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Reaction coordinates for elucidating reaction dynamics with anharmonic couplings

Shinnosuke Kawai*

In many chemical reactions, the dynamics occurring in the region around a saddle point play an essential role in determining the reactivity. The dynamics appears complicated when there exist significant couplings between the reactive and vibrational degrees of freedom. The present review describes recent studies of coordinate transformations designed to disentangle the couplings and reveal the underlying structure of the dynamics.

Abstract

Saddle points can be found on the potential energy surface between the reactants and products regions in many chemical reactions. The dynamics occurring in the vicinity of a saddle point play an essential role in the study of reaction dynamics because the reactivity of a trajectory is primarily determined in the saddle region. There are many cases where a well-defined boundary (called *reactivity boundary* here) between reacting and non-reacting trajectories can be located in the phase space. Locating the reactivity boundary, however, becomes challenging when anharmonic couplings between the reaction coordinate and the vibrational coordinates complicate the reaction dynamics. The aim of this paper is to present a review of recent studies that use nonlinear coordinate transformations to disentangle the anharmonic couplings. The reaction coordinates constructed through such nonlinear coordinate transformations are de-coupled from the other coordinates as much as possible, thus simplifying analysis of reaction dynamics. Several options are introduced for nonlinear coordinate transformations which should be appropriately chosen by examining the extent of the anharmonic couplings. Under certain conditions, special reaction coordinates constructed by a suitable nonlinear coordinate transformation reveals the existence of a clear reactivity boundary in the phase space even when there are strong anharmonic couplings.

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INTRODUCTION

Chemical reaction is the process of molecules changing their configurations from “reactants” to “products”. Physically it can be regarded as a motion of atoms described in the configuration space with a set of coordinates specifying the current positions of the atoms. A point (in the classical mechanics) or a wavepacket (in the quantum mechanics) changes its location from a region classified as “reactants” in the configuration space to another region classified as “products”. In many cases, the regions corresponding to reactants and the products are valleys in the potential energy landscape. Between these valleys there is often found a region with higher potential energy than the reactants and the products regions, giving rise to a “barrier” region that the system must pass through in order to get from the reactants region to the products region. In such a “barrier” region one can usually find a *rank-one saddle point* where the potential energy is maximum along one direction associated with the path from the reactants region to the products region and is minimum along all the other directions. The importance of the saddle point firstly lies in the fact that it gives the minimum amount of the energy necessary for the process of surmounting the barrier for the reaction. In the case where the energy of the system is not very high, the system must necessarily pass through the vicinity of the saddle point in the process of chemical reaction. It is the dynamics occurring in the vicinity of the saddle point that determine whether a given system undergoes the process of chemical reaction by successfully surmounting the barrier or bounces back to the reactants region, that is, the dynamics in the vicinity of the saddle point determine the *reactivity*.

Interest in the dynamics occurring in the saddle region primarily arose in the context of calculating the reaction rate constant. The transition state theory^{1,2} attempts to calculate the reaction rate by first postulating a dividing surface, called *transition state* (TS), in the saddle region and then measuring the flux passing through the TS. A crucially important assumption in the concept of the TS is the so-called *non-recrossing* property of the TS: if a trajectory is to go from the reactants side to the products side, it must necessarily cross the TS dividing surface between them, *and*, once a trajectory has crossed the TS, it must go down into the products region without ever returning to the TS again. This assumption is based on the intuition that the motion taking place in the saddle region primarily determines the occurrence of the reaction while the motion after passing the saddle region is simply that

of “sliding down the slope”. This assumption enables the calculation of the reaction rate using only the information of the local region around the saddle point without simulating global trajectories. Note, however, the dynamics outside the saddle region is important when the state-to-state rate constant¹ is concerned or when the system has significant amount of global recrossing³.

