

# Local Regularity and Non-recrossing Paths in Transition States of Chemical Reactions

Tamiki Komatsuzaki<sup>†</sup>, R. Stephen Berry<sup>\*</sup>

We analyze saddle crossings of a 6-atom Lennard-Jones cluster to demonstrate a) how one may choose a canonical coordinate system in which the transmission coefficient for the classical reaction path is unity from threshold up to a moderately high energy, above which the transition state is chaotic; b) that near the threshold energy, all or almost all the system's degrees of freedom are essentially regular, with near-constant action, in the region of the transition state, and c) that the degree of freedom associated with the reaction coordinate remains essentially regular through the region of the transition state, even to moderately high energies.

Submitted to *Science* (1998)

---

The pervasive concept of the mechanism of the most common class of chemical reactions is that of a system moving on a single effective potential surface (typically in a space of  $3N-6$  independent variables, for an  $N$ -body system) from one local minimum, which corresponds to the state of the reactants, across a saddle or transition state, to a second local minimum, that of the products. If the system begins in thermal equilibrium, and if conditions justify assuming a quasi-equilibrium between the reactants and systems crossing the transition state in the forward direction (i.e., to the products) along the reaction coordinate  $q_1$ , then the full apparatus of "transition-state theory" in any of several forms [1,2] can be brought into use to evaluate the rate coefficient of the reaction. The greater part of the effort in using any of the specific methods of this approach is evaluating the density of systems in the transition state and in the reactant state regions, that is, partition functions of both the states. However the theory has a "correction factor," a multiplier of the ratio of the two relevant partition functions, which is called the "transmission coefficient  $\kappa$ ," a quantity between 0 and 1. This factor is intended to take into account the possibilities that the reaction coordinate  $q_1$  may exchange energy with other coordinates in the transition state region [3], and that there may be also quantum mechanical effects in the process of passage. [2]

How a system actually traverses the transition state region, and what kinds of trajectories carry the system through, are questions considerably more demanding than, for example, how the reaction rate depends on temperature. It is these that we address here, using

---

The authors are at Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, U.S.A.

<sup>†</sup> Institute for Fundamental Chemistry, 34-4 Takano-Nishihirakicho, Sakyo-ku, Kyoto 606 Japan (-March 1998)

<sup>\*</sup> To whom correspondence should be addressed

isomerization of a 6-atom cluster as our illustrative vehicle. We have applied a canonical transformation of the coordinates and momenta to give a representation of the trajectories of reacting systems in which, up to moderately high energies above the saddle energy, the classical transmission coefficient is unity, and the degree of freedom associated with the reaction coordinate is *locally* regular with nearly constant action and frequency, in the region of the saddle. The crux of the method is the application of Lie canonical perturbation theory [4] to generate a nonlinear coordinate transformation, from an arbitrary, initial set of coordinates for the atoms of the reacting system, into a new set in which the individual degrees of freedom are as regular as possible, at the degree of expansion in perturbation theory one chooses to use.

The method of constructing the transformation is described in a fuller publication. [5] Here we describe it briefly. Then we present results for the model system we have used to test the method, the 6-atom cluster held together by pairwise Lennard-Jones forces, which one can think of as a reasonably good representation of the  $\text{Ar}_6$  cluster.

These results are the essential content of this report. (All results are given in the universal reduced units of the Lennard-Jones potential; energies are in units of the energy scale  $\epsilon$ .) They show that i) if the system has only a bit more energy than the absolute minimum required to traverse the saddle, ca.  $0.05\epsilon$  above that saddle, and go from reactants to products, then all the degrees of freedom are fairly regular and the action in each is rather well conserved *in the region of the transition state*; ii) throughout a considerably wider range of energies, up to at least  $0.5\epsilon$  above a saddle, the one degree of freedom corresponding to the reaction coordinate remains rather regular and conserves its action in the region of the transition state, even when all other degrees of freedom have become chaotic and strongly coupled; iii) at still higher energies, the reactive degree of freedom becomes chaotic and coupled to the other degrees of freedom in the saddle region. In other words, up to moderately high energies, any system entering the neighborhood of the saddle point (or, more generally, the dividing hypersurface), with enough energy in the reactive degree of freedom to cross the hypersurface, then it certainly will, because that degree of freedom decouples from all the rest and retains both its action and its (imaginary) frequency during its transit. However this is not apparent in ordinary coordinate systems; the system provided by Lie canonical perturbation theory is the only one we know in which this near-integrability can be seen.

