Probing remnants of invariants to mediate energy exchange in highly chaotic many-dimensional systems

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A technique is presented to scrutinize a piece of remnants of invariants [R. B. Shirts and W. P. Reinhardt, J. Chem. Phys. **77**, 15 (1982)] buried in chaos in many degrees of freedom (DOF) dynamical systems in terms of canonical perturbation theory based on Lie transforms. The transformed canonical variables are often evaluated by the truncation of the coordinate transformation at a finite order in the original Hamiltonian system. However, the truncation of canonical variables gives rise to a loss of the symplectic property of the system. This results in apparent abrupt fluctuation of the action integrals, which yields a misinterpretation. We demonstrate, in a three-DOF Hamiltonian system of HCN isomerization reaction, that our technique can detect remnants of invariants buried in the potential well even at energies higher than the potential barrier, although the conventional truncation scheme fails to do so. This technique makes it possible to shed light on the physical insight into how the reactive mode exchanges its energy with the other modes and through which resonance the energy exchange takes place in reacting systems.

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The mechanism of transport in a space is one of the most fundamental subjects in a variety of fields such as chemistry [1–3], celestial mechanics [4–6], fluid mechanics [7], environmental science [8], and biology [9]. For instance, the selective control of the yield of a desired product state is a long-cherished dream for chemists [10]. For this purpose, a thorough knowledge of how the system wanders through the space of the reactant state before leaving to the product state and how the reactive mode acquires sufficient energy to climb over the saddle from the reactant to the product states is imperative. The question of how spacecrafts or asteroids are transported under the gravitational force is still one of the fundamental issues in celestial mechanics. The problem of finding the most efficient route for space missions using the least possible energy has recently been addressed [6]. Without a firm understanding of nonlinear dynamics on how a spacecraft is captured or wanders through the region of each planet, its mission would not be achieved.

Several transport phenomena, such as chemical reactions and a spacecraft or an asteroid in the planetary system, look quite different from each other, but recent advances in dynamical system theory have been successful in bridging some aspects of these apparently different phenomena on the common basis of the underlying geometrical structure of phase space in many-body systems. Most efforts have been devoted to understanding the phase-space geometry in the region around a hyperbolic fixed point that has one prominent stable and unstable direction compared with the other directions. This has led to a description of a roadmap in the phase space to *necessarily* mediate the transport from one local region to the other [1–4]. However, the questions of how the system travels within the local region that is remote from the region of the saddle, and what kinds of phase-space structures the system experiences, such as Arnold web [11] and remnant of invariant [12], have not yet been clarified for highly chaotic many-body systems. Some previous studies have revealed the existence of a variety of anomalies in the phase-space transport in Hamiltonian systems, e.g., sticky motion in the stagnant layer [13], fractional kinetics [14], and very slow dynamics [15–19]. These must be a manifestation of the nonuniform nature of the underlying phase space. In order to reveal the underlying mechanism behind such anomalous transport phenomena in the same footing and also to understand their physical consequences, such as nonuniform energy exchange processes among the different vibrational modes in molecular systems, it is highly desirable to develop a technique to explore invariant, or remnant of invariant, manifolds buried in chaos.

In this Brief Report, we present a technique to scrutinize remnant of invariants based on the formula originally developed by Hori [20] and later by Deprit [21]. The key strategy is the use of virtual time evolution derived from a series of appropriate generating functions in canonical perturbation calculation. It is found that this technique can capture the underlying remnants of invariants to mediate the energy exchange among modes at energies so high above the potential barrier that the conventional procedure resting on the finite truncation of the coordinate transformation cannot.

We begin with a brief outline of the procedure, which is based on canonical perturbation theory (CPT), a classical analogue of Van Vleck perturbation theory in quantum mechanics, written in the language of Lie algebras [22]. Suppose that the Hamiltonian H of the N degrees of freedom (DOF) system is analytic with respect to the canonical coordinates and the conjugate momenta $(\mathbf{p},\mathbf{q}) = (p_1,\ldots,p_N,\ q_1,\ldots,q_N)$, and that H can be expanded in the neighborhood of a stationary point as

$$H(\mathbf{p},\mathbf{q}) = \sum_{k=2}^{\infty} H_k(\mathbf{p},\mathbf{q}). \tag{1}$$

Here, we denote H_2 by

$$H_2 = \frac{1}{2}\sum_{i=1}^{N} \omega_i (p_i^2 + q_i^2) \tag{2}$$

and H_k by the coupling terms composed of the kth-order power series in $(\mathbf{p},\mathbf{q})$, and ω_i is either real or imaginary.