In addition to the calculational technique for reaction rates, the theory of the saddle region dynamics provides fundamental understanding of what is occurring during the process of chemical reaction. By offering an intuitive image of the motion of reacting trajectories, it provides insights that help to answer the question of what differentiates the reacting trajectories that go from the reactants region to the products region and the non-reacting trajectories that start in the reactants region but are reflected by the barrier back into the reactants region again. Recent theoretical studies⁴⁻⁹ of the saddle region dynamics from the viewpoint of nonlinear dynamics elucidated the existence of well-defined boundaries in the phase space that divide the reacting trajectories from the non-reacting ones, even in cases with anharmonic coupling that complicates the dynamics. Hereafter such boundaries will be called *reactivity boundaries*. The present review provides a brief summary of the basic aspects of the recent theoretical developments concerning the saddle region dynamics, mainly in the classical mechanical description. Readers interested in the extension of the theory to the quantum mechanical regime may refer to Refs. 10,11. It is also possible to utilize the concept of the reactivity boundary for elucidating the mechanism of reaction control by laser fields and apply it to the design of the optimal pulse shape to obtain desired products.^{11,12}

SADDLE REGION DYNAMICS IN HARMONIC APPROXIMATION

Let us start the discussion with a simple case. As the (rank-one) saddle point is defined as a stationary point of the potential energy surface that is maximum along only one direction, the lowest order terms in the Taylor expansion of the potential energy $V(\mathbf{q})$ for the nuclear coordinates $\mathbf{q}$ are as follows:

$$V(\mathbf{q}) \approx -\frac{\lambda^2}{2}q_1^2 + \sum_{\ell=2}^n \frac{\omega_\ell^2}{2}q_\ell^2 \quad (1)$$

where the origin of the coordinate system is taken at the saddle point and the normal mode coordinates $(q_1, \dots, q_n)$ have been introduced to diagonalize the potential energy. Here we assume mode 1 is the unstable direction with potential curvature $-\lambda^2/2$. This unstable mode corresponds to the motion of “sliding down the barrier”. The other modes are vibrational modes with frequencies ω_ℓ .

The Hamiltonian is then

$$\begin{aligned} H(\mathbf{q}, \mathbf{p}) &= \frac{p_1^2}{2} - \frac{\lambda^2}{2} q_1^2 + \sum_{\ell=2}^n \left(\frac{p_\ell^2}{2} + \frac{\omega_\ell^2}{2} q_\ell^2 \right) \\ &= \lambda x_1 \xi_1 + \sum_{\ell=2}^n i \omega_\ell x_\ell \xi_\ell, \end{aligned} \quad (2)$$

where the following variables have been introduced for later convenience:

$$\begin{aligned} x_1 &\stackrel{\text{def}}{=} \frac{\lambda q_1 + p_1}{\sqrt{2\lambda}}, & \xi_1 &\stackrel{\text{def}}{=} \frac{p_1 - \lambda q_1}{\sqrt{2\lambda}}, \\ x_\ell &\stackrel{\text{def}}{=} \frac{\omega_\ell q_\ell - i p_\ell}{\sqrt{2\omega_\ell}}, & \xi_\ell &\stackrel{\text{def}}{=} \frac{p_\ell - i \omega_\ell q_\ell}{\sqrt{2\omega_\ell}}. \end{aligned} \quad (3)$$

This transformation defines a skewed coordinate system (x_1, ξ_1) in the (q_1, p_1) -plane.

The action variable defined by $I_1 \stackrel{\text{def}}{=} x_1 \xi_1$ for the reaction mode is an invariant of motion with the Hamiltonian given by Eq. (2). Therefore the trajectories run along the hyperbolas given by $I = \text{const.}$ as shown in Fig. 1.

Suppose that $q_1 = -\infty$ corresponds to the “reactants” (*i.e.*, before the reaction), and $q_1 = +\infty$ to the “products” (after the reaction). The trajectories with $x_1 > 0$ and $\xi_1 > 0$ are “forward reactive” because they start from the reactants region, pass over the barrier, and go into the products region (*i.e.*, the reaction progresses from the reactants to the products). On the other hand, the trajectories with $x_1 < 0$ and $\xi_1 > 0$ are “forward non-reactive” because they start from the reactants region, are reflected by the barrier, and go back into the reactants region. Similarly, the trajectories with $x_1 < 0$ and $\xi_1 < 0$ are “backward reactive,” and those with $x_1 > 0$ and $\xi_1 < 0$ are “backward non-reactive.” Thus the sets $\{x_1 = 0\}$ and $\{\xi_1 = 0\}$ constitute the *reactivity boundaries* between the reactive and the non-reactive trajectories.