Indicative symptoms of local regularity appeared in theoretical studies of small atomic clusters that compared local Liapunov functions and Kolmogorov entropies in saddle regions and other regions of potential surfaces [6–12]. Experiments by Lovejoy et al. on decomposition of vibrationally-excited ketene showed rates with quantized steps [13]; Marcus suggested that this could be a signature of existence of approximate invariants of motion in the transition state region. [14] More recently, Komatsuzaki and Nagaoka [15,16] used Lie canonical perturbation theory (LCPT) to construct a coordinate system to study a system with four degrees of freedom, a model of proton transfer in malonaldehyde; their analysis indicated that the proton transfer behaves, in the saddle region, as fully regular in all four degrees of freedom, with the corresponding four approximate constants of motion, and that the trajectories with energy in the reactive degree of freedom adequate to cross the saddle exhibit no re-crossings, i.e., have unit transmission coefficient. Here we address a system with 15 internal (vibrational + rotational) degrees of freedom, which we take as typical of real systems of moderate size. Fig. 1 shows the relevant stable structures, octahedron (OCT) and capped trigonal bipyramid (CTBP), and the energies of these structures and the saddles

linking them.

The method we employ to establish the coordinate system maximizing the local regularity in as many degrees of freedom as possible is, in brief, the following. The Hamiltonian is expressed in a region around a saddle point of interest as an expansion in a small parameter, so that the lowest-order term or zero-th order Hamiltonian is regular in that region; specifically, it is written as a sum of harmonic-oscillator Hamiltonians. Then the maximum order of perturbation is fixed, in our case at second-order. The first- and second-order terms of the Hamiltonian are expressed as sums of cubic and quartic terms in the normal coordinates of the system, and the three zero-frequency modes associated with the motion of the center of mass are removed. The transformation to the new coordinates proceeds by the method of “algebraic quantization,” [15,17] first by transforming from normal coordinates and conjugate momenta to “raising” and “lowering” operators in the customary way, and then expressing these in terms of action and the conjugate angle variables. The requisite equations to solve are those that minimize the angle-dependencies of the new Hamiltonian, thereby making the action variables as nearly constant as possible. We suppose here that the saddle is of rank 1, so that it has only one negative force constant, one imaginary frequency and one imaginary action.

Near a stable fixed point, it is well known that trajectories are regular or nearly so at low energies. Here, however, we deal with an unstable fixed point. At energies very slightly above the energy of the saddle, virtually all the energy of the system must be potential when the system is on a trajectory carrying it across the saddle, i.e., when the trajectory is that of a reaction. In that case, the motion of the system in the saddle region is governed almost entirely by the zero-order Hamiltonian and is therefore entirely regular. At low but slightly higher energies in the vicinity of an unstable stationary point, many modes remain nearly integrable, i.e. maintain nearly constant action while in the saddle region. Simulations bear this out; the actions in most new transformed modes of vibration are very nearly constant if the energy is only  $0.05\epsilon$  above either of the two kinds of saddles for the  $\text{Ar}_6$  cluster. Fig. 2A shows the action, evaluated with second-order LCPT, for several modes at this energy, along a typical saddle crossing trajectory over saddle I. As shown in Fig. 1, this is the saddle linking the OCT structure, the global minimum, with the CTBP, one other stable structure for this system. The results are very similar for the trajectories over saddle II, the saddle connecting one CTBP structure with another. Almost all the modes have nearly constant action in the saddle region at this low energy.