The goal of CPT is to find generating functions $F_3, F_4, \ldots, F_m$ (up to a certain order m) so that the original Hamiltonian H can be transformed into a simpler form $\hat{H}$ by sequential canonical transformations,

$$\hat{H} = e^{L_m} \cdots e^{L_3} H = H_2 + \hat{H}_3 + \cdots + \hat{H}_m + (\text{terms whose order is higher than } m). \tag{3}$$

Here $e^{L_k} = e^{\{F_k,\cdot\}}$ is written in terms of the Poisson bracket $\{A,B\} \equiv \Sigma_{i=1}^{N} (\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i})$ and

$$e^{L_k} f \equiv f + \{F_k, f\} + \frac{1}{2}\{F_k, \{F_k, f\}\} + \cdots . \tag{4}$$

F_k and $\hat{H}_k$ are sums of monomials of order k in the canonical variables $(\mathbf{p},\mathbf{q})$. The generating function F_k is determined so that $\hat{H}_k$ satisfies $\{H_2, \hat{H}_k\} = 0$ and becomes as simple as possible [22].

There are mainly two different approaches to extract the geometrical structure of phase space in terms of CPT. The first and most prevailing approach is to transform H such as Eq. (3) and truncate it at $(m+1)$th order. If one can confirm that a solution of the truncated Hamiltonian is close to the solution of the original Hamiltonian H (see, e.g., [23]), one can assign the geometrical structures associated with H in terms of the truncated Hamiltonian. However, in general, it is very difficult to prove that the two solutions are equivalent unless they are both sufficiently close to the stationary point. The other approach is the following: One traces the new coordinates and momenta $(\hat{\mathbf{p}}^{(m)}, \hat{\mathbf{q}}^{(m)})$ in $\hat{H}$ as functions of $(\mathbf{p},\mathbf{q})$ obeying the original Hamiltonian H,

$$\hat{p}_i^{(m)}(\mathbf{p},\mathbf{q}) = e^{-L_m} e^{-L_{m-1}} \cdots e^{-L_3} p_i,$$

$$\hat{q}_i^{(m)}(\mathbf{p},\mathbf{q}) = e^{-L_m} e^{-L_{m-1}} \cdots e^{-L_3} q_i. \tag{5}$$

It is known that this transformation preserves the symplectic property if $(\mathbf{p},\mathbf{q})$ are symplectic (see, e.g., [20,21]). For example, if the system is transformed into a set of isolated oscillators by $(\mathbf{p},\mathbf{q}) \to (\hat{\mathbf{p}}^{(m)}, \hat{\mathbf{q}}^{(m)})$, the associated action integrals $\hat{I}_i^{(m)}(\mathbf{p},\mathbf{q}) \equiv \frac{1}{2}\{[\hat{p}_i^{(m)}(\mathbf{p},\mathbf{q})]^2 + [\hat{q}_i^{(m)}(\mathbf{p},\mathbf{q})]^2\}$ should, in principle, be constants of motion during the dynamical evolution obeying $H(\mathbf{p},\mathbf{q})$.

Considering the former approach, one can neither extract the underlying remnants of invariants structures such as vague tori [12], which might behave as a bottleneck during the transport in phase space, nor reveal intermittent hopping motion between such remnants of invariants. This shortage is a consequence of the fact that the truncated Hamiltonian always provides a globally integrable or near-integrable representation, such that the system never or hardly ever evolves in different regions of remnants of invariants. On the other hand, the latter approach using Eqs. (5) to trace the dynamical evolution obeying the original Hamiltonian should reveal how the system enters and escapes from remnants of invariants by means of the evolution of the action integrals $\hat{I}_i^{(m)}$. Furthermore, one can also grasp the order of resonance through which the energy exchange takes place by monitoring the ratios between the frequencies $\partial\hat{H}/\partial\hat{I}_i^{(m)}$.

