1]Hokkaido Univ.)

[*J. Phys. Chem. A* **103**, 6715 (1999)]

The validity of the J-shift or the energy-shift approximation is investigated numerically by taking the reaction O(^{3}P) + HCl → OH + Cl as an example. The approximation based only on the results of J (total angular momentum quantum number) = 0, which is the ordinary J-shift approximation, cannot reproduce the exact reaction dynamics well, especially when the initial rotational quantum number is high. The reaction rate constants for specified initial rovibrational states are over- or underestimated depending on the initial state and temperature. The good agreement with the accurate result of the thermal rate constant seems to be rather accidental because of the cancellations of these over- and underestimates. An extended J-shift approximation is proposed, in which accurate calculations should be carried out up to $J = j_i$ with $|\Omega| \le \Omega_{\max}$ when $j_i \le \Omega_{\max}$, or up to $J = \Omega_{\max}$ when $j_i > \Omega_{\max}$, where $\Omega_{\max}$ is the maximum of the absolute values of the body-fixed projection quantum number Ω that give noticeable contributions to the reaction dynamics. When the maximum J required to have a well converged cross-section and rate constant is much larger than j_i it is recommended to carry out accurate calculations at some representative J values and to use these values to estimate probabilities at other J values by an appropriate interpolation or extrapolation procedure.

I-F-5 Electronically Adiabatic Chemical Reactions Analyzed by the Semiclassical Theory of Nonadiabatic Transition

ZHU, Chaoyuan; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[1]
([1]Hokkaido Univ.)

The previously proposed qualitative conceptualization of heavy-light-heavy (HLH) chemical reactions on single potential energy surface (PES) as vibrationally nonadiabatic transitions at avoided crossings along the potential ridge lines is confirmed and further extended. An analytical as well as quantitative analysis of three-dimensional HLH reactions is carried out by applying the new semiclassical theory of nonadiabatic transition established by Zhu and Nakamura. About one thousand of avoided crossings which appear in the sea of adiabatic potential curves obtained in the hyperspherical coordinate approach are classified into relevant and irrelevant ones for reactive transitions by introducing a diabatic decoupling procedure based on the dimensionless parameter of the new semiclassical theory. Thus about one hundred of three kinds of avoided crossings relevant for reactive transitions are specified and treated analytically. The cumulative reaction probabilities can be quite nicely reproduced quantitavely. This indicates that the clarification and conceptualization of reaction mechanisms can be done even analytically. State-to-state reaction processes can be qualitatively nicely comprehended as before, but cannot be quantitatively well reproduced, simply because inelastic transitions are not necessarily localized and cannot be well comprehended in terms of nonadiabatic transitions. An interesting series of avoided crossings responsible for rotationally inelastic transitions are found at energies lower than the threshold of reaction in the case of exo- (or endo-)ergic reaction.

I-G Theory of Nonadiabatic Transition

I-G-1 Patterns of Time Propagation on the Grid of Potential Curves

OSTROVSKY, Valentin N.[1]**; NAKAMURA, Hiroki**
([1]Inst. Phys., Univ. St. Petersburg, Russia)

[*Phys. Rev. A* **58**, 4293 (1998)]

Time-propagation patterns are studied for a network formed by two bands of equidistant rectilinear parallel diabatic potential curves that cross each other. In the case of weak coupling between the bands the propagation proceeds mostly via a diabatic path. In the case of strong coupling a different regime of anti-diabatic propagation is revealed. For the intermediate case of coupling strength the propagation is basically described by an overlay of diabatic and antidiabatic patterns; interestingly, the adiabatic propagation is never operative. The present dynamic quantum model is compared with those models that assume a reduction of the problem to a succession of pairwise transitions between the states.

I-G-2 Analytic Solution of Two-State Time-Independent Coupled Schrödinger Equations in an Exponential Model

OSHEROV, Vladimir I.[1]**; NAKAMURA, Hiroki**
([1]IMS and Inst. Chem. Phys., Russia)

[*Phys. Rev. A* **59**, 2486 (1999)]

Quantum mechanically exact analytical solutions are obtained for a two-state exponential model, in which the exponent of diabatic coupling is one-half of that of the diabatic potential curve. A very simple and accurate semiclassical formula is found for the nonadiabatic transition probability.This gives a direct generalization of the Landau-Zener and Rosen-Zener formulas.

I-G-3 Semiclassical Theory of Nonadiabatic Transitions in a Two-State Exponential Model

PICHL, Lukas[1]**; OSHEROV, Vladimir I.**[2]**; NAKAMURA, Hiroki**
([1]GUAS; [2]IMS and Inst. Chem. Phys., Russia)

The two-state exponential model (repulsive potential case) is investigated and the two channel scattering problem is solved by means of semiclassical theory and high energy approximation. The analytical expression for the nonadiabatic transition matrix agrees with the previous attractive case. The only variables in this formula are the model-independent adiabatic momenta contour integrals. Oscillations of the overall transition probability when the energy is below the crossing of diabatic potentials can be observed in the case of large coupling. Unified theory of nonadiabatic transitions, covering the Landau-Zener-Stueckelberg and Rozen-Zener-Demkov models, is the aim of the present study.

I-H New Way of Controlling Molecular Processes

I-H-1 New Way of Controlling Molecular Processes by Time-Dependent External Fields

TERANISHI, Yoshiaki[1]**; NAKAMURA, Hiroki**
([1]GUAS)

[*J. Chem. Phys.* **111**, 1415 (1998)]

A new idea of controlling molecular processes by time-dependent external fields is proposed. Molecular processes in external fields are considered to be composed of a sequence of time-dependent nonadiabatic transitions in which the external fields play a role of adiabatic parameters. Unit final transition probability can be achieved with the use of the interference effects among various paths created by nonadiabatic transitions. The basic idea is to sweep the external field periodically at each avoided crossing and to control the transition there completely as we desire. This idea is quite general, and can hold whatever the external field is. Various control schemes can be proposed corresponding to the various types of time-dependent nonadiabatic transitions. The methods of π-pulse and chirped laser pulse with the adiabatic rapid passage may be considered as special cases of the present idea. As an example, a one-dimensional model of the laser-induced ring-puckering isomerization of trimethylenimine is considered, and comparative studies on the effectiveness and the stability of the various control schemes proposed in this paper are made together with presentation of numerical examples.

I-H-2 Control of Molecular Photodissociation with Use of the Complete Reflection Phenomenon

NAGAYA, Kuninobu[1]**; TERANISHI, Yoshiaki**[2]**; NAKAMURA, Hiroki**
([1]GUAS; [2]Inst. Phys. Chem. Res.)

In the one-dimensional nonadiabatic tunneling type curve crossing, there always occurs the intriguing phenomenon of complete reflection at certain discrete energies. We may think of controlling molecular processes with use of this phenomenon by applying a strong static laser field. By dressing up the electronic ground state of a molecule and adjusting the laser frequency appropriately, we can create the nonadiabatic tunneling potential surface crossing and the complete reflection condition to stop the dissociation into a certain direction. Although the complete reflection cannot be “complete” in a multi-dimensional space, we can control molecular photodissociation to some extent. Even in the case that a molecule cannot dissociate into a certain direction because of a high potential barrier in the excited state, we can dissociate that molecule into such a channel with use of the present method in principle. Two-dimensional model systems mimicking HOD and CH_3SH molecules are numerically studied.

I-I Molecular Switching with Use of the Complete Reflection Phenomenon

I-I-1 Molecular Switching in a Two-Dimensional Constriction

NAKAMURA, Hiroki

[*J. Chem. Phys.* **110**, 10253 (1999)]

The new idea of molecular switching discussed previously for the one-dimensional system [Nanbu, Nakamura and Goodman; *J. Chem. Phys.* **107**, 5445 (l997)] is extended to a two-dimensional constriction model. Analytical formulation is provided with use of the Mathieu functions and the semiclassical theory of nonadiabatic transition. Numerical demonstrations are also carried out. Both reflection and transmission, and thus the switching cannot be complete like in the one-dimensional case, but the switching is demonstrated to be quite effective. Although this is a purely theoretical model at this stage, some practical implications are discussed.

I-J Theoretical Study of Dissociative Recombination

I-J-1 Analytical Treatment of Singular Equations in Dissociative Recombination

PICHL, Lukas[1]**; NAKAMURA, Hiroki; HORACEK, Jiri**[2]
([1]GUAS; [2]IMS and Charles Univ., Czech Rep.)

[*Comput. Phys. Commun.* in press]

The Lippmann-Schwinger type singular integral equation, which arises in the multi-channel quantum defect theory of dissociative recombination process, is investigated. The singularity of its kernel is treated analytically by introducing an energy dependent quadrature. In many cases of physical interest the energy-dependent coupling potential, which gives the integral kernel of the equation, is quasi-separable in a way that allows to write down an analytical solution. The analytical treatment as well as the new solution are illustrated by taking the H_2^+ as an example. Our method is demonstrated to be much better than the conventional ones, such as the first order perturbation theory and the grid method.