Here it is helpful to make a brief comment on the usage of the term *reaction coordinate*. In the case of a rank-one saddle point, there is only one reaction coordinate (q_1) in the configuration space. When we look at the phase space, however, both the position coordinates and their conjugate momenta are called coordinates in the phase space. Therefore both q_1

and p_1 are called *reaction coordinates* here. In the following, the coordinates x_1 and ξ_1 , which have been constructed by mixing q_1 and p_1 , will also be called reaction coordinates.

NONLINEAR COORDINATE TRANSFORMATION FOR ANHARMONIC SYSTEMS

As the total energy of the system increases, the harmonic approximation Eq. (2) becomes no longer valid. We have higher order terms in the Taylor expansion of the Hamiltonian:

$$H(\mathbf{q}, \mathbf{p}) = \lambda x_1 \xi_1 + \sum_{\ell=2}^n i\omega_{\ell} x_{\ell} \xi_{\ell}, \\ + H'(x_1, x_2, \dots, x_n, \xi_1, \xi_2, \dots, \xi_n), \quad (4)$$

where H' is a polynomial function containing cubic and higher order terms. Due to the existence of H' , the action $I_1 = x_1 \xi_1$ of the reactive mode is no longer a constant of motion. The motion along the reaction mode (q_1, p_1) is affected by the current values of the other coordinates. This is an effect known as *coupling*. A plot like Fig. 1 with only q_1 and p_1 therefore cannot capture the correct view of the dynamics due to the loss of information about the other coordinates.

The passage from the low-energy harmonic regime to higher energies was remarked on in Ref. 5 in the study of the trajectories of an inert gas cluster system. This and other studies⁴⁻⁹ then showed that it is possible to introduce a coordinate transformation $(x_1, \dots, x_n, \xi_1, \dots, \xi_n) \mapsto (\bar{x}_1, \dots, \bar{x}_n, \bar{\xi}_1, \dots, \bar{\xi}_n)$ that casts the Hamiltonian into the following form:

$$H(\mathbf{q}, \mathbf{p}) \approx \bar{H}(\bar{x}_1, \dots, \bar{x}_n, \bar{\xi}_1, \dots, \bar{\xi}_n) \\ = \lambda \bar{x}_1 \bar{\xi}_1 + \sum_{\ell=2}^n i\omega_{\ell} \bar{x}_{\ell} \bar{\xi}_{\ell} \\ + f_1(\bar{I}_1, \bar{x}_2, \dots, \bar{x}_n, \bar{\xi}_2, \dots, \bar{\xi}_n) \\ + f_2(\bar{x}_2, \dots, \bar{x}_n, \bar{\xi}_2, \dots, \bar{\xi}_n). \quad (5)$$

In this form, the total Hamiltonian depends on $\bar{x}_1$ and $\bar{\xi}_1$ only through the action $\bar{I}_1 \stackrel{\text{def}}{=} \bar{x}_1 \bar{\xi}_1$. Here f_1 and f_2 contain anharmonic terms, and, in particular, f_1 is defined so that $f_1 = 0$ when $\bar{I}_1 = 0$. When the Hamiltonian is in the form of Eq. (5), it can be proved, by some

elementary calculations with Hamilton's equations of motion, that the new action variable $\bar{I}_1$ is an invariant of motion. This means that the same picture as Fig. 1 is valid if the names of the axes are changed to $\bar{x}_1$ and $\bar{\xi}_1$.