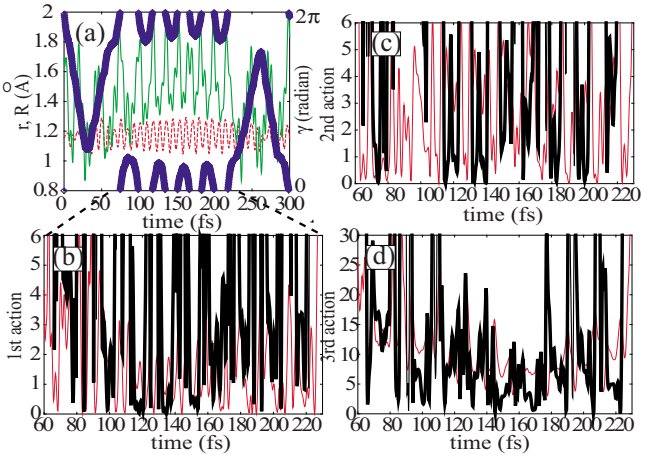

FIG. 1. (Color online) (a) A representative reactive trajectory of HCN isomerization, r (dotted line), R (thin solid line), and γ (thick solid line). Here total energy is set to be $E=-0.420$ kcal/mol, where the potential barrier height to connect the HCN and HNC wells is -0.444 kcal/mol. $\gamma \approx 0$, $\approx \pi$ and $\gamma \approx \pm 1.168$ rad correspond to the HCN and HNC well and a saddle point to link the two wells, respectively. One can see that γ takes around 0 between $t=50$ and 225 fs, which means that the system traverses the HCN well in this interval. (b)–(d) The action integrals $\hat{I}_i^{(4)}$ (thin solid line) and $\hat{I}_i^{(7)}$ (thick solid line) obtained from Eq. (6) for each DOF in the HCN well.

In common CPT calculations, the transformed variables in Eqs. (5) are usually written as an expansion series truncated at a certain finite order, e.g., $(m+1)$th order,

$$\hat{p}_i^{(m)} \approx p_i - \{F_3, p_i\} + \cdots + (\text{terms of } m\text{th order}),$$

$$\hat{q}_i^{(m)} \approx q_i - \{F_3, q_i\} + \cdots + (\text{terms of } m\text{th order}). \tag{6}$$

In Fig. 1, we show an example of the evolution of the three action integrals along a potential well in the isomerization process of the HCN molecule. HCN is modeled by a three-DOF Hamiltonian with zero total angular momentum: $H = \frac{1}{2\mu}p_r^2 + \frac{1}{2m}p_R^2 + \frac{1}{2}(\frac{1}{\mu r^2} + \frac{1}{mR^2})p_\gamma^2 + V(r,R,\gamma)$. Here, r denotes the distance between the C and the N atoms, R is the distance between H and the center of mass between C and N, and γ is the angle between H and C as seen from the center of mass of C and N in Jacobi coordinates. μ and m are, respectively, the reduced mass of the CN diatom and the mass of the full system. As for the potential $V(r,R,\gamma)$, we use the surface introduced by Murrel *et al.* [24]. First, we expand the Hamiltonian as a power series with respect to the normal coordinates $(\mathbf{p},\mathbf{q})$ around a potential minimum according to the procedure outlined in Eqs. (1) and (2). The new actions $\hat{I}_i^{(m)}$ are evaluated in terms of $(\hat{p}_i^{(4)}, \hat{q}_i^{(4)})$ and $(\hat{p}_i^{(7)}, \hat{q}_i^{(7)})$ via Eqs. (6). Here, $\hat{I}_1$ and $\hat{I}_2$ roughly correspond to the stretching motions along the coordinates r and R, respectively, and $\hat{I}_3$ to

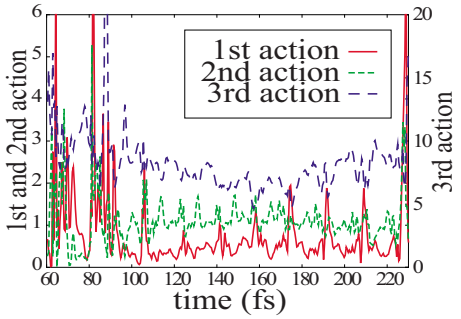

FIG. 2. (Color online) The new actions calculated by virtual time evolution using F_k $(k=3,4,\ldots,7)$ for each DOF along the same trajectory shown in Fig. 1.

