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Exploring remnants of invariants buried in a deep potential well in chemical reactions[1]

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How the reacting system climbs through saddles from one basin to another on potential energy surface has been one of the most intriguing subjects not only in chemistry but also physics and biology. This decade significant progress has been achieved in establishing the concept of the so-called transition state (TS), that is, a hypersurface of co-dimension one through which the system passes through only once from one basin to another [1-3]. However, there exist still open problems to be resolved; 1) how the no-return TS ceases or bifurcates as the energy increases [4], 2) how the stable/unstable invariant manifolds emanating from the normally hyperbolic invariant manifold *wander* in deep potential wells in many-degrees of freedom (dofs) systems [5] or how one can generalize the *remnant of invariant manifolds* [6] to many-dofs systems, 3) how one can generalize the concept of no-return TS besides the region of first-rank saddles. Related to the problem 2), most of all the chemical reaction theories assume that all of the available energy redistributes *statistically* through the dofs of system in the reactant well before the reaction takes place. It is implicitly expected that the ratio of the measure occupied by tori in phase space to that of the ambient space decreases exponentially as the dimensionality of the system increases. Here we present a novel technique to scrutinize the remnant of invariants buried in chaos in many-degrees of freedom systems [7]. This is regarded as the remnants of a destroyed invariant manifold that may dominate the transport in phase space even at high energy regions where most of all tori vanish. We demonstrate the potentiality of our technique for HCN isomerization, where the conventional procedure based on a finite order truncation in the coordinate transformation of canonical perturbation theory prevent us from detecting remnants of invariants.

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