Let us here look into technical details of constructing such a coordinate transformation. The core of the method is known as the Lie canonical perturbation theory^{13,14}. The Hamiltonian Eq. (4) is first expanded in a series:

$$H = \sum_{\nu=0}^{\infty} \epsilon^{\nu} H_{\nu}, \quad (6)$$

where ϵ is a formal parameter of perturbation that will be set equal to 1 after all the calculations have been done. The zeroth order part of the Hamiltonian is taken as the harmonic approximation:

$$H_0 = \lambda x_1 \xi_1 + \sum_{\ell=2}^n i \omega_{\ell} x_{\ell} \xi_{\ell}, \quad (7)$$

and the higher order term H' in Eq. (4) is put into $H_1, H_2, \dots$ in Eq. (6). The canonical transformation is given by solving the following differential equations:

$$\begin{aligned} \frac{d}{d\tau} \mathbf{q}(\tau) &= - \frac{\partial}{\partial \mathbf{p}(\tau)} F(\mathbf{q}(\tau), \mathbf{p}(\tau)), \\ \frac{d}{d\tau} \mathbf{p}(\tau) &= \frac{\partial}{\partial \mathbf{q}(\tau)} F(\mathbf{q}(\tau), \mathbf{p}(\tau)), \end{aligned} \quad (8)$$

with the initial condition corresponding to the original coordinate:

$$\begin{aligned} \mathbf{q}(0) &= \mathbf{q}, \\ \mathbf{p}(0) &= \mathbf{p}. \end{aligned} \quad (9)$$

And the transformed coordinates are given as the final values at $\tau = \epsilon$:

$$\begin{aligned} \bar{\mathbf{q}} &= \mathbf{q}(\epsilon), \\ \bar{\mathbf{p}} &= \mathbf{p}(\epsilon). \end{aligned} \quad (10)$$

Note the differential equations Eq. (8) are Hamilton's equations of motion as if the function $-F(\mathbf{q}, \mathbf{p})$ were the "Hamiltonian" and the parameter τ were the "time". The function F is called a generating function. The transformation thus constructed is automatically canonical because the Hamiltonian time evolution is canonical.

The formal solution of Eq. (8) is given by

$$\begin{aligned}\mathbf{q}(\tau) &= \exp(-\tau \text{ad}_F) \mathbf{q}, \\ \mathbf{p}(\tau) &= \exp(-\tau \text{ad}_F) \mathbf{p},\end{aligned}\tag{11}$$

where the operator ad_F donotes the operation of the Poisson bracket

$$\begin{aligned}\text{ad}_F G &= \{G, F\} \\ &= \sum_{\ell} \left(\frac{\partial G}{\partial q_{\ell}} \frac{\partial F}{\partial p_{\ell}} - \frac{\partial F}{\partial q_{\ell}} \frac{\partial G}{\partial p_{\ell}} \right).\end{aligned}\tag{12}$$

After the transformation, the Hamiltonian is expressed in terms of the new coordinates

$$H(\mathbf{q}, \mathbf{p}) = \bar{H}(\bar{\mathbf{q}}, \bar{\mathbf{p}}).\tag{13}$$

This Hamiltonian function is given by

$$\bar{H} = \exp(\epsilon \text{ad}_F) H.\tag{14}$$

Note the sign is opposite to Eq. (11). The final Hamiltonian $\bar{H}$ is expanded in a series as $\bar{H} = \sum_{\nu=0}^{\infty} \epsilon^{\nu} \bar{H}_{\nu}$. When Eq. (6) is substituted into Eq. (14) and the exponential operator is also expanded, the $O(\epsilon^1)$ part of Eq. (14) reads

$$\bar{H}_1 = H_1 + \text{ad}_F H_0.\tag{15}$$

If we express H_1 , F , and $\bar{H}_1$ as polynomials

$$\begin{aligned}H_1 &= \sum_{\mathbf{j}, \mathbf{k}} h_{\mathbf{j}\mathbf{k}}^1 x_1^{j_1} \dots x_n^{j_n} \xi_1^{k_1} \dots \xi_n^{k_n}, \\ F &= \sum_{\mathbf{j}, \mathbf{k}} f_{\mathbf{j}\mathbf{k}}^1 x_1^{j_1} \dots x_n^{j_n} \xi_1^{k_1} \dots \xi_n^{k_n}, \\ \bar{H}_1 &= \sum_{\mathbf{j}, \mathbf{k}} \bar{h}_{\mathbf{j}\mathbf{k}}^1 x_1^{j_1} \dots x_n^{j_n} \xi_1^{k_1} \dots \xi_n^{k_n},\end{aligned}\tag{16}$$

then, after some calcuation using Eq. (15) and the definition of ad_F in Eq. (12), the coefficients in $\bar{H}_1$ are given by

$$\bar{h}_{\mathbf{j}\mathbf{k}}^1 = h_{\mathbf{j}\mathbf{k}}^1 + \left(\lambda(k_1 - j_1) + \sum_{\ell} i\omega_{\ell}(k_{\ell} - j_{\ell}) \right) f_{\mathbf{j}\mathbf{k}}^1.\tag{17}$$