the bending motion associated with the angle γ. Note that, if the actions are well defined in the potential well, they are expected to exhibit approximate constants or evolve slowly along trajectories inside the well. In Fig. 1, one can, however, observe that all actions abruptly fluctuate. The increase of the perturbation order does not resolve this problem. Padé resummation techniques have often been employed to extrapolate to higher orders in terms of a set of truncated calculations [12]. It was found, however, that the Padé coefficients cannot be determined for these abruptly changing actions. One might conjecture that the fluctuations of action integrals are caused by the nonintegrability of the system due to the high nonlinearity of the potential at energies above the potential barrier.

As was shown here, the truncation of the CPT transformation can lead to abrupt fluctuations of the new action integrals when they are traced in the original system. This phenomenon results from the fact that Eqs. (6) do not represent a symplectic system due to the truncation in $(\mathbf{p},\mathbf{q})$. These apparent fluctuations in the action integrals have so far remained unnoticed in the literature. It is difficult to assign the origin of the fluctuations, as both the truncation or intrinsic chaos might be important, especially for the evolution in the potential well at such high energies.

We present a technique that preserves the symplectic property in the transformed variables based on the Lie transforms [20,21]. Their formula is as follows: provided that a generating function W is calculated analytically in advance, the canonical transformation associated with W,

$$(\mathbf{P},\mathbf{Q}) = e^{\{W,\cdot\}}(\mathbf{p},\mathbf{q})\big|_{(\mathbf{p},\mathbf{q})=(\mathbf{p}_0,\mathbf{q}_0)}, \tag{7}$$

can be determined by solving the set of ordinary differential equations,

$$\frac{d\mathbf{p}(\epsilon)}{d\epsilon} = -\frac{\partial W}{\partial \mathbf{q}}, \quad \frac{d\mathbf{q}(\epsilon)}{d\epsilon} = \frac{\partial W}{\partial \mathbf{p}}, \tag{8}$$

with the initial condition $(\mathbf{p}_0,\mathbf{q}_0)=(\mathbf{p}(0),\mathbf{q}(0))$. The new canonical variables $(\mathbf{P},\mathbf{Q})$ are identified as $(\mathbf{p}(1),\mathbf{q}(1))$. The canonical transformation in Eqs. (7) can easily be generalized for any observable $A(\mathbf{p},\mathbf{q})$, e.g., the action integrals and the frequencies $\partial\hat{H}/\partial\hat{I}_i$, with the help of the relation of $e^{\{W,\cdot\}}A(\mathbf{p},\mathbf{q})=A(e^{\{W,\cdot\}}\mathbf{p},e^{\{W,\cdot\}}\mathbf{q})=A(\mathbf{P},\mathbf{Q})$ [20,21]. We make use of this idea by replacing W by $-F_k$ in Eqs. (8). First, we

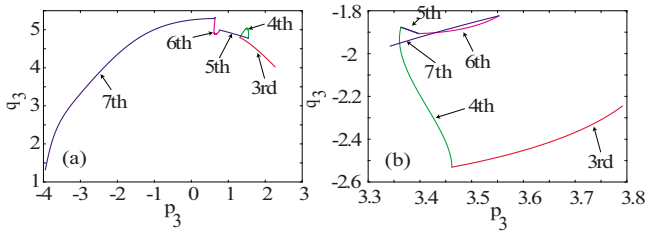

FIG. 3. (Color online) The projection of the consecutive, virtual time evolutions obeying $-F_k$ $(k=3,4,\ldots,7)$ on (p_3,q_3), where the initial phase-space point $(\mathbf{p},\mathbf{q})$ is taken at (a) $t_1=81.76$ fs and (b) $t_2=115.14$ fs.