As the energy is increased more and more, to at least  $0.5\epsilon$  above the saddle energy, the actions of more and more modes become nonconstant in the saddle region. However the action in the mode of the reaction coordinate, as determined by LCPT, remains constant throughout the saddle region. This behavior is shown in Fig. 2B, again for saddle 1, and for trajectories with energies  $0.5\epsilon$  above that saddle, i.e., at  $-11.579\epsilon$ . The local frequency of the reactive mode, also, remains relatively constant in second-order LCPT, even when the local frequencies of other modes are quite variable; this will be discussed in a fuller description of this work [5].

All the transmission coefficients  $\kappa$  for this system are relatively close to unity, even for energies up to  $1.0\epsilon$  above the saddle. Those in zero- and first-order perturbation theory, however, do deviate; at energies of  $0.5$  and  $1.0\epsilon$ , the zero-order transmission coefficients approach  $0.99$ , 1% below unity. However the transmission coefficients evaluated with second-order LCPT are essentially unity at energies up to  $0.5\epsilon$  and deviate by only about  $0.002$  even

at energies of  $1.0\epsilon$ . These results are shown in Fig. 3. Put quantitatively, typical numbers of recrossings decrease (out of 10,000 total) from 217 in zero order to 18 to 0, over saddle 1 at an energy of  $0.1\epsilon$ .

The separatrix in the transformed space is a hypersurface naturally defined by the condition that the coordinate of the one imaginary mode has the value 0 about the unstable fixed point in the new coordinates. This separatrix is a complex, momentum-dependent function, and is properly defined only in infinite order of perturbation. Here we approximate this by using the unstable fixed point in second order of perturbation. Because of its momentum dependence, and the high degree of nonlinearity of the transformation, the separatrix is not easy to visualize. However is possible to tabulate or graph distributions of projections of this hypersurface onto low-dimensional subspaces of the principal coordinates. Such projections reveal how the complexity of the separatrix grows with energy [5].

The results of this investigation indicate that a suitable representation of the behavior of a reacting system reveals a high degree of separability and regular character of the reaction coordinate in the region of the transition state, where its force constant is negative and its frequency is imaginary. This is, as Hernandez and Miller pointed out [18], because any arbitrary combination of modes cannot satisfy commensurable conditions to make an unstable mode mix with modes stable in that region. Only if the energy is so high that the trajectory can encounter places on the potential with sizeable local Liapunov function along the reaction coordinate, i.e., places where quasi-constant action zone along the reaction coordinate is extremely small, does the reactive mode mix with the other modes. At those energies, the reactive mode and all the others are coupled together into a fully-chaotic system.

## REFERENCES AND NOTES

---

- [1] Early references are H. Eyring, *J. Chem. Phys.* **3**,479 (1935); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.* **31**, 875 (1935); E. Wigner, *Trans. Faraday Soc.* **34**, 29(1938); S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (New York, McGraw-Hill, 1941).
- [2] Recent reviews are D. G. Truhlar, B. C. Garrett, and S. J. Kippenstein, *J. Phys. Chem.* **100**, 12771(1996); D. C. Chatfield, R. S. Friedman, S. L. Mielke, G. C. Lynch, T. C. Allison, D. G. Truhlar, and D. W. Schwenke, in *Dynamics of Molecules and Chemical Reactions* edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996), p323.
- [3] R. A. Marcus, *J. Chem. Phys.* **43**, 1598 (1966); *ibid.* **45**,4493(1966).
- [4] G. Hori, *Pub. Astro. Soc. Japan* **18**, 287(1966); A. Deprit, *Celest. Mech.* **1**,12(1969); A. J. Dragt and J. M. Finn, *J. Math. Phys.* **17**, 2215(1976); *ibid.* **20**, 2649(1979); review articles are J. R. Cary, *Phys. Rep.* **79**,130(1981); A. J. Lichtenberg and M. A. Lieberman, *Regular and Chaotic Dynamics 2nd Ed.* (Springer-Verlag, New York, 1992).
- [5] T. Komatsuzaki and R. S. Berry, *J. Chem. Phys.* submitted for publication.
- [6] D. J. Wales and R. S. Berry, *J. Phys. B* **24**, L351 (1991).
- [7] R. J. Hinde, R. S. Berry, and D. J. Wales, *J. Chem. Phys.* **96**, 1376 (1992).
- [8] C. Amitrano and R. S. Berry, *Phys. Rev. Lett.* **68**, 729(1992); *Phys. Rev. E* **47**, 3158 (1993).
- [9] R. J. Hinde and R. S. Berry, *J. Chem. Phys.* **99**, 2942 (1993).