Thus, by setting

$$f_{\mathbf{j}\mathbf{k}}^1 = -\frac{h_{\mathbf{j}\mathbf{k}}^1}{\lambda(k_1 - j_1) + \sum_{\ell} i\omega_{\ell}(k_{\ell} - j_{\ell})}\tag{18}$$

the terms with $j_\ell \neq k_\ell$ in H can be cancelled in Eq. (15) and the transformed Hamiltonian $\bar{H}$ contains only terms with $j_1 = k_1$. This gives the final form of $\bar{H}$ specified by Eq. (5) as desired. The description given above is a simplified explanation, focusing only on the first order of perturbation in the Lie canonical perturbation method used in the previous studies. More technical details including the higher order terms can be found in literature^{4–9,13–15}.

In the literature, the form of Eq. (5) has been called ‘partial normal form (PNF)’ as the transformation is designed to make only the action $\bar{I}_1$ of the reaction mode a constant of motion. It is also possible to construct a transformation that makes all the transformed actions constants of motion^{6,7,9}. In the latter case the final form of the Hamiltonian is called ‘full normal form (FNF)’. The different strategies for constructing the transformation lead to differences in its convergence properties. Since the normal form transformation is based on the series expansion, it may suffer from divergence mainly arising from the appearance of nonlinear resonances among the modes when the system has significant nonlinear couplings in the high energy regime. In general, the convergence becomes better when the generating function contains a smaller number of terms and therefore the transformation is closer to the identity transformation. In Ref. 16 the present author has suggested another form of normal form,

$$\begin{aligned} \bar{H}(\bar{x}_1, \dots, \bar{x}_n, \bar{\xi}_1, \dots, \bar{\xi}_n) \\ = \lambda \bar{x}_1 \bar{\xi}_1 + \sum_{\ell=2}^n i\omega_\ell \bar{x}_\ell \bar{\xi}_\ell \\ + \bar{I}_1 g_1(\bar{x}_1, \dots, \bar{x}_n, \bar{\xi}_1, \dots, \bar{\xi}_n) \\ + g_2(\bar{x}_2, \dots, \bar{x}_n, \bar{\xi}_2, \dots, \bar{\xi}_n). \end{aligned} \quad (19)$$

This functional form is closer to the original Hamiltonian than the other NFs in that it allows for any form of g_1 and g_2 . The only requirement in the form of Eq. (19) is that the function g_1 is multiplied by $\bar{I}_1$. It is therefore expected to have a better convergence property. Under the Hamiltonian given by Eq. (19), the action variable $\bar{I}_1$ is no longer a constant of motion. However, it is shown by simple calculations that the sets $\{\bar{x}_1 = 0\}$ and $\{\bar{\xi}_1 = 0\}$ are still invariant manifolds and no trajectories can cross them. These two sets therefore play the role of reactivity boundaries. The form of Eq. (19) has been called “minimal normal form (MNF)” because it is a minimal functional form for obtaining the invariance of the manifolds.

NUMERICAL EXAMPLES

For the purpose of demonstration, examples of trajectories in the saddle region are plotted in the usual normal mode coordinates and in the transformed coordinates in Fig. 2. The numerical calculations have been done for a model system of a hydrogen atom in crossed electric and magnetic fields used in previous studies^{6,7,16}. The field parameter ε for the strength of the electric field is set to 0.45 in the scaled units. Figure 2(a) and (b) show the trajectories with energy 0.05 above the saddle point in the scaled units. The same trajectories are plotted in the normal mode coordinates in (a) and in the transformed coordinates in (b). While the trajectories look very complicated in the usual coordinates, the plot with the transformed coordinates reveals the existence of regular structure.