propagate $(\mathbf{p}(\epsilon),\mathbf{q}(\epsilon))$ starting from the initial point $(\mathbf{p}(\epsilon=0),\mathbf{q}(\epsilon=0))=(\mathbf{p}_0,\mathbf{q}_0)$ by using the third-order generating function F_3 until ϵ becomes 1. The resultant $(\mathbf{p}(1),\mathbf{q}(1))$ are the transformed canonical variables at the third order, i.e., $(\hat{\mathbf{p}}^{(3)},\hat{\mathbf{q}}^{(3)})$, which corresponds to the first operation $e^{-L_3}p_i$ and $e^{-L_3}q_i$ in Eqs. (5). Second, starting from the point $(\hat{\mathbf{p}}^{(3)},\hat{\mathbf{q}}^{(3)})$, we further propagate the system in terms of the fourth-order generating function F_4 using the same procedure as before. By iterating this step, one can precisely evaluate the new canonical variables up to a chosen order m, $(\hat{\mathbf{p}}^{(m)},\hat{\mathbf{q}}^{(m)})$. Note that Eqs. (5) themselves remain symplectic if $(\mathbf{p},\mathbf{q})$ is symplectic [20,21]. Therefore, our procedure does not lose the symplectic property, and the validity range of the new canonical coordinates is expected to be much wider compared to the truncated approach using Eqs. (6).

Figure 2 shows the three actions at seventh order calculated by our technique using F_k $(k=3,4,\ldots,7)$ along the same trajectory as in Fig. 1(a). One can notice that, compared to Figs. 1(b)–1(d), the abrupt fluctuations are much more suppressed, and fewer spontaneous peaks appear, though the same generating functions have been used. In addition, one observes that some fluctuations persist in certain intervals of time, e.g., between $t=80$ and 90 fs. This indicates the existence of intrinsic chaos in a certain region of the multidimensional phase space. Figures 3(a) and 3(b) illustrate the consecutive time evolution according to $-F_k$ $(k=3,4,\ldots,7)$ initiated at $(\mathbf{p}(t),\mathbf{q}(t))$ at $t_1=81.76$ fs and $t_2=115.14$ fs, respectively. Here, the trajectories are projected onto the place of (p_3,q_3). One can expect that the trajectory initiated at t_1, when large fluctuation occurs, sig-

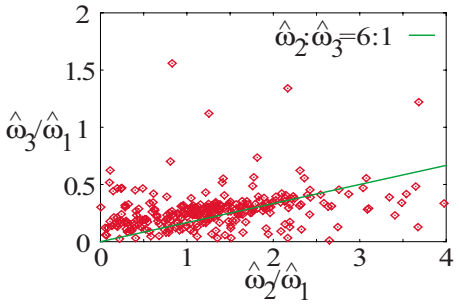

FIG. 4. (Color online) The ratio of the three frequencies $\omega_i = \partial\hat{H}/\partial\hat{I}_i^{(m)}$ calculated in terms of F_k $(k=3,4,\ldots,7)$ using the virtual time evolution procedure of Eq. (8) along the same trajectory in Fig. 1.

nificantly evolves, whereas the trajectory at t_2 shows the tendency to converge into a certain value. We also found that the largest local Lyapunov exponent underlines the difference between the two points in the local divergence rate in phase space. The most important result of our approach is the finding of slowly varying actions in the interval from $t=90$ to 200 fs. This result implies that some remnants of invariants are buried in HCN even at the high-energy region above the potential barrier. This means that the concept of the modes still exists and is well defined in the time interval. In Fig. 2, one observes that the action of the third mode, which is associated with the reactive mode, gradually decreases from $t=90$ to 150 fs, implying the release of energy into the two other modes. Then, from that point in time, the action gradually turns to increase and gains energy from the bath modes. Moreover, the comparison of frequency ratios shows that the energy exchange occurs through the $\hat{\omega}_2:\hat{\omega}_3=6:1$ resonance as shown in Fig. 4. This assignment of modes and the resonance through which the energy exchange takes place cannot be demonstrated with a truncated scheme such as Eqs. (6).

We expect that our technique can overcome the drawback of the conventional truncation scheme that spoils the symplectic property of the original variables and can capture the underlying remnants of invariants that make it possible to investigate not only energy exchange processes but also their relation to chemical reaction processes of how the reactive mode acquires (loses) its energy in order to climb over the potential barrier (to be trapped in the potential well) and through which resonance the energy transfer occurs.

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