- [10] R. S. Berry, *Chem. Rev.* **93**, 237 (1993).
- [11] R. S. Berry, *Int. J. Quantum. Chem.* **58**,657(1996).
- [12] K. Ball, R. S. Berry, R. E. Kunz, F-Y. Li, A. Proykova, and D. J. Wales, *Science* **271**, 963 (1996).
- [13] E. R. Lovejoy, S. K. Kim and C. B. Moore, *ibid.* **256**, 1541(1992); E. R. Lovejoy and C. B. Moore,*J. Chem. Phys.* **98**, 7846(1993); S. K. Kim, E. R. Lovejoy, and C. B. Moore,*ibid.* **102**, 3202(1995).
- [14] R. A. Marcus, *Science* **256**, 1523(1992).
- [15] T. Komatsuzaki and M. Nagaoka, *J. Chem. Phys.* **105**, 10838 (1996).
- [16] T. Komatsuzaki and M. Nagaoka, *Chem. Phys. Lett.* **265**, 91 (1997).
- [17] L. E. Fried and G. S. Ezra, *J. Chem. Phys.* **86**, 6270(1987); *Comp. Phys. Comm.* **51**, 103(1988); *J. Phys. Chem.* **92**, 3144(1988).
- [18] R. Hernandez and W. H. Miller, *Chem. Phys. Lett.* **214**, 129(1993).
- [19] T.K. would like to dedicate this paper to Prof. Kenichi Fukui at Institute for Fundamental Chemistry (deceased January 1998). This research was supported by the Japan Society for the Promotion of Science (JSPS) and the National Science Foundation.

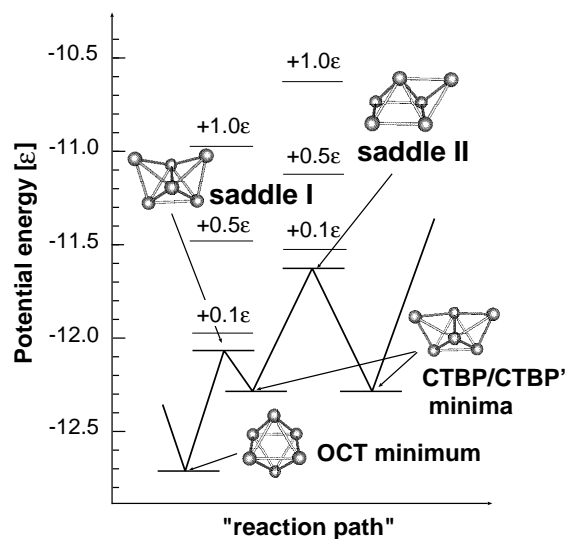


FIG. 1. Schematical picture of the potential energy surface of  $\text{Ar}_6$ . CTBP' is a permutational isomer of the CTBP minimum neighboring on the OCT minimum.

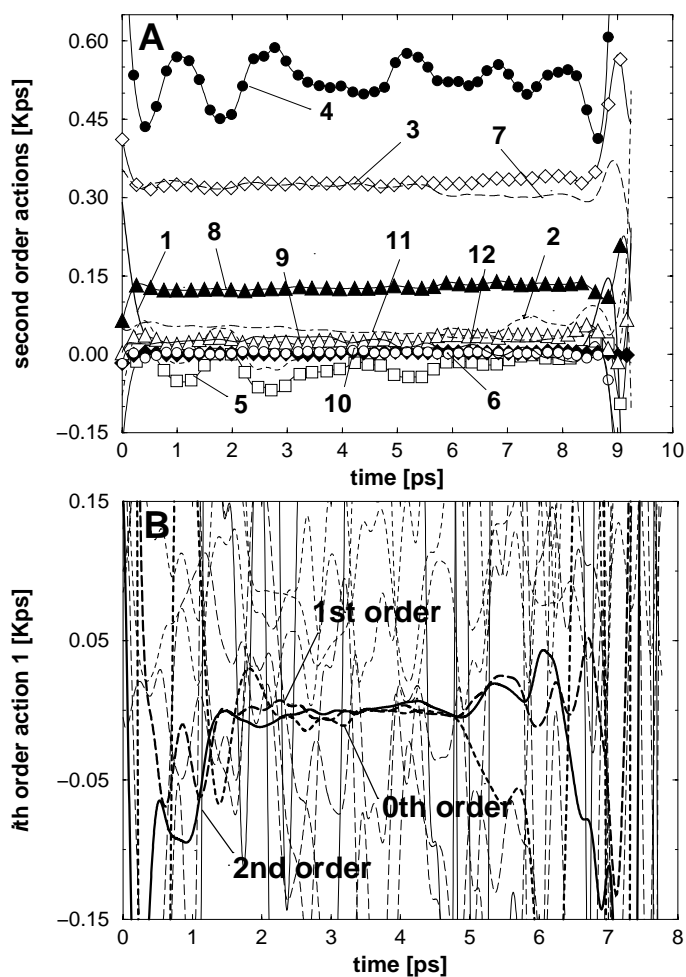


FIG. 2. **(A)** The time evolutions of the new actions at second-order, determined by LCPT, along a typical saddle-crossing trajectory at  $0.05\epsilon$ . The bold-solid, dashed, open-diamond, filled-circle, square, filled-diamond, long-dashed, filled-triangle, open-triangle, open-circle, dot-dashed, and solid lines denote 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, respectively; **(B)** those of the new action associated with the reactive mode 1 in chaotic motions of the other stable modes at  $0.5\epsilon$ . All the dotted, dashed, and solid lines denote the zero, first, and second order's, respectively. For mode 1 the units of action must be multiplied by a factor of an imaginary number  $i$  because it is imaginary. The other stable modes are in such an order that the associated real frequencies,  $0 < \bar{\omega}_2 \leq \bar{\omega}_3, \dots, \leq \bar{\omega}_{12}$ .

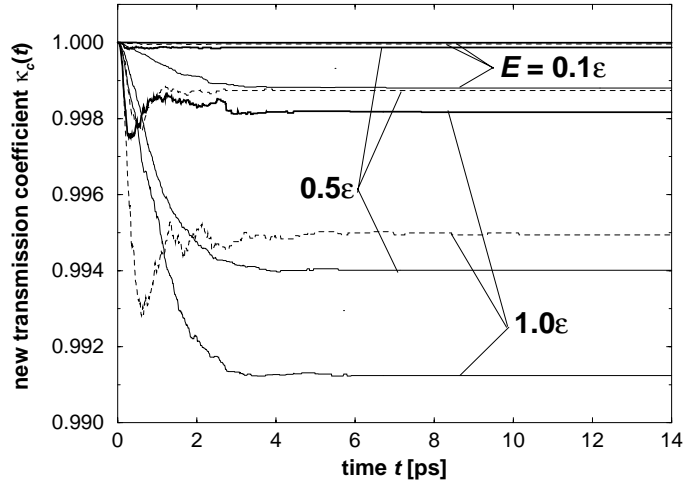


FIG. 3. The new transmission coefficients  $\kappa(t)$  at  $E=0.1, 0.5,$  and  $1.0\epsilon$  for saddle I, evaluated from 10,000 saddle crossing molecular dynamics trajectories. [5] The solid, dashed, and bold-solid lines, respectively, correspond to the  $\kappa$ 's in terms of the zero-order dividing surface, i.e., a conventional transmission coefficient, the first, and second order dividing surfaces. The time  $t = 0$  is set to be the time when the system first crossed the given dividing surface. The convergent values are 0.9988(0), 0.99996(1), 1.00000(2) (at  $E = 0.1\epsilon$ ); 0.9940(0), 0.9987(1), 0.9999(2) (at  $E = 0.5\epsilon$ ); 0.9912(0), 0.9949(1), 0.9982(2) (at  $E = 1.0\epsilon$ ) whose number in the parentheses is the order of the LCPT.