The laminar flow in Fig. 2(b) shows the constancy of the action $\bar{I}_1$ in the transformed reaction coordinates. By using this fact the reactivity boundaries are identified as $\bar{I}_1 = 0$. It is seen in the figure that no trajectories can cross this boundary due to the constancy of the action variable. Figure 2(c) and (d) show the trajectories with higher energy (0.15 above the saddle point in the scaled units). At this energy, the convergence of the partial normal form has been found to be poor, and the minimal normal form (Eq. (19)) is used to construct the transformation. Trajectories plotted in Fig. 2(d) with the transformed coordinates show some crossings of different trajectories. This fact shows that the action $\bar{I}_1$ is no longer a constant at this energy even in the transformed coordinates. However, one can still see the existence of the reactivity boundaries and identify them analytically as the sets $\{\bar{x}_1 = 0\}$ and $\{\bar{\xi}_1 = 0\}$. According to Eq. (19), no trajectories can cross these boundaries.

TOWARD “GLOBAL” UNDERSTANDING OF CHEMICAL REACTIONS

The use of coordinate transformation to reveal the structure of the dynamics in the saddle region has been reviewed and demonstrated. A system with intense couplings between multiple modes showing complicated motions when seen in usual coordinates may possess regular structure, specifically a clear boundary separating reactive and non-reactive trajectories in the phase space. The method of coordinate transformation presented here is designed to find special coordinates that are de-coupled from each other as much as possible and thus make

the analysis of the dynamics as simple as possible. The method is able to reveal regular structure that is hidden in the seemingly complicated motions of the usual coordinates, and is therefore expected to contribute to our understanding of chemical reaction dynamics.

The present method relies on the polynomial expansion around the saddle point. This is based on the intuition that the motion occurring in the saddle region is most important in determining the reactivity of a trajectory. However, a chemical reaction is a process traveling all the way from the reactants to the products, not occurring only in the saddle region. The excitation in the reactants required to climb up the hill and reach the saddle region is also an essentially important part for the understanding of chemical reactions. Distribution of the heat of reaction after passing the saddle region affects the state distribution of the nascent products, constituting an important research field of state-to-state reaction dynamics¹. In a reaction with a long lived collision complex, a significant amount of recrossing occurs due to the dynamics outside the saddle region³. Another important issue is whether the transformed coordinate $\bar{q}_1$ still divides the whole space into the correct reactants and products regions. Actually it was shown in the study of reaction dynamics through a rank-two saddle point that the reactivity boundary identified as $\bar{x}_1 = 0$ correctly indicates the future sign of $\bar{q}_1$ but the sign of $\bar{q}_1$ is not identical to the sign of q_1 that corresponds to the correct reactants and products¹⁷. All these issues show the importance of understanding the reaction dynamics in the global space from the reactants region to the products region. It should be noted here that efforts are continuously being made to increase the convergence radius of the normal form transformation^{9,16,18,19}. The concepts of the intrinsic reaction coordinate²⁰ and the reaction path Hamiltonian²¹ may also serve as good starting points to find global reaction coordinates that minimize couplings. It is the author's opinion that the exploration of dynamical reaction coordinates in the global space is an important and challenging future work.

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Figure 1: Phase space flow along the normal mode reaction coordinates plotted for the harmonic approximation around the saddle point. Trajectories run along the contours of the action variable $I_1 = \frac{p_1^2}{2} - \frac{\lambda^2}{2} q_1^2 = \lambda x_1 \xi_1$. The x_1 -axis and the ξ_1 -axis running diagonally in the figure constitute boundaries between reactive and nonreactive trajectories.

Figure 2: Example trajectories before and after the coordinate transformation. (a) Trajectories with lower energy above the saddle point plotted in the usual normal mode coordinates. (b) The same trajectories as (a) plotted in the partial normal form coordinates. (c) Trajectories with higher energy above the saddle point plotted in the usual normal mode coordinates. (d) The same trajectories as (c) plotted in the minimal normal form coordinates.

Figure 1
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Figure